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Research paper

Risk assessment of not meeting environmental objectives related to protection of human health and groundwater quality: The tiered approach in the context of the EU water framework directive

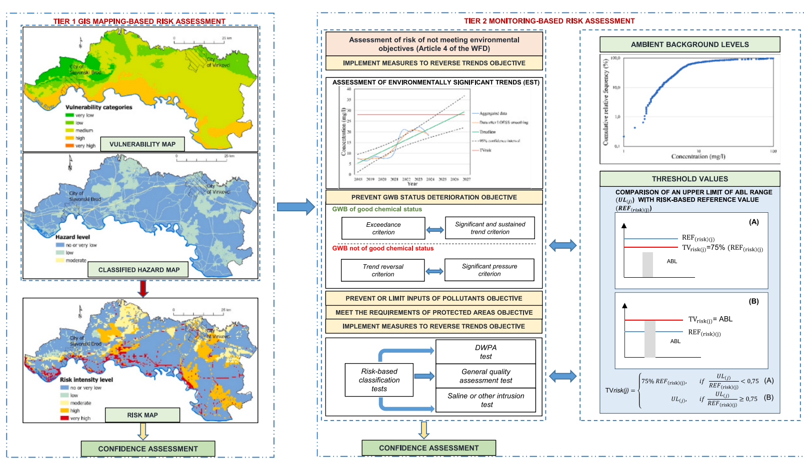
Zoran Nakić *, Dario Perković, Zoran Kovač, Borna-Ivan Balaž

University of Zagreb, Faculty of Mining, Geology and Petroleum Engineering, Pierottijeva 6, 10000, Zagreb, Croatia

HIGHLIGHTS

- The tiered approach to risk assessment refers to protection of human health and groundwater.
- Multiple risk screening and assessment tools address data uncertainty and confidence assessment.
- The Tier 1 risk screening results in development of the GIS-based risk map for groundwater body.
- The Tier 2 risk assessment combine multiple criteria to characterize the risk of deterioration of groundwater quality.
- A high-quality data from a high-resolution conceptual model of groundwater body is to be used.

GRAPHICAL ABSTRACT



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ABSTRACT

This paper presents the tiered approach to risk assessment, aiming to recognize groundwater bodies for which it can be unequivocally defined, with an established confidence level, whether they are at risk of not meeting environmental objectives of the EU Water Framework Directive (WFD) related to the protection of drinking water protected areas and groundwater itself. As an upgrade of the risk screening tools derived in the context of the Common Implementation Strategy (CIS) of the WFD, the robust and comprehensive approach to risk assessment extensively addresses data uncertainty and confidence assessment. If a risk assessment is conducted with low confidence, further data collection on pressures, chemical status and hydrogeological characteristics is carried out, which lasts until data are of sufficient quality to make a reliable prediction in outcomes. The tiered approach is combined with the confidence assessment focusing the research to areas of high uncertainty and low degree of confidence. To test this approach, groundwater chemical data from the groundwater body (GWB), which is typical for the Pannonian region of Croatia, were used. The Tier 1 semi-quantitative risk screening

* Corresponding author.
E-mail addresses: zoran.nakic@rgn.unizg.hr (Z. Nakić), dario.perkovic@rgn.unizg.hr (D. Perković), zoran.kovac@rgn.unizg.hr (Z. Kovač), borna-ivan.balaz@rgn.unizg.hr (B.-I. Balaž).

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resulted in development of the GIS-based risk map for the selected GWB. The Tier 2, monitoring-based risk assessment, was carried out by applying: a) relevant criteria to conduct trend analysis and to characterize the risk of deterioration of GWB chemical status and b) risk-based classification tests, in combination with the confidence assessment of tests results. Results of the assessment of risk of not meeting the “implement measures to reverse trends” and the “prevent GWB status deterioration” objectives for the selected GWB did not reveal an existence of environmentally significant trends and an exceedance of risk-based quality standards and threshold values with arithmetic and/or spatial means of targeted substances. The risk-based classification tests results confirmed no significant risk of not meeting good GWB chemical status related to the protection of human health and groundwater. All results demonstrate that proposed approach to risk assessment is straightforward and operational for use if a high-quality data derive from a high-resolution conceptual model of a GWB.

List of Abbreviation

Full Term Name	Abbreviation
Ambient Background Level	ABL
Arithmetic Mean	AM
Arithmetic Mean of concentration data for all values < LOQ set to 0	AM0
Arithmetic Mean of concentration data for all values < LOQ set to LOQ	AM100
Background Level	BL
Common Implementation Strategy	CIS
Confidence Assessment	CA
Confidence Level	CL
Drinking Water Protected Areas	DWPA
Drinking Water Protected Areas classification test	$DWPA_{risk}$
Drinking Water Standard	DWS
Driver, Pressure, State, Impact, Response	DPSIR
Environmental Quality Standard	EQS
Environmentally Significant Trend	EST
European Union	EU
General Quality Assessment classification test	GQA_{risk}
Groundwater dependent terrestrial ecosystem	GWDTE
Groundwater body “Eastern Slavonia – Sava River Basin”	GWB CSGI_29
Groundwater Directive	GWD
Hazard Index	HI
Hazard Index Classes	HIC
Lepeltier Method	LM
Limit of Detection	LOD
Limit of Quantification	LOQ
Monitoring Station	MS
Nitrate Vulnerable Zones	NVZ
Not Available data	NA
Non-point Pollution sources	NPP
Point Pollution sources	PP
Preselection Method	PM
Prevent or limit inputs of pollutants	P/L
Protected Areas	PA
Quality Standard	QS
Raw Water (pumped water)	RW
Reference Value	REF
Representativity Index	R_u
Risk Assessment	RA
Risk-based Reference Value	REF_{risk}
Risk-based Threshold Value	TV_{risk}
Risk Intensity Index	RII
River Basin	RB
River Basin Management Plan	RBMP
Saline or other intrusion classification test	SOI_{risk}
Source-Pathway-Receptor	SPR
Spatial Mean	SM
Statistically Significant Trend	SST
Targeted Substances	TS
Threshold Value	TV
Upper Limit of 95% confidence intervals around regression line	UL_{95}
Upper Limit of the range of natural concentrations	UL
Weighted Spatial Mean	SM_w
Water Framework Directive	WFD

1. Introduction

Numerous approaches are used for assessing groundwater quality and pollution hazards. For that purpose, it is very common to use Water Quality Indices (Aouiti et al., 2021; Peiyue et al., 2010), GIS techniques (Megahed, 2020) and statistical methods (Gulgundi and Shetty, 2018; Kovač et al., 2018; Krishna et al., 2019). Many researchers use combination of different tools and techniques, e.g., integration of GIS tools with statistical methods and/or Water Quality Indices (Jha et al., 2020; Judeh et al., 2021; Silva et al., 2021).

To mitigate the impacts of point and non-point pollution sources on groundwater quality, the risk assessment is fundamental for an effective groundwater protection. As an example, the common approach worldwide today is determination of a health risk-based threshold concentrations of pollutants in groundwater, which relies either on use of a single threshold value of pollutants to estimate the risk hazard (Zhang et al., 2018; Cai et al., 2019) or on use of probabilistic methods to evaluate health risks (Saha et al., 2017; Qiu et al., 2021). Other approaches include risk maps, developed to prioritize environmental hazard with respect to groundwater vulnerability through overlying process of both hazard and vulnerability maps (Aliewi and Al-Khatib, 2015), probabilistic risk analysis used to deal with the parametric and structural uncertainties of geological media (Zhang et al., 2013) or quantitative and semi-quantitative models, e.g. Groundwater Risk Assessment Model that is based on a multi-barrier approach to wellfield protection (Somaratne et al., 2013). Some routine risk assessments of polluted land apply generic frameworks for assessing and managing risks, which is based on soil threshold values determined through back-calculation of the soil-groundwater transport using generic models (Augustsson et al., 2020).

The source-pathway-receptor (SPR) paradigm (Commission of the European Communities, 2010) is proposed to address the actual or potential consequences on the health of the specific receptor (public water supply well-fields or groundwater dependent ecosystems) of pollution arising from specific pollution source via a defined subsurface pathway. Following recommendations from the Analysis of Pressures and Impacts – Guidance Document No 3 (Commission of the European Communities, 2003), many researchers apply the Driver, Pressure, State, Impact, Response (DPSIR) analytical framework, designed by the Organization for Economic Co-operation and Development (OECD; 1993), to draw a causal chain linking impacts and pressures of pollution sources to the outcome on human and environmental health (Potschin, 2009; Balderacchi et al., 2013; Nakić et al., 2013; Mattas et al., 2014; Malmir et al., 2021). By this framework, Driver is an anthropogenic activity affecting the environment, Pressure is the direct effect of a driver, State is the environmental condition resulting from the pressure, Impact is an environmental effect of a pressure and Responses are the measures taken for improving the state (Balderacchi et al., 2013).

The assessment of the risk of failure to achieve good chemical status of groundwater bodies in Europe are requested by the Water Framework Directive, WFD (EU, 2000b) and the Groundwater Directive, GWD (EU, 2006). According to requirements of the WFD, EU Member States conduct the analysis of pressures and impacts of human activity on the quality of groundwater with a view to identifying groundwater bodies presenting a risk of not achieving WFD environmental objectives. In the Common Implementation Strategy (CIS) of the WFD guidance document No. 26 (Commission of the European Communities, 2010), a coherent approach on how to assess the risk caused by different pressures at different scales was specified. As a follow-up, EU member states use this guidance document in the implementation phase of the WFD and GWD. For example, in the River Basin Management Plan of the Republic of Croatia until 2027 (RBMP, 2023) the risk assessment of not achieving good chemical status of groundwater bodies in Croatia was carried out according to the approach proposed in this guidance document.

In this paper, the tiered approach to risk assessment (RA) is presented, aiming to recognize groundwater bodies for which it can be unequivocally defined, with an established confidence level (CL), whether they are at risk of not achieving good chemical status. If a RA is conducted with low confidence, further data collection on pressures,

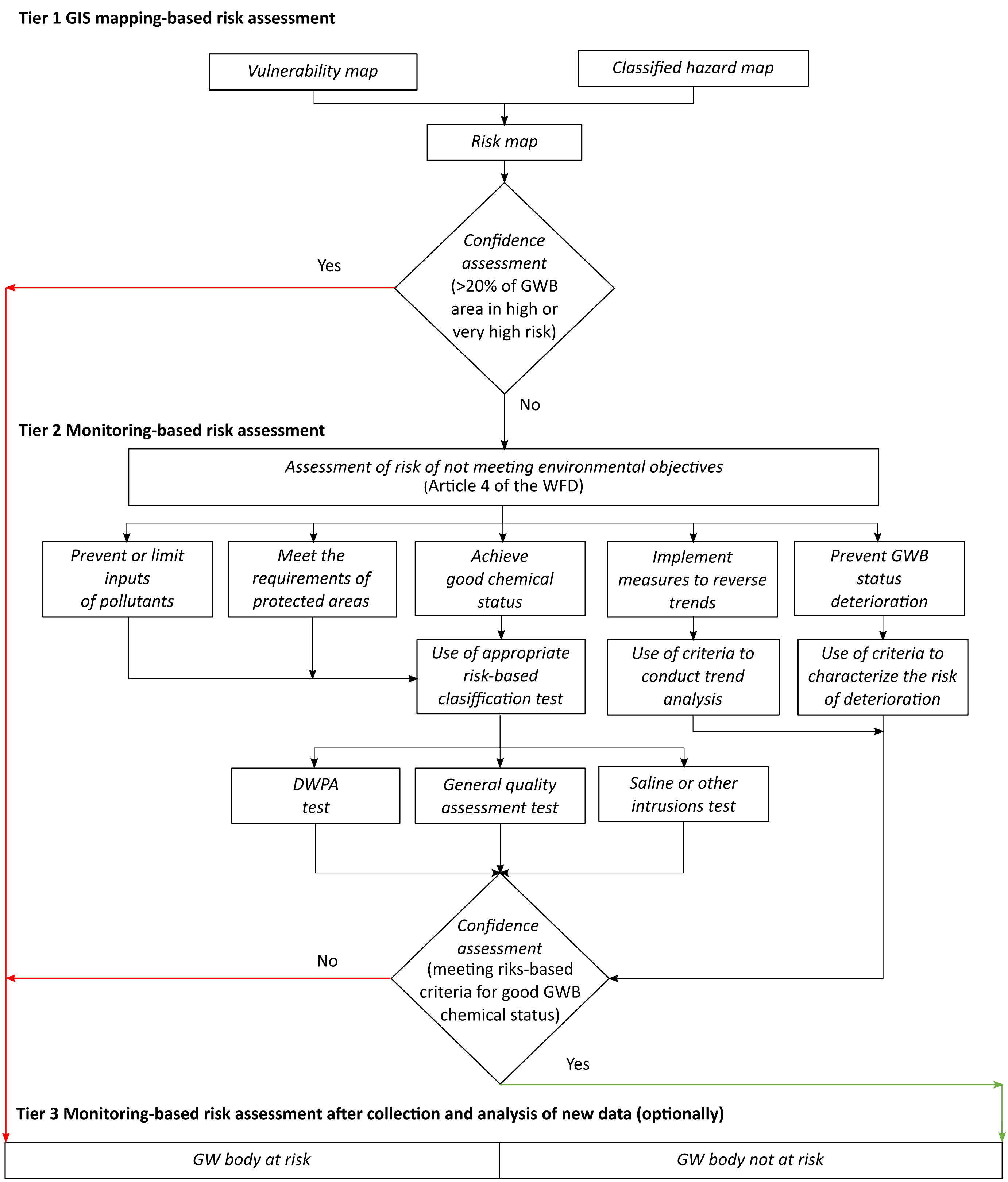


Fig. 1. Flow diagram illustrating the tiered approach to risk assessment.

chemical status, hydrogeological characteristics, etc. is carried out, which lasts until the data are of sufficient quality to make a reliable prediction in outcomes. Basically, the tiered approach to RA is combined with the confidence assessment (CA) focusing the research to areas of high uncertainty and low degree of confidence. We have tested this approach assessing the risk of not meeting environmental objectives related to protection of human health and groundwater quality of the groundwater body "Eastern Slavonia - Sava River Basin" (GWB CSGI_29), which is typical, according to the aquifer typology, for the Pannonian region of Croatia.

The main aim of our work was to define and test a robust and comprehensive methodology for a RA of not meeting environmental objectives for groundwater and protected areas, defined by the Article 4 of the WFD. To the best of our knowledge, this study is a rare example of the application of the RA procedure in the context of the WFD, which extensively addresses data uncertainty and confidence assessment.

2. Materials and methods

2.1. Risk assessment methodology

The tiered approach to RA, described and tested in this paper, provides a methodological framework for an assessment of risk of not meeting environmental objectives of the Water Framework Directive, WFD (EU, 2000b) related to protection of drinking water protected areas (DWPA) and groundwater itself. The environmental objectives to groundwater, related to good chemical status of groundwater bodies defined in the WFD Annex V, apply at different scales for a wide range of source-pathway-receptor (SPR) relationships. A RA for the WFD Article 4 objectives looks forward in time and attempts to predict the status of groundwater bodies at the end of the River Basin Management Plan (RBMP) period.

In the context of the CIS of the WFD, the guidance document No. 26 (Commission of the European Communities, 2010) outlines the concept of the RA based on the use of qualitative, semi-quantitative or quantitative risk screening tools aiming to divide groundwater bodies that are "not at risk" and "at risk" failing to meet the WFD environmental objectives. For groundwater bodies for which a RA has been carried out with a low confidence level (CL), additional data collection and analysis is done until bodies can be assessed with acceptable degree of reliable prediction.

The tiered approach to RA, presented in this paper (Fig. 1), represents the upgrade of this concept. Applying Tier 1, semi-quantitative GIS mapping-based risk screening, described in Section 2.1.1, groundwater bodies are divided into those for which it can be unequivocally determined, with a high CL, whether they are at risk. The Tier 1 CA is based on the *surface criterion* from the CIS guidance document No. 18 (Commission of the European Communities, 2009). For groundwater bodies with a low confidence of Tier 1 assessment, a Tier 2, monitoring-based RA of not meeting environmental objectives defined by the Article 4 of the WFD (Section 2.1.2), is applied. The Tier 2 CA is based on criteria specifically designed for determining the CL of GWB risk assessment that are integral part of the Tier 2 RA for the WFD Article 4 objectives. Optionally, the collection and analysis of new data continues as a part of the Tier 3, until the data are of sufficient quality to make a risk assessment with the highest possible CL.

Evidently, the tiered approach should be based on the use of appropriate conceptual model of the groundwater system, which is, by definition, the current understanding of the groundwater system based on the knowledge of its natural characteristics (Grath et al., 2007). The accuracy of a conceptual model is higher as the amount of, and confidence in, the available environmental information increase, leading to more reliable and effective description of groundwater system (Balderacchi et al., 2013).

2.1.1. Tier 1: GIS mapping

The Tier 1 semi-quantitative risk screening is characterized by development of a GIS based risk map derived in the overlay process of both groundwater vulnerability and hazard maps. It provides a conceptual understanding of an impact of pollution pressures in relation to an intrinsic property of a groundwater system.

Vulnerability mapping is usually performed by methods like DRASTIC (Aller et al., 1985), GOD (Foster, 1987), PI method of European COST Action 620 (Goldscheider, 2003) or SINTACS (Civita and De Maio, 1997). Any of these methods can be applied for vulnerability mapping, however the choice of method mostly depends on realistic evaluation of the number, type, distribution and reliability of the available data (Civita, 2010). For testing the tiered approach to RA, we applied the GIS based vulnerability map of the Pannonian region of Croatia (HR, 2023), developed by the SINTACS method. A vulnerability index ($I_{SINTACS}$), used to distribute hydrogeological settings of the Pannonian region of Croatia over the six degrees of intrinsic vulnerability, was calculated for each cell of a discretisation grid that was overlaid on the base map of Pannonian region using progressive rating P, ranging from 1 to 10 and given to each value interval and/or declared types of seven parameters/factors used in the model (Brkić et al., 2009): Depth to groundwater (S), Effective infiltration (I), Unsaturated zone infiltration capacity (N), Soil/overburden attenuation capacity (T), Saturated zone characteristics (A), Hydraulic conductivity (C), Topographic surface slope (S), multiplied with additional relative weight describing a hydrogeologic and impact setting of each parameter/factor.

$$I_{SINTACS} = \sum_{J=1}^{7} P_j w_j \quad [1]$$

Hazards can be defined as potential point and non-point sources of pollution on the surface of groundwater body resulting from human activities. For the Tier 1 GIS based risk screening, the classified hazard map of the GWB CSGI_29 was developed following the approach proposed by De Ketelaere et al. (2003). All potential sources of pollution were classified according to the type of land use, namely infrastructural, industrial, and agricultural activities, considering additional criteria for weighting hazards based on the estimation of toxicity and quantities of pollutants infiltrated below the surface and associated with each hazard. The potential degree of harmfulness of each source of pollution was estimated by calculating the Hazard Index, HI (De Ketelaere et al., 2003):

$$HI = H\ Q_n\ R_f \quad [2]$$

where *H* is the weighting value of each hazard indicating estimated toxicity, solubility and mobility of pollutants, varying from 10 (the lowest level of toxicity) to 100 (the highest level of toxicity); Q_n is the ranking factor indicating estimated quantity (low to high amounts) of potentially toxic substances within the same hazard type category released to environment (0.8–1.2); Rf is the reduction factor which provides an assessment of the probability for a pollution event to occur (0–1), considering the technical factors like state of maintenance, preservation and security measures in facilities/installation. If no information on these technical factors is available, then Rf is set to 1.

The classified hazard map was then developed by aggregating HI values in five HI classes (HIC), showing the spatial distribution of varying levels of hazards.

The risk of polluting groundwater denotes the probability of suffering adverse consequences from the possible pollution resulting from hazardous events. The intensity of potential impact of pollution sources affecting groundwater quality may be estimated by a risk intensity map, which involves the combination of vulnerability map and classified hazard map. It is based on the calculation of the risk intensity index (RII) or the probability that pollutants reach the surface of groundwater. The calculation of the RII may be carried out in different ways, for example by combining the vulnerability and hazard indices by matrix technique (Hötzl et al., 2003) or using a mathematical approach (Aliewi and Al-Khatib, 2015).

The risk intensity map of the GWB CSGI_29 was developed following the approach of aggregation of vulnerability map and classified hazard map proposed by Malik and Svasta (2003). First, to calculate HI values all identified hazard types were transferred into aerial hazards by creating buffers around their areas of influence. Then, for aggregation purpose, two different point counting systems, hazard and vulnerability indices, were transformed in relative scale (0–100%). In the next step, log RII values, reflecting significant variability of risk values over several magnitude, were calculated by multiplication of these two relative values. Finally, the GIS based risk intensity map of the GWB CSGI_29 was classified in five RII classes, showing the spatial distribution of varying levels of risk, from very low to very high.

The Tier 1 CA is carried out by determining the proportion of the area of a GWB represented by high and very high risk (A_{MH}) compared to the total area of a GWB (A_{TOT}). If $A_{MH} > 20\%\ A_{TOT}$, a GWB is at risk with high CL. If $A_{MH} \leq 20\%\ A_{TOT}$, then it cannot be unequivocally determined, with a high CL, whether a GWB is at risk and Tier 2 monitoring-based risk assessment is applied (Fig. 1). The Tier 1 CA *surface criterion* (20% of the total area of a GWB) is based on the concept of the *extent of exceedance criterion* (C_{ee}) of the "General quality assessment test" (Commission of the European Communities, 2009), which determines an acceptable portion of the total area or volume of a GWB in which the mean value of a substance exceeds a respective groundwater quality standard (QS_{GW}) or threshold value (TV_{GW}). According to the C_{ee}, if an extent of exceedance (of total area or volume of a GWB) is >20% then a GWB is in risk of not meeting the WFD environmental objective "Achieve good groundwater chemical status".

2.1.2. Tier 2: Monitoring-based risk assessment

The Tier 2 RA of not meeting environmental objectives, defined by the Article 4 of the WFD, is characterized by application of appropriate criteria and risk-based classification tests in which chemical data collected over the previous river basin (RB) planning cycles are used to predict what the GWB chemical status will be at the end of the next RBMP period. It provides a quantitative approach to RA, based on data uncertainty and confidence assessment of meeting risk-based criteria for good GWB chemical status related to protection of human health and groundwater itself.

The Tier 2 RA of not meeting *Prevent or limit inputs of pollutants* and *Meet the requirements of protected areas* objectives is conducted through an application of risk-based classification tests (Fig. 1). The rationale for these objectives implementation is described in Section S1.

2.1.2.1. Implement measures to reverse any significant and sustained upward trend objective. Deteriorating effect of a range of point and non-point sources of pollution or other uncontrolled pressures on a GWB can be revealed by an assessment of significant and sustained upward trends of substances, which is, based on definition from the GWD Article 2, any statistical or environmental increase of pollutants, group of pollutants or indicators of pollution resulting from the impact of human activity. According to the WFD Article 4, any significant and sustained upward trends need to be reversed by implementing measures to progressively reduce the pollution and prevent further deterioration of groundwater quality, as requested by the GWD Article 5. To verify the statistical significance of upward trends, EU Member States use different approaches, e.g., the parametric or the non-parametric statistical tests (Grima et al., 2015; Gourcy and Lopez, 2019). Furthermore, any statistically significant trend, which may lead to failure to achieve one or more environmental goals, defined by the Water Framework Directive, can be interpreted as environmentally significant trend (Commission of the European Communities, 2009). Some EU member states consider a trend as environmentally significant if a trend line of pollutant concentrations, obtained from measured or extrapolated data, exceeds the threshold value (TV) or some predetermined percentage of TV for that pollutant (Gourcy and Lopez, 2019; Frollini et al., 2021).

The Tier 2 RA of not meeting the requirements of implementing measures to reverse trend objective considers the long-term impact of man-made activities. It extensively addresses prediction uncertainty inherent to data variability and/or high percentage of limit of quantification (LOQ) or limit of detection (LOD) values in data set and is carried out by using temporal and spatial criteria for aggregating data from individual monitoring stations (Fig. 2) to assess statistically and environmentally significant trends of pollutants or indicators of pollution at a GWB or a monitoring station (MS) level (Fig. 3).

Homogeneity of groundwater monitoring network, reflecting spatial representativity of monitoring stations, is a basis for statistical or trend assessment of monitoring data (Grath et al., 2001; Hosseinimarandi et al., 2014; Thakur, 2017; Farlin et al., 2019; Sarris et al., 2022). To assess the homogeneity of monitoring network, the Tier 2 RA data aggregation procedure apply Representativity Index, R_u, defined as the average minimum distance between any location in the area to the closest sampling site and expressed as percentage of the average minimum distance for an optimal network (Grath et al., 2001):

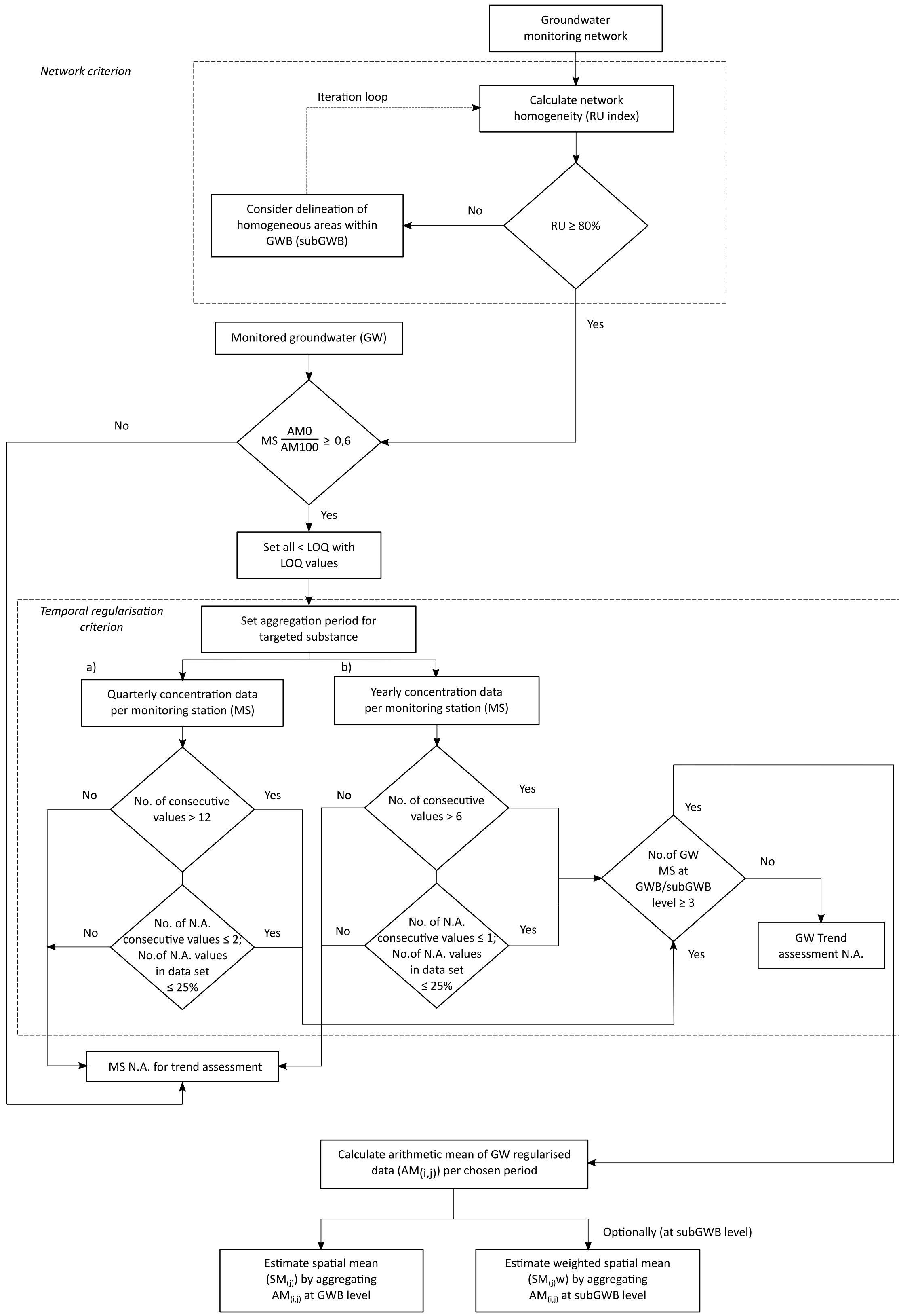
$$R_U = \frac{37,7}{dist_{ave}\sqrt{\frac{k}{Area}}}\ [\%] \quad [3]$$

where k is number of sampling sites; $dist_{ave}$ is average minimum distance between any location in the area to the closest sampling site; *Area* is the size of the investigated area. However, the spatial representativity of a monitoring network can be guaranteed only in homogeneous units or areas within a natural system, in relation to hydrogeological, hydrogeochemical or climatological characteristics. The importance of applying the principle of homogeneity, especially when determining natural background concentrations in groundwater systems, is noticed by numerous researchers (Matschullat et al., 2000; Wendland et al., 2005; Müller et al., 2006; Molinari et al., 2012). To satisfy the *criterion of homogeneity of groundwater monitoring network*, a hydrogeologically heterogeneous GWB can be divided into homogeneous sub-bodies.

Following the recommendations from Grath et al. (2001), the Tier 2 RA data aggregation procedure consists of temporal regularisation of concentration data for each monitoring site and a spatial aggregation of the regularised data at a GWB or sub-bodies level. *Temporal regularisation criterion* is fulfilled if number of consecutive quarterly or annual concentration data for targeted substance at each sampling site is equal or higher than twelve or six respectively, or number of not available (NA) consecutive quarterly or annual concentration data for targeted substance at each sampling site is equal or less than two or one respectively (Fig. 2). *Spatial regularisation criterion* is fulfilled if the number of monitoring sites at a GWB or sub-bodies level is equal or higher than three and the ratio of arithmetic mean of concentration data at each sampling site, for all values < LOQ set to 0 (AM0), and arithmetic mean of concentration data at each sampling site, for all values < LOQ set to LOQ (AM100), is equal or higher than 0.6. Spatial aggregation of arithmetic mean of regularised concentration data ($AM_{(i,j)}$) per monitoring site is conducted by estimating spatial mean ($SM_{(j)}$) or weighted spatial mean ($SM_{(j)}w$), respectively the kriging mean, by aggregating $AM_{(i,j)}$ at a GWB or sub-body level.

An assessment of statistically and environmentally significant trends of pollutants or indicators of pollution at a GWB or at a MS level is carried out in two steps. First, linear regression is applied to determine the existence of a statistically significant trend (SST), and if it is proven, then regression line is extrapolated into the future to assess an environmentally significant trend (EST) (Fig. 3).

The starting point for trend assessment of time series of arithmetic mean ($AM_{(j)}$) of groundwater concentration data and/or of time series of spatial mean ($SM_{(j)}$) or weighted spatial mean ($SM_{(j)}w$) of groundwater concentration data is determined, according to the GWD Article 2, as a *baseline value*, referring to an average value of concentration data



Note:
GWB - groundwater body;
LOQ - limit of quantification;
AM_0 - arithmetic mean of concentration data, all values <LOQ set to 0;
AM_{100} - arithmetic mean of concentration data, all values < LOQ set to LOQ ;
$AM_{(i,j)}$ - arithmetic mean of concentration of (j) substance at (i) monitoring station;
$SM_{(j)}$ - spatial mean of concentration of (j) substance at (i) monitoring stations;
$Sm_{(j)w}$ - weighted spatial mean of concentration of (j) substance at (i) monitoring stations.

Fig. 2. Roadmap for applying temporal and spatial criteria for aggregating data used to conduct trend analysis.

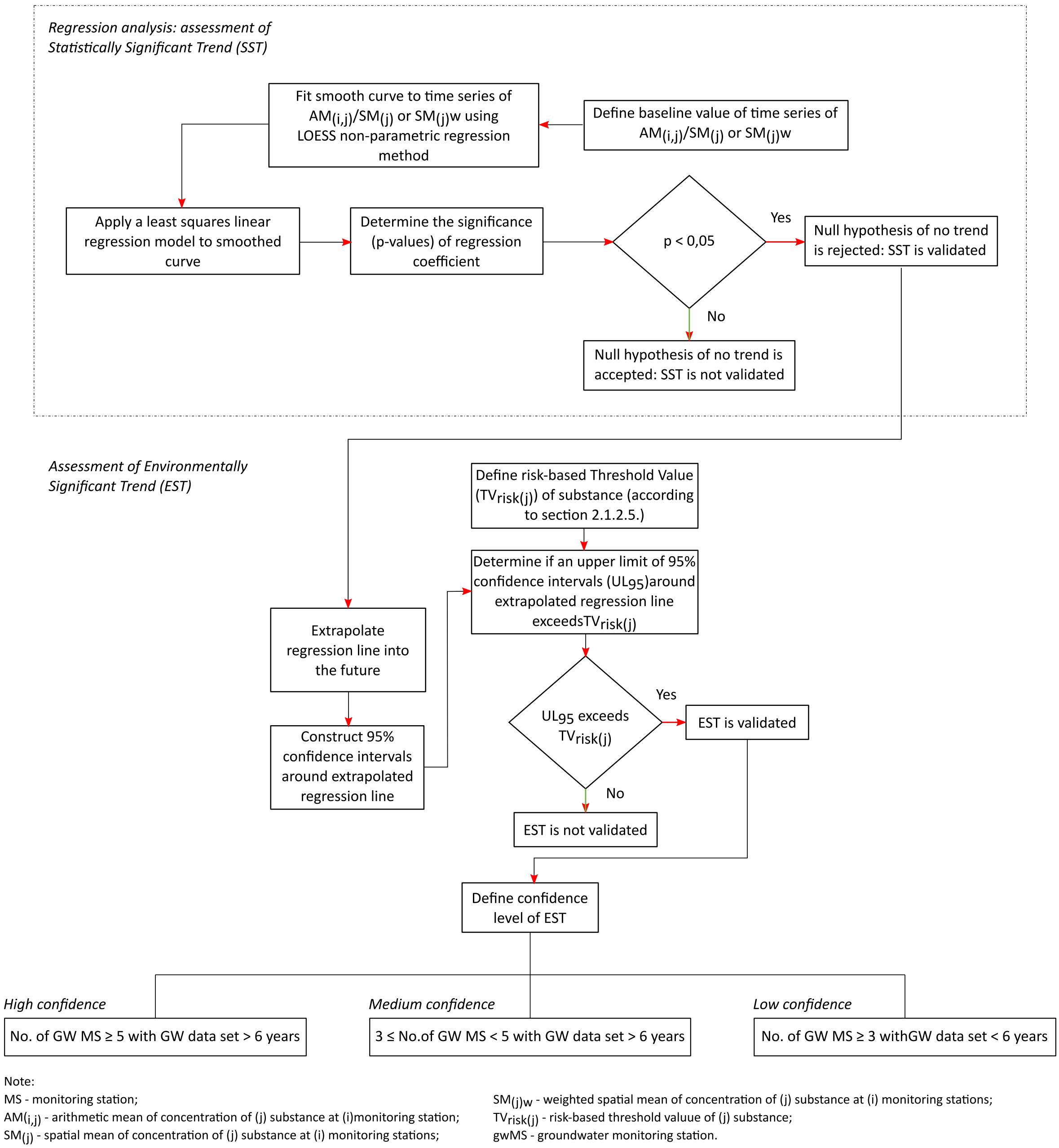


Fig. 3. Roadmap for conducting statistically and environmentally significant trend analysis.

calculated for the first aggregation period (quarter or year) for which a *temporal regularisation criterion* of data aggregation procedure is fulfilled. To reduce the impact of large and medium-sized deviations or outliers in the data on trend estimation, it is effective to use LOESS non-parametric regression as a data smoothing method, which combines the simplicity and pragmatics of linear regression with the flexibility of nonlinear regression (Cleveland, 1979; Cleveland and Devlin, 1988; Jacoby, 2000). The LOESS method fits simple models (for example, polynomials of the first or second degree) to local subsets of the data, which it then fits into a continuous curve that well describes the deterministic variation of the data. The procedure to fit smooth curves to time series of arithmetic means of regularised concentration data ($AM_{(i,j)}$) and to time series of spatial means ($SM_{(j)}$) or weighted spatial means ($SM_{(j)}w$) is described in Section S1.

To estimate whether statistically significant trend may lead to failure to achieve one or more environmental goals, defined by the WFD, firstly a regression line is extrapolated within one planning cycle of the RBMP, in accordance with the risk assessment time frame defined by the WFD and the GWD, depending on the length of the time series of measured data. To reduce the impact of the variability of spatial mean ($SM_{(j)}$) or weighted spatial mean ($SM_{(j)}w$) of groundwater concentration data, 95% confidence intervals around extrapolated regression line is determined (Fig. 4), applying the procedure described in Section 1.

The environmentally significant trend is confirmed if an upper limit of 95% confidence intervals around extrapolated regression line exceeds a risk-based threshold value of substance *j* ($TV_{risk(j)}$). Following recommendations from the WFD guidance document No. 26 (Commission of the European Communities, 2010), a $TV_{risk(j)}$ is determined in accordance with the *precautionary principle* (EU, 2000a), which may be implemented if there is a risk of detrimental effects on groundwater quality resulting from human influence and if it is not possible to determine the risk of failure to achieve one or more environmental goals, defined by the WFD, with a high degree of confidence. Considering that a risk-based threshold value is necessary for applying the

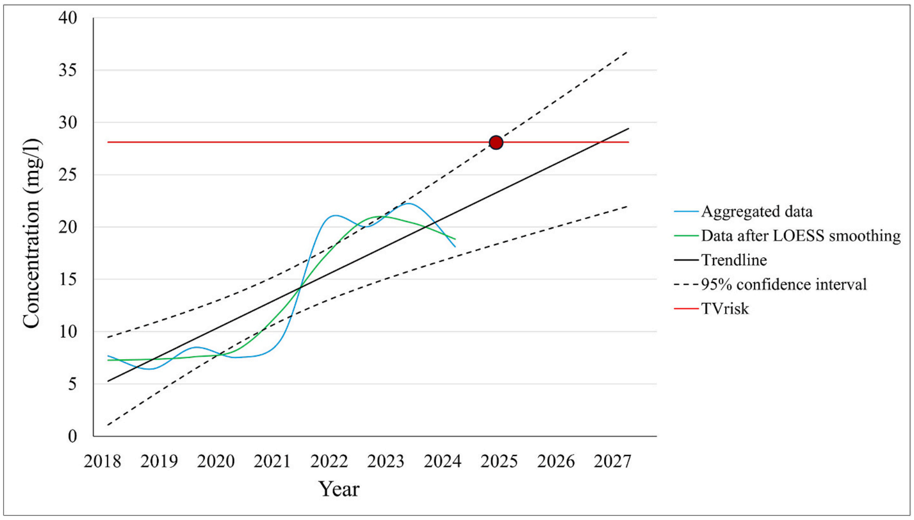


Fig. 4. Assessment of environmentally significant trends.

risk-based classification tests used in RA of not meeting the environmental objective "Achieve good groundwater chemical status", it is presented in detail in Section 2.1.2.3.

To validate the environmental significance of trend of pollutants or indicators of pollution, the confidence level of EST is estimated using criteria applied by some EU member states (Gourcy and Lopez, 2019), considering the length of time series of spatial mean ($SM_{(j)}$) or weighted spatial mean ($SM_{(j)}w$) of groundwater concentration data and density of the monitoring network at GWB or sub-body level (Fig. 3).

If the CL of trend assessment is high, then the Tier 2 RA of not meeting the requirements of this objective continues with trend reversal assessment, if appropriate. Considering that the RA of not meeting the requirements of implementing measures to reverse trend objective is closely related to the RA of deterioration of groundwater quality status (Commission of the European Communities, 2010), which is, in the tiered approach to RA described and tested in this paper, based on *trend reversal* and *significant pressure criteria*, a trend reversal assessment procedure is presented in the following Section 2.1.2.2.

2.1.2.2. Prevent GWB status deterioration objective. Article 3 of the GWD stipulates that the assessment of the groundwater chemical status is carried out using EU groundwater quality standards and threshold values established by EU member states for pollutants, groups of pollutants and pollution indicators that have been determined to contribute to the body or group of groundwater bodies being at risk of not achieving good status. Inherent to the procedure set out in Part A of the Annex II of the GWD, threshold values are directed towards the protection of GWDTE and surface waters, but also to the protection of drinking water and others legitimate types of water use. Accordingly, chemical status assessment is carried out against relevant classification tests that address different set of receptors at risk (Commission of the European Communities, 2009) and the risk of failing the "prevent GWB status deterioration" objective can be assessed through characterization of impact of pressures at different scales. Since numerous studies have indicated significant time lags between direct or indirect input of pollutants and impact on groundwater, reflected through deterioration of the chemical composition due to pollution (Meals et al., 2010; Lapworth et al., 2012; Vero et al., 2018; Pérez-Lucas et al., 2018; Kim et al., 2020; Castaldo et al., 2021), it might be expected that some GWB deteriorate from good to poor chemical status (Commission of the European Communities, 2010). In that sense, the Tier 2 RA of not meeting "prevent GWB status deterioration" objective is carried out by using criteria that differ depending on whether the GWB is in good or not of good chemical status.

For a GWB of good chemical status, the Tier 2 RA procedure is based on *exceedance* and *significant and sustained trend criteria* (Fig. 5). It results from the requirements of assessing groundwater chemical status from the Annex III of the GWD. The aim is to estimate the extent of the GWB having an annual mean arithmetic concentration of pollutant higher than relevant groundwater quality standard (QS_{GW}) or higher than groundwater threshold value (TV_{GW}), which is determined as a part of the regular procedure of carrying out the "General Quality Assessment" (GQA) test to assess the chemical status of the GWB (Commission of the European Communities, 2009). The *exceedance* criterion is complemented by trend analysis carried out against risk-based QS_{GW} or TV_{GW} defined with reference to the precautionary principle set by the Communication from the Commission on the precautionary principle (EU, 2000a) and CIS guidance document No. 26 (Commission of the European Communities, 2010).

The first step of the RA procedure, based on *exceedance criterion*, is calculation of (Fig. 5): a) the arithmetic mean (AM_{ij}) of the concentration of substance *j* that contribute to a body of groundwater being at risk of not achieving the environmental objectives for groundwater for each monitoring site *i* and b) the spatial mean (SM_j) of the concentration of substance *j*, that is AM of the AM_{ij} to estimate the arithmetic mean of substance *j* at the level of a GWB, using the appropriate aggregation procedure, described in Section 2.1.2.1., of monitoring results at an individual monitoring site level and at the level of a GWB. Following the calculation of AM_{ij} and SM_j, the extent of exceedance of appropriate QS_{GW} or TV_{GW} values is determined by comparing: a) AM_{ij} of the concentration of substance *j* with QS_j and/or TV_j values defined for the assessment of groundwater chemical status by the "General quality assessment test", proposed by the CIS guidance document No. 18 (Commission of the European Communities, 2009), and b) SM_j of the concentration of substance *j* with QS_{risk} or TV_{risk} values defined for the RA of not meeting environmental objectives related to protection of human health and groundwater itself by the risk-based "General quality assessment test". In the next step, the procedure based on the *significant and sustained trend criterion* is carried out by assessment of the statistically and environmentally significant trends (SST, EST) of substance *j* at the level of a GWB. It is determined whether an upper limit of 95% confidence intervals around extrapolated regression line (UL_{95}) exceeds QS_{risk} or TV_{risk} values during 6-year cycle of RBMP.

For a GWB of not of good chemical status, the Tier 2 RA procedure is based on *trend reversal* and *significant pressure criteria* (Fig. 6). Trend reversal assessment is used to test the fulfilment of requirements from the Article 5 and Annex IV of the GWD to reverse trends which present significant risk of harm to the, inter alia, quality of human health or

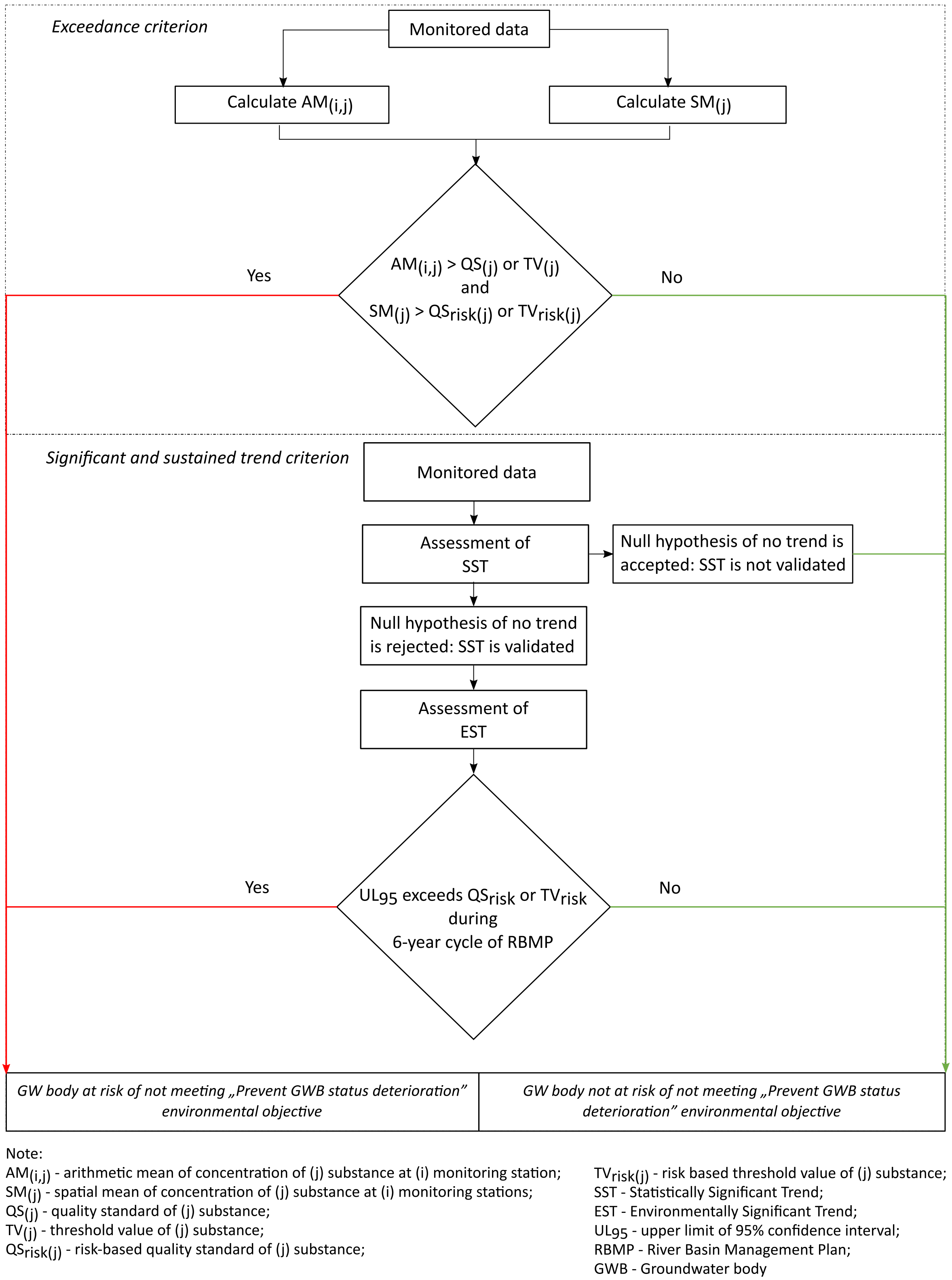


Fig. 5. Roadmap for applying exceedance and significant and sustained trend criteria used to characterize the risk of status deterioration for GW body of good chemical status.

legitimate uses of groundwater.

Testing the significance of the break in an upward trend of the concentration of substance *j* at the level of GWB, by the test statistic F in the Two-sections model proposed by Grath et al. (2001), may be carried out in cases when the concentration of substances reaches the starting point for trend reversal. In the Tier 2 RA procedure the starting point is identified as 75% of the parametric values of risk-based QS_{GW} or TV_{GW} defined with reference to the precautionary principle, considering the guideline from the Annex IV, part B of the GWD. Significant pressure assessment, which is carried out as a part of the Tier 2 RA procedure

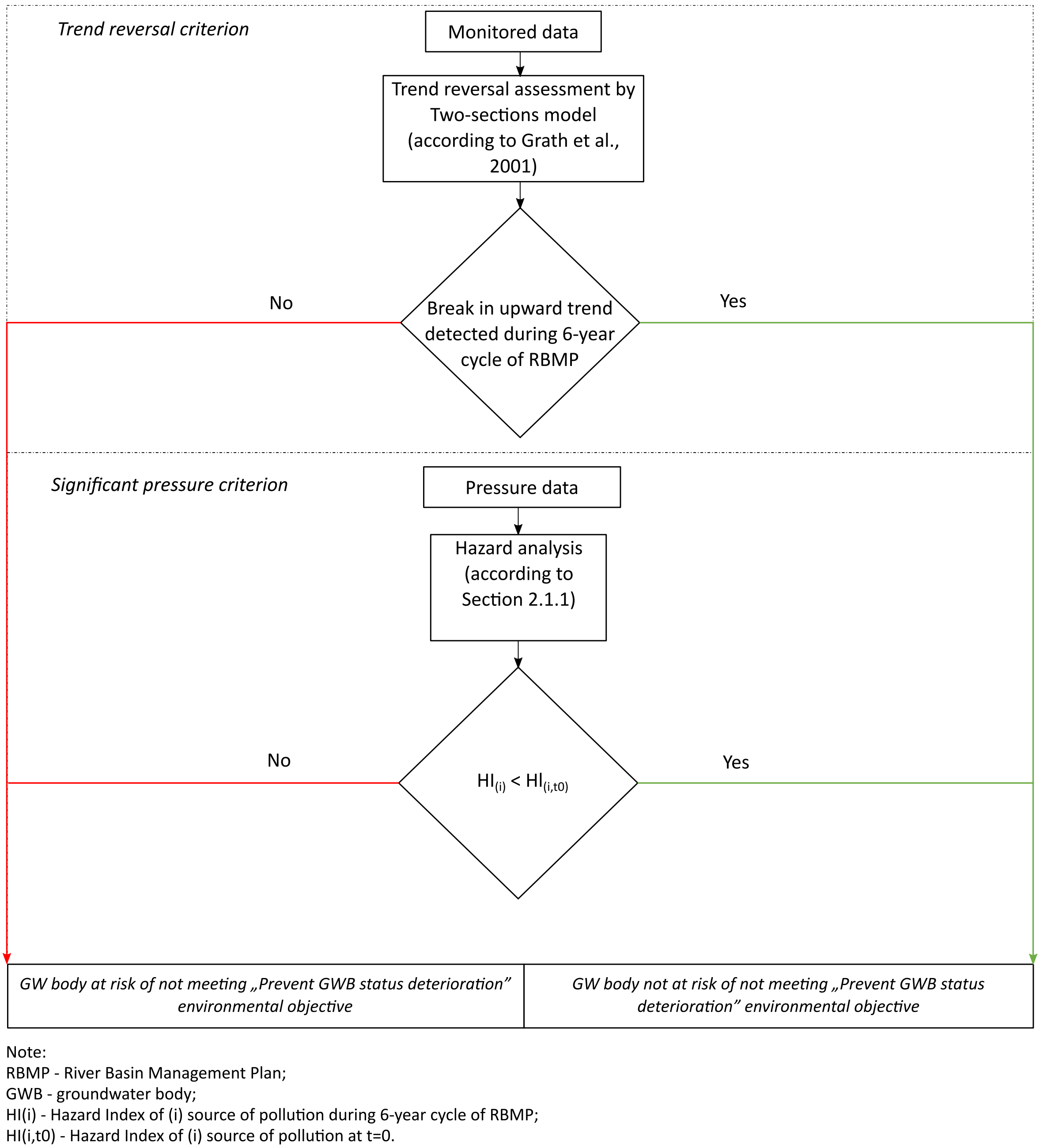


Fig. 6. Roadmap for applying trend reversal and significant pressure criteria used to characterize the risk of status deterioration for GW body not of good chemical status.

through the hazard analysis, is used to test the fulfilment of requirements from the Article 6 of the GWD to prevent the input into groundwater of hazardous substances or limit the input into groundwater of non-hazardous substances, listed in Annex VII to the WFD. The hazard analysis, described in Section 2.1.1, is carried out to assess the risk of harm to the quality of human health or legitimate uses of groundwater that, according to the CIS guidance document No. 26 (Commission of the European Communities, 2010), is associated with: a) a failure to have a sufficient prevent and limit measures in place and/or b) residual pollution in unsaturated or saturated zones that could impact in time the chemical status of GWB because of time lags between direct or indirect input of pollutants and impact on groundwater.

2.1.2.3. Achieve good chemical status objective. The Tier 2 RA of not meeting "Achieve good chemical status" objective, described and tested in this paper, is based on the application of appropriate risk-based classification tests for DWPA and groundwater, in which groundwater chemical data collected over the previous RB planning cycles are used to assess the risk of not meeting the good chemical status for each applied test. To undertake the risk assessment for the next planning cycle, the baseline conditions from which this assessment can take place is to be defined (Commission of the European Communities, 2010). In the Tier 2 RA procedure, it is carried out by comparing the arithmetic and/or spatial mean value of a pollutants or indicators of pollution that contribute to the body or group of groundwater bodies being at risk of not achieving good chemical status substance with respective risk-based TV_{GW}, in combination with an assessment of statistically and environmentally significant trends of pollutants or indicators of pollution at the monitoring site level. The RA procedure, based on the use of risk-based classification tests, addresses outliers and/or high percentage of LOQ or LOD values in data set applying set of *network criterion* and *temporal and spatial criteria* for aggregating data from individual monitoring stations described in section 2.1.2.1. and in Fig. 2.

The Groundwater Directive (EU, 2006) establishes specific measures for the prevention and control of groundwater pollution, which includes the adoption of common criteria for the chemical status and risk assessment, based on groundwater quality standards (QS), which are adopted at the EU level, and threshold values (TV) of pollutants, which are determined by EU member states. The EU research project BRIDGE (Background cRiteria for the IDentification of Groundwater thrEsholds) proposed the tiered approach for determining TV (Müller et al., 2006; Hinsby et al., 2008) to support the development of common methodology for EU member states. It is implemented in the CIS guidance document No. 18 (Commission of the European Communities, 2009) and includes application of both background level (for naturally occurring substances) and a relevant "reference value" for receptors outlined by a conceptual model of GWB (Hinsby et al., 2008), which may be drinking water standard (DWS), if drinking water is a relevant receptor in GWB, or in cases of other legitimate or environmental use, any other type of environmental quality standards (EQS). In this paper we modified the tiered approach for determining TV proposed by the BRIDGE project. We developed our own approach to determine background levels, and threshold values are defined with reference to the precautionary principle, which is set by the Communication from the Commission on the precautionary principle (EU, 2000a) and CIS guidance document No. 26 (Commission of the European Communities, 2010). This principle, in essence, require that emphasis should be placed on dealing with the causes, rather than the results, of environmental damage (Quevauviller, 2007).

Background level (BL) can be defined as a relative measure for distinguishing between natural and anthropogenically conditioned concentrations of an element or compound in a real set of samples (Matschullat et al., 2000) and is a consequence of the interaction between the rock matrix and water, chemical and biological processes in unsaturated and saturated zone, groundwater retention time and chemical composition of precipitation (Preziosi et al., 2014). Article 2 of the GWD specifically defines the background value as: "the concentration of a substance or the value of an indicator in a body of groundwater corresponding to no, or only very minor, anthropogenic alterations to undisturbed conditions".

The BRIDGE project proposed the use of two methods for determining BL. The Component separation method is based on the separation of the relative frequency of the concentration of a chemical substance into natural and anthropogenic components, which are modelled by separate distributions, and is applied when a large amount of data is available for a chemical substance (Wendland et al., 2005). The Pre-selection method is used in cases where a limited set of data is available and when chemical samples show no or very little human influence (Hinsby et al., 2008). It is applied by numerous researchers (Griffioen et al., 2008; Coetsiers et al., 2009; Gemitzi, 2012; Voutchkova et al., 2021).

Considering that the chemical composition of groundwater is a reflection of the cumulative effect of both natural processes that cause significant natural variability of chemical substances (Kwiatkowski, 1991; Matschullat et al., 2000), as well as pollution due to the influence of human activities (Edmunds and Shand, 2008), it is imperative to investigate a large number of samples in order to distinguish the effects of natural and anthropogenic factors on the chemical composition of groundwater (Voigt et al., 2005). Most of the scientific and technical problems associated with the assessment of variability of chemical composition can be successfully addressed by applying model-based objective methods, which are based on the separation of a set of measured data into subgroups with characteristic probability density functions that reflect relevant natural geochemical processes and/or pollution events in an area (Sinclair, 1991). Some researchers (Reimann and Garrett, 2005; Kelly and Panno, 2008) believe that natural background concentrations of chemical substances no longer exist due to human influence on the entire planet, even in areas that are generally considered to be "untouched" by human activity. Motivated by the thought that in many parts of the world the influence of man on the environment has been present for such a long time that it is pointless to try to determine the natural background concentrations of substances in groundwater, Reimann and Garrett (2005) devised the concept of *ambient background levels* (ABL), which describes immeasurably disturbed and no longer intact background concentration of substances in groundwater, which is the result of long-term human influence on all environmental compartments.

In the tiered approach to RA we use selected method belonging to the group of model-based objective methods to determine ABL, in accordance with the concept proposed by Reimann and Garrett (2005), in a GWB or sub-GWB that meets the condition of hydrogeochemical homogeneity (Fig. 7), following the recommendations of researchers (Matschullat et al., 2000; Preziosi et al., 2010; Molinari et al., 2012), who point out that the geochemical background concentration of a chemical substance needs to be determined in spatial conditions characterized by homogeneous, mainly climatological, lithological and pedological characteristics.

Based on results of statistical simulation study, in which we compared the reliability and robustness of several model-based objective methods based on common criteria (Nakić et al., 2018), we have selected the Lepeltier method (LM) for determining ABL for the purpose of the Tier 2 RA of not meeting "Achieve good chemical status" objective. LM analyzes a deviation from the log-normal distribution on a graph with logarithmic scales (Lepeltier, 1969), which is displayed as a sudden change, so-called "elbow" in the graph, and all values that are less than or equal to that point, of sudden change, are the result of the cumulative effect of natural processes that cause significant natural variability. In the original work of Lepeltier (1969), the background level was determined graphically as the mean value of the range of concentrations smaller than or equal to x, however, in this paper, after defining the range of concentrations smaller than or equal to x (Fig. 8), its $\mu + 2\sigma$ was calculated, following the approach described by Matschullat et al. (2000). The determined upper limits of data dispersion are accepted as UL of background level of a substance.

The confidence level (CL) of determining ABL by model-based LM, defined from a statistical simulation study (Nakić et al., 2018), is showed in Table S1. It is based on two criteria, the number of data (N) and the proportion of < LOQ values (in %) in statistical sample, considering the guidelines from the literature (Lepeltier, 1969; Matschullat et al., 2000) indicating the minimum number of data that must be used to define an ABL of substance with a high CL.

In cases where, due to a small number of available data and/or a significant proportion of < LOQ or < LOD values in the data set, it is not advisable to use LM, then the Preselection method (PM) is applied to estimate the background levels, which was designed within the framework of the BRIDGE project. It assumes that concentrations of certain pollution indicators can indicate on the presence or absence of anthropogenic influences at locations where sampling is carried out for the purposes of determining BL. In cases where the concentrations of pollution indicators exceed some predefined value, then the sample is considered polluted and excluded from the further procedure (Müller et al., 2006). The process of identification and possible exclusion of polluted samples includes the criteria described in Section S1.

Relevant "reference values", i.e., their aliases, "criteria values" as defined by the CIS guidance document No. 18 (Commission of the European Communities, 2009), are determined for targeted substances (TS) that contributes to the risk of not meeting environmental objectives

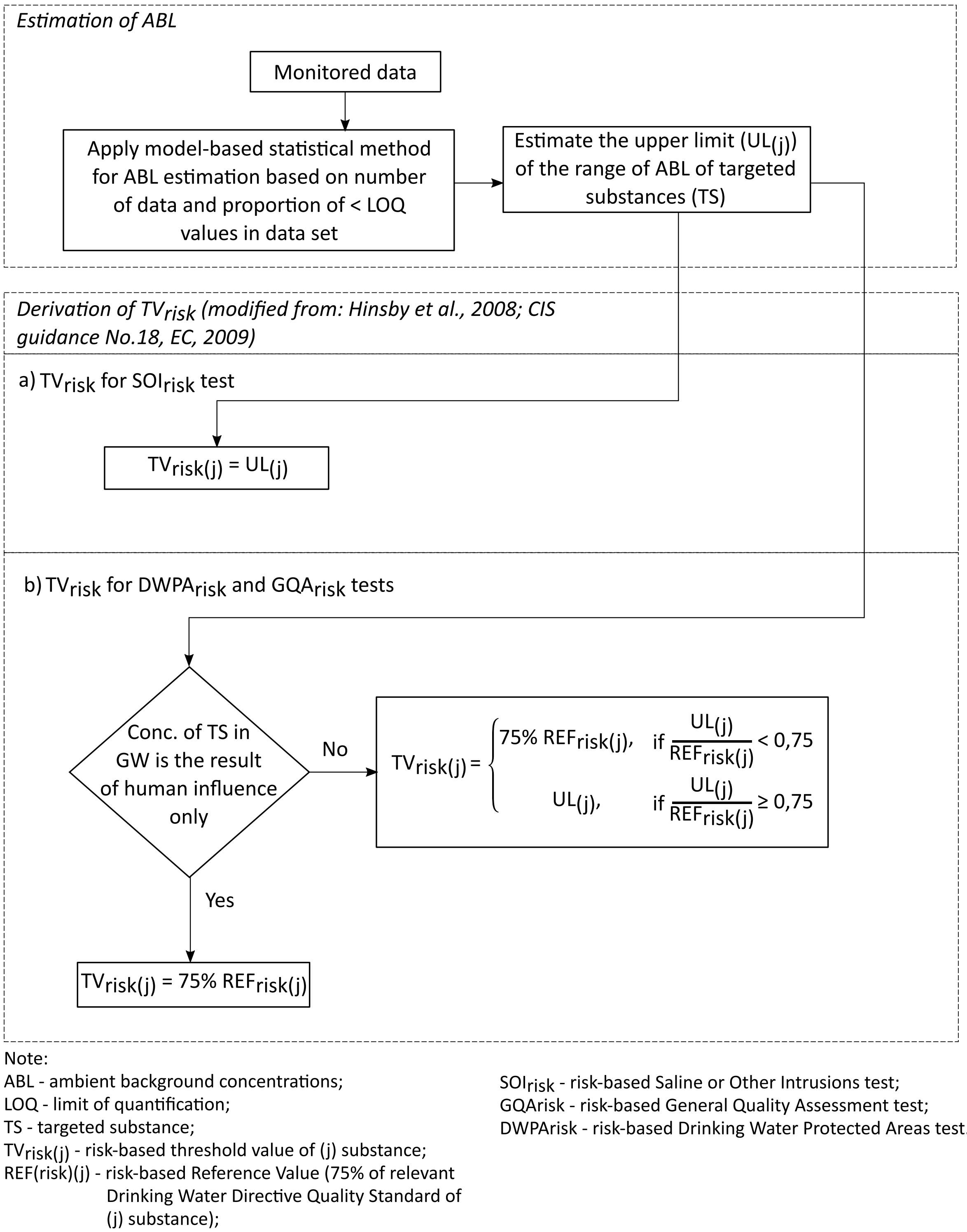


Fig. 7. Roadmap of determining ambient background levels and risk-based threshold values of substances in the tiered approach to risk assessment.

of the WFD related to protection of DWPA and groundwater itself, for each receptor that is potentially at risk, modifying the procedure described in Hinsby et al. (2008) and the CIS guidance document No. 18. If groundwater is used for a specific purpose, such as drinking water or industrial water or water for irrigation, then the "risk-based reference values" of TS are determined with reference to the precautionary principle (EU, 2000a; Commission of the European Communities, 2010), by applying "usage criteria", as 75% of a relevant drinking water standard of TS for a protection of drinking water in DWPA or as 75% of some other quality/usage standard if the water is used for some other purpose. The 75th percentile of the water quality standard is introduced into the Tier 2 RA procedure as a "safety factor", in line with conclusions of Marsland and Roy (2015), because risk-based QS_{GW} or TV_{GW} for targeted substance j is not compared with measured concentrations of substance j at monitoring station i, but rather with the arithmetic and/or spatial mean values of the concentrations of substance j, which are aggregated at the level of the monitoring station i or at the level of a GWB respectively. If there is a risk of salinization, i.e., intrusion of salt

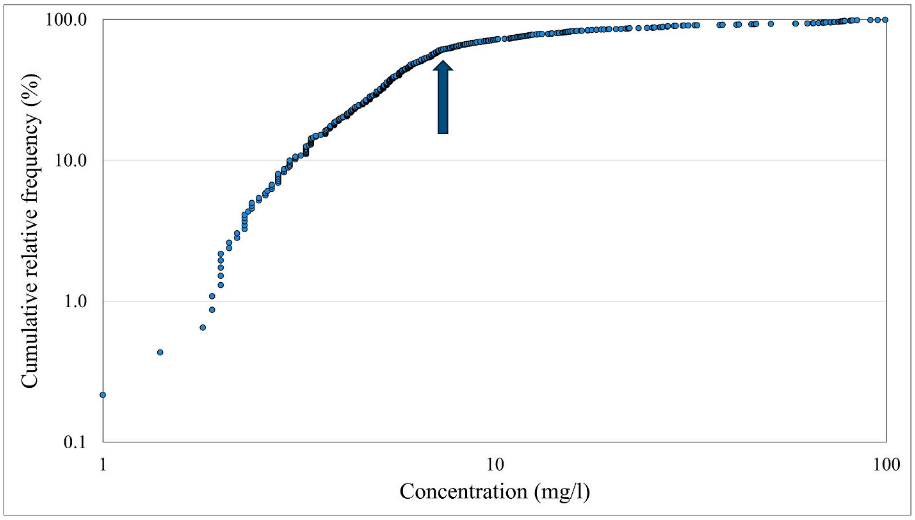


Fig. 8. Cumulative relative frequencies of concentrations of substance *j* at the level of a groundwater body.

water or some other similar intrusion caused by natural processes, which deteriorate groundwater quality, the reference value is determined, by applying the relevant "environmental criteria", as the UL of the ABL range of the relevant indicator of salinity or other intrusions of natural origin, for example saline intrusion from geological sources.

Risk-based threshold values of targeted substances (TV_{risk}) are determined for carrying out risk-based classification tests for groundwater itself and DWPA. For the "Saline or other intrusions (SOI_{risk})" classification test, the TV_{risk} of targeted substance *j,* which may be a relevant intrusion indicator like sulphate, chloride, or electrical conductivity, is equal to its respective "risk-based reference value" and is determined as the UL of the ABL range of measured concentration of substance *j* (Fig. 7). For the "Drinking Water Protected Areas ($DWPA_{risk}$)" and "General Quality Assessment (GQA_{risk})" classification tests, the procedure for determining the TV_{risk} of targeted substance *j* depends on its origin (Fig. 7). If concentrations of TS in groundwater are results of human influence only, then:

$$TV_{risk(j)} = 75\%\ REF_{(risk)(j)} \quad [4]$$

where $REF_{(risk)(j)}$ is a risk-based reference value of a substance *j*. If concentrations of TS in groundwater are results of natural conditions and human influence, then:

$$TV_{risk(j)} = \begin{cases} 75\%\ REF_{(risk)(j)},\ \text{if}\ \dfrac{UL_{(j)}}{REF_{(risk)(j)}} \langle 0,75 \\ UL_{(j)},\ \text{if}\ \dfrac{UL_{(j)}}{REF_{(risk)(j)}} \geq 0,75 \end{cases} \quad [5]$$

where $UL_{(j)}$ is the upper limit of the ABL range of a substance *j* (Fig. 9).

The Tier 2 RA procedure for risk-based classification tests, SOI_{risk}, $DWPA_{risk}$ and GQA_{risk}, is shown in Fig. 10.

SOI_{risk} test is carried out by comparing arithmetic mean values of TS, intrusion indicators, with respective risk-based TV_{GW}, in combination with an assessment of statistically and environmentally significant trends of intrusion indicators at the monitoring site (MS) level. $DWPA_{risk}$ test is carried out by comparing arithmetic mean values of TS, pollutants or indicators of pollution, with respective risk-based TV_{GW}, in combination with an assessment of statistically and environmentally significant trends of pollutants or indicators of pollution at the MS level. During the implementation of both tests, $DWPA_{risk}$ and SOI_{risk}, it is determined whether the requirements from Article 7.3 of the WFD, which refer to avoiding deterioration of groundwater quality to reduce the level of treatment required, have been met. The GQA_{risk} test is carried out by comparing arithmetic and spatial mean values of a TS, pollutants or indicators of pollution, with respective risk-based TV_{GW}. An integral part of the GQA_{risk} and SOI_{risk} tests is the *extent of exceedance*

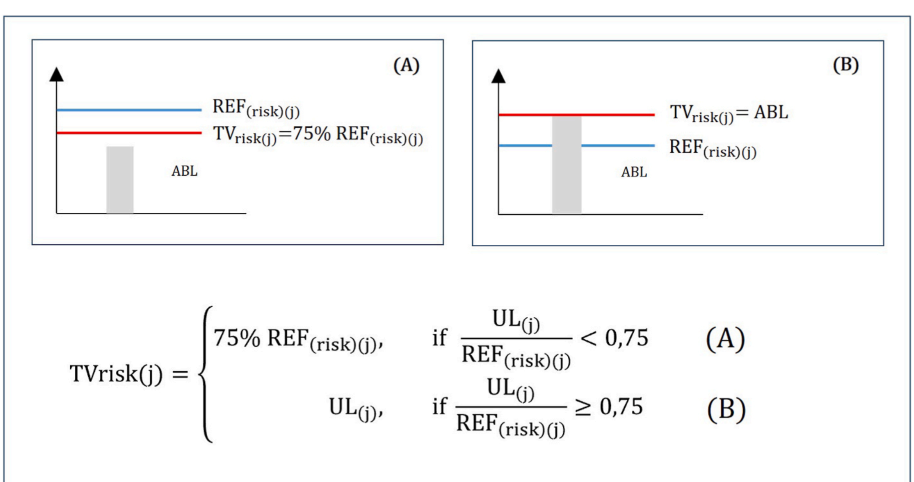
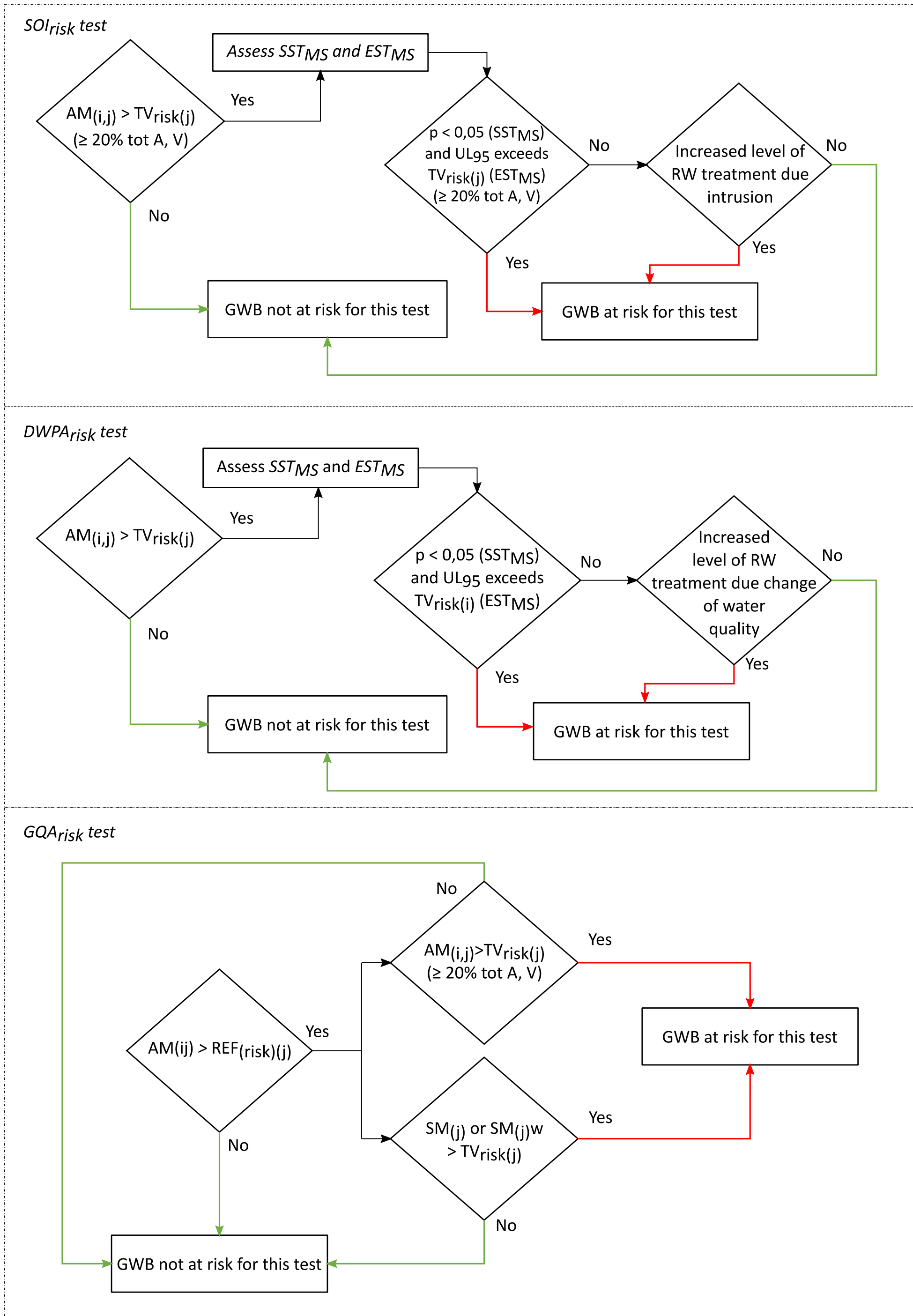


Fig. 9. Assessment of risk-based threshold values for substances of natural and anthropogenic origin.



Note:

SOI_{risk} - risk-based Saline or Other Intrusions test;
GQA_{risk} - risk-based General Quality Assesment test;
$DWPA_{risk}$ - risk-based Drinking Water Protected Areas test
$AM_{(i,j)}$ - arithmetic mean of concentration data of (j) substance at (i) monitoring station;
$SM_{(j)}$ - spatial mean of the concentration of (j) substance at the GWB level;
$SM_{(j)w}$ - weighted spatial mean of the concentration of (j) substance at the GWB level;
$TV_{risk(j)}$ - risk-based threshold value of (j) substance
$REF_{(risk)(j)}$ - risk-based Reference Value (75% of relevant Drinking Water Directive Quality Standard of (j) substance);
A - surface of the groundwater body;
V - volume of the groundwater body;
SST_{MS} - Statistically Significant Trend at the level of monitoring station;
EST_{MS} - Environmentally Significant Trend at the level of monitoring station;
UL_{95} - upper limit of 95% confidence interval;
RW - raw water (pumped water);
GWB - groundwater body.

Fig. 10. Roadmap of the Tier 2 RA procedure for risk-based classification tests.

criterion (C_{ee}) of the "General quality assessment test" that is developed for an assessment of groundwater quality status (Commission of the European Communities, 2009). If arithmetic mean value of one or more TS exceeds a respective risk-based TV_{GW} or environmentally significant trend (EST) of one or more TS has been confirmed (for the purpose of carrying out the SOI_{risk} test) at the level of MS that are representative of more than 20% of the total area or volume of a GWB, then a GWB is at risk for these tests.

2.2. Hydrogeological setting

The GWB CSGI_29 is one of the fifteen groundwater bodies in the Pannonian part of Croatia identified in the "River Basin Management Plan of the Republic of Croatia" (HR, 2023). Geographically, it is in the Sava River valley in the eastern part of Croatia and extends for about 3330 km^2 (Fig. S1).

Within this GWB, the number of aquifers ranges from two, near the Sava River, to eleven in the northern part of the Sava River depression (Fig. S2). The main characteristics of this series of aquifers are the high share of permeable layers in the total thickness of sediments and relatively low mineralization of water (Kopić, 2016). The thickness of the single aquifers is rarely greater than 30 m (Ujević et al., 2010). The aquifer thickness decreases from the Sava River to the north, while the content of fine sediments, specifically sand and silt, increases (Kopić, 2016). Shallow unconfined and deeper semi-confined and confined aquifers are of Quaternary age. The gravelly and sandy aquifers near the Sava River are found at depth of 20–70 m (Nakić et al., 2020). These fan-shape coarse grained clastic sediments were deposited during warm and humid interglacial periods with high water energy. Fine grained sand, silt and clay were deposited during cold water periods with low water energy (Mutić, 1993; Brkić et al., 2016). The thickness of the overlying silty-clay or sandy-silty deposits is less than 10 m along the Sava River and towards the north it significantly increases up to 40 m. Due to the large aquitard thickness, the natural vulnerability of aquifers, estimated by the SINTACS method, is moderate to low (HR, 2023). The exception is the narrow area along the Sava River, with increased aquifer vulnerability. The aquifer bedrock consists of poorly permeable clay at a depth of 80–85 m.

Based on the measurement of tritium contents at locations far from the Sava River to the north, Brkić et al. (2016) found that the relative mean residence time of groundwater is prior to 1950s. Groundwater flows towards the Sava River for most of the year, while groundwater recharge from the river occurs only during the high-water levels. The main source of the aquifer recharge is the infiltration of precipitation (Brkić, 2017).

Chemical composition of groundwater in deep aquifers of the Sava River depression is mainly controlled by natural processes, mostly by dissolution of carbonate and weathering of silicates in alluvial deposits (Mutić, 1993). High concentrations of arsenic, manganese, iron and ammonium frequently occur in groundwater indicating the existence of naturally reducing environment of aquifer systems (Kopić, 2016; Nakić et al., 2020). This condition is typical for the groundwater of the Pannonian Basin (Oreščanin, 2013) indicating an impact of lithological, sedimentological and palaeographic factors on groundwater geochemical composition (Rowland et al., 2011). Groundwater pollution caused by agricultural activity and urbanization has been recorded in shallow aquifers. Elevated concentrations of nitrogen, potassium and chloride in groundwater have been detected in aquifers that are in direct hydraulic connection with the Sava River (Brkić et al., 2016).

2.3. Land use and pressure data

Pollution pressure results from point (PP) and non-point (NPP) sources of pollution with potential to deteriorate groundwater quality and chemical status of the GWB. PP and NPP data sources in the study area originate from the GIS Web Feature Services of *Croatian Agency for Environment and Nature of Croatia* (CAEN, 2022). PP sources include locations of industrial plants, landfills, and data from the Croatian *Environmental Pollution Register* on wastewater discharge points and location of waste disposal into the environment (Fig. S3). By aggregating CORINE Land Cover Croatia layer from 2018 (CAEN, 2022) and geospatial data layer from the project "Impact of agriculture on surface and groundwater pollution in the Republic of Croatia" (Romić et al., 2014), five categories of land use categories have been obtained (Fig. S4). Based on (CAEN, 2022), 61% of the investigated area is used for agriculture, 32% is covered by forest, 5% are settlements and 2% are wetlands and water bodies. The category of artificial surfaces includes urban areas, industrial or commercial facilities, road and railway network and associated land, mineral exploitation sites, large landfills, and construction sites.

The unclassified hazard map (Fig. S5) indicates all hazards as geometrical objects organised in GIS environment. According to their spatial extension, three types of hazards are distinguished – point, line and polygon (areal, diffuse) hazards. All hazards are initially coloured red, before geospatial objects are assigned their attribute values necessary for the calculation of the Hazard Index (De Ketelaere et al., 2003).

2.4. Available chemical data sets

The risk assessment (RA) for the GWB CSGI_29 was based on groundwater chemical data from fourteen observation wells (Fig. S2) that were obtained from the national database of Croatian Waters: "National monitoring program of groundwater quality". Some of the observation wells are in the immediate vicinity of the active wellfields, Jelas and Trslana, from which groundwater is pumped with quantities of up to 400 l/s and 100 l/s respectively, and near the reserve wellfields, Otok and St. Jankovci, which, if necessary, individually pump up to 15 l/s.

To assess the homogeneity of monitoring network in the study area, Ru index was calculated applying the procedure explained by Grath et al. (2001). Ru index of groundwater quality monitoring network at the level of the GWB CSGI_29 is 62%, indicating sub-optimal (sub-homogeneous) monitoring network, meaning that estimated spatial mean values, obtained by data aggregation method, might be biased.

Chemical substances have been selected from the list of the substances indicated by the Annex I and II of the GWD (EU, 2006) and by the Commission Directive 2014/80/EU (EU, 2014), which amend Annex II of the GWD (EU, 2006). Annex I of the GWD specify nitrates (NO_3) and pesticides (and their metabolites) as groundwater quality standards at the EU level. Annex II specifically lists the substances which need to be considered when setting national groundwater quality standards (threshold values): a) substances or ions or indicators which may occur both naturally and/or as a result of human activities: arsenic (As), cadmium (Cd), lead (Pb), mercury (Hg), ammonium (NH_4), chloride (Cl), sulphate (SO_4), nitrites (NO_2), total phosphorus (P)/phosphates (PO_4); b) man-made synthetic substances: trichloroethylene (TCE), tetrachloroethylene (PCE); c) parameters indicative of saline or other intrusions: conductivity (EC). Following the recommendation of Müller et al. (2006), which proposed that determination of groundwater threshold values should also be carried out for naturally occurring substances that may occur in high concentrations due to human activity, iron (Fe) and manganese (Mn) have also been added to the list of TS for carrying out the RA. Both chemical species are particularly sensitive to change in redox condition due to groundwater abstraction that can lead to their elevated concentration in groundwater. In general, all substances that contribute to the groundwater body's risk of failing to meet the objectives set out in the Water Framework Directive may be used in a RA.

3. Results and discussion

3.1. GIS mapping-based hazard and risk analysis

The vulnerability map of the GWB CSGI_29 (Fig. S6) was obtained from the vulnerability map of the Pannonian region of Croatia (HR, 2023), which was developed by applying the SINTACS method. Fig. S6 indicates that most of the GWB has moderate to low potential to be vulnerable to pollution of the groundwater resources. The geospatial data from the vulnerability map reveal that only 0.32% of the study area is classified as very high, 18.28% as high, 57.60% as medium, 17.46% as low, and 6.34% as very low vulnerability.

The classified hazard map is shown in Fig. 11. Most of the geographical information systems store the data in specialized file structures and every layer or subclass can only include one type of shape (e.g. either points, lines, or polygons). Thus, it is generally expected that the hazards would be stored separately according to their spatial properties. It is also recommended that the hazards should be arranged in separate layers according to the hazard inventory list (De Ketelaere et al., 2003). Within one layer the data are organised in tables, in which the rows correspond to each of the individual hazards and the columns to their corresponding attributes. For the calculation and storage of the Hazard Index (HI), it is recommended that all required coefficients, including Hazard Index and the Hazard Index Class, be entered in separate columns in the attribute tables (Table S2). This data structure allows an easy way to display the different hazards with appropriate symbols, and in the colour corresponding to the relevant Hazard Index Class, according to the guidelines set by De Ketelaere et al. (2003).

The assessment of the ranking factor (Q_n) value of each hazard type defined in the hazard inventory list is carried out by grouping all possible values of the ranking factor (0.8 … 1.2) into three discrete values, specifically 1.2, 1.0 and 0.8, attributing the ranks of quantity of potentially toxic substances from particular hazard released to groundwater to different permeabilities of hydrogeological units of GWB CSGI_29, namely primary aquifers, secondary aquifers and areas without any significant aquifer respectively. Thus, each hazard receives only one discrete value depending on the geospatial location within the corresponding hydrogeological unit. Since the state of maintenance, preservation and security measures in hazard facilities or installations was unknown, it was not possible to estimate the probability of pollution from individual hazards. Therefore, in accordance with the guidelines proposed by De Ketelaere et al. (2003), reduction factors (Rf) for all hazards are set to 1.

The risk intensity map of the GWB CSGI_29 (Fig. 12) was developed by aggregating hazard and vulnerability indices point counting systems into log RII values that are classified in five RII classes showing the spatial distribution of the risk intensity. Risk map, after applying spatial tabular analysis, reveals that 67% of area has minimum risk (no or very low), low risk has only 2% of area, moderate has 12.4%, high has 13% and very high has 5.6%. Given that the area of the GWB CSGI_29, represented by high and very high risk (A_{MH}), is 18.6 % of the total area of GWB (A_{TOT}), that is $A_{MH} \leq 20\% \ A_{TOT}$, it may be concluded that it cannot be unequivocally determined that GWB CSGI_29 is at risk with high confidence level. According to criteria described in Section 2.1., the Tier 2 monitoring-based risk assessment (RA) is applied, and results are presented below.

3.2. Monitoring-based risk assessment

The Tier 2 monitoring-based RA of not meeting the environmental objectives defined by the Article 4 of the WFD was conducted using groundwater chemical data from the Croatian "National monitoring program of groundwater quality", which refer to the GWB CSGI_29. Number of samples, arithmetic means, data variability and proportions of <LOQ values in data set are indicated in Table S3. Since many chemical substances data contain a high proportion of <LOQ values, leading to non-fulfilment of both temporal and spatial regularisation criteria for those substances, the Tier 2 data aggregation procedure, applying quarterly concentration data, was carried out only for targeted substances (TS): EC, NH_4, total P, Cl, SO_4 and Mn, using data from monitoring stations (MS) that fulfil aggregation criteria (Table S3). A high data variability of EC and redox-sensitive substances (Fe, Mn) point out to the lithological and hydrogeochemical heterogeneity of aquifer system of the GWB CSGI_29, meaning that estimated ambient background levels (ABL) of naturally occurring substances at the level of GWB, might be biased. Namely, it is well known from the literature (Matschullat et al., 2000; Molinari et al., 2012) that background levels of substances, especially those that are sensitive to changes in oxidation-reduction conditions in aquifers, increase with depth. Furthermore, geochemical and hydrogeological stratification, even at

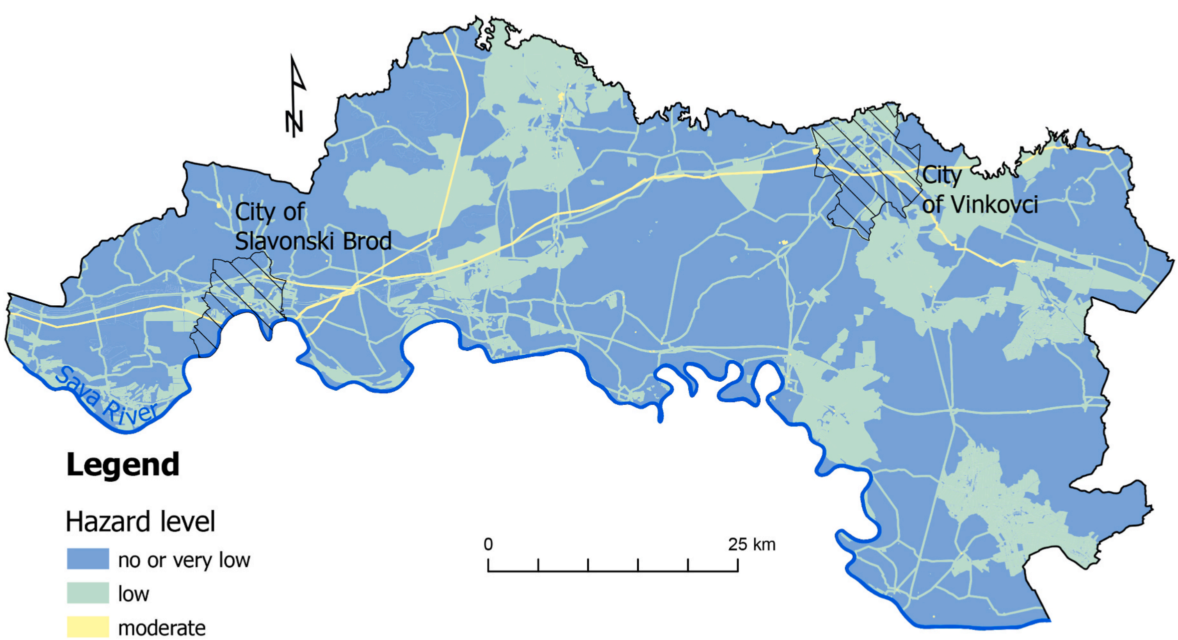


Fig. 11. Classified hazard map for the GWB CSGI_29.

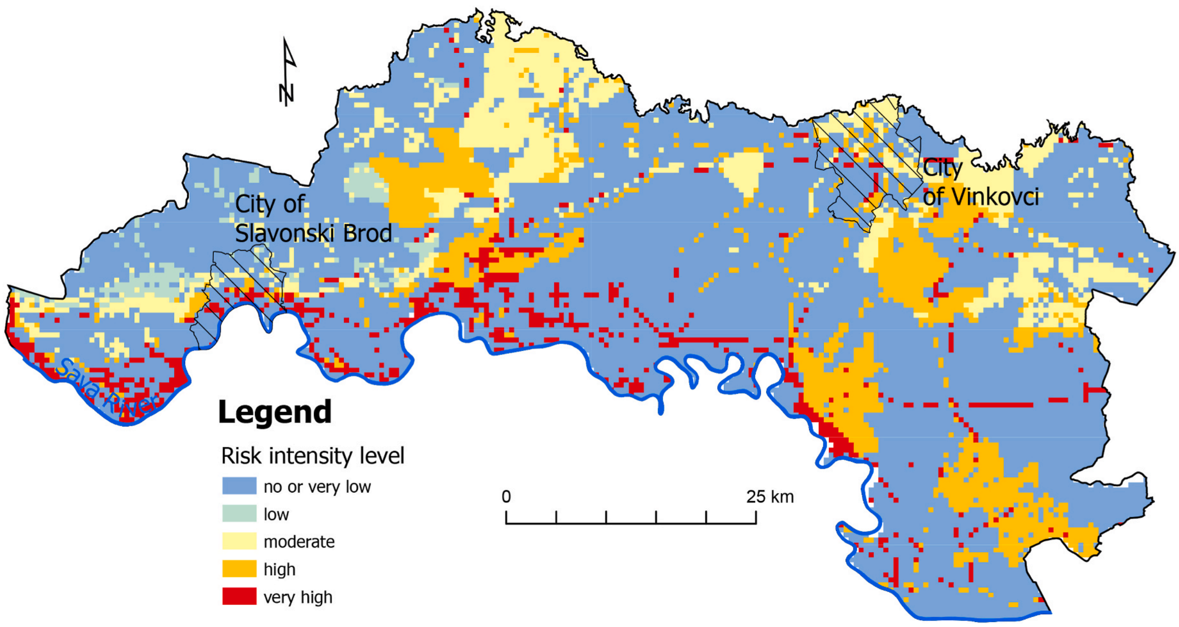


Fig. 12. Risk intensity map of the GWB CSGI_29.

the level of individual aquifers, can influence background levels, which is confirmed by Preziosi et al. (2010), who showed that the background levels of some chemical substances, determined at the level of the groundwater body, significantly differ from the background levels of the same substances, determined in homogeneous areas within the same groundwater body. Given that no high-quality hydrogeological and hydrogeochemical spatial data (e.g. S and O stable isotopes in $SO4^{2-}$ and O and H isotopes in H_2O) is available for the GWB CSGI_29, which would enable its hydrogeochemical stratification by depth and its partition into homogeneous sub-bodies, the Tier 2 RA was made at the level of the GWB.

The assessment of statistically and environmentally significant trends for TS at the level of the GWB was carried out to examine the possible deteriorating effect of point and non-point pollution sources on groundwater quality and to assess the risk of not meeting the *Implement measures to reverse any significant and sustained upward trend* objective for the GWB CSGI_29. Results shown in Table 1 reveal that statistically and environmentally significant upward trends have not been verified for TS, indicating no risk of not meeting this environmental objective.

In the River Basin Management Plan of the Republic of Croatia until 2027 (HR, 2023) it is demonstrated that the GWB CSGI_29 is in the good chemical status. Therefore, the Tier 2 RA of not meeting the *Prevent GWB status deterioration* objective for the GWB CSGI_29 was carried out using the procedure based on *exceedance* and *significant and sustained trend* criteria, which is to be implemented for any GWB that is in the good chemical status. In the RA for this objective, all TS were used, except of Total P, for which it was not possible to determine reference and threshold values, because there is no relevant drinking water standard for that substance. Results of comparison of arithmetic (AM_{ij}) and spatial means (SM_j) of TS with corresponding threshold values (TV_j) and risk-based threshold values ($TV_{risk(j)}$), as well as of assessment of the SST and EST (Table 2), indicate no risk of not meeting this environmental objective.

The Tier 2 RA of not meeting: *Prevent or limit inputs of pollutants, Meet the requirements of protected areas*, and *Achieve good chemical status* objectives for the GWB CSGI_29 was conducted by applying “Saline or other intrusions (SOI_{risk})”, “Drinking Water Protected Areas ($DWPA_{risk}$)” and “General Quality Assessment (GQA_{risk})” risk-based classification tests, which are relevant for drinking water protected areas (DWPA) and groundwater itself. To perform these tests, it was necessary to determine relevant ABL and threshold values (TV) for all TS. Methods for ABL have been applied based on criteria described in Section 2.1.2.3. As shown in Table S4, the modified Lepeltier method (LM) and the Preselection method (PM) were used to determine the upper limit (UL) of the range of

Table 1
Assessment of the statistically (SST) and environmentally (EST) significant trends of targeted substances at the level of the groundwater body "Eastern Slavonia - Sava River Basin" (GWB CSGI_29).

Substance	Time period	N observation wells	N quarterly data	Trend direction	p-value	SST ($\alpha = 0.05$)	EST (significant if UL_{95} exceeds QS_{risk} or TV_{risk})	EST_{SL} (confidence level)
EC (μS/cm)	2018–2022	9	20	Descending	5.47E-02	No	[a]	
Cl (mg/L)	2018–2022	11	20	Ascending	7.17E-02	No		
SO4 (mg/L)	2018–2022	10	20	Descending	8.93E-01	No		
NH4 (mgN/L)	2018–2022	11	20	Descending	4.28E-04	Yes	No	Low
Total P (mgP/L)	2018–2022	10	20	Descending	6.66E-04	Yes	No	Low
Mn (μg/L)	2018–2022	11	20	Descending	5.23E-02	No	[a]	

Note.
[a] It is not determined according to the criteria for conducting environmentally significant trend analysis.

Table 2
Results of testing the "Preventing GWB status deterioration objective" for the groundwater body "Eastern Slavonia - Sava River Basin" (GWB CSGI_29).

Substance	Time period	N monitoring stations	N quarterly data	TV_{risk}	TV	Testing exceedance of $TV_{risk(j)}$ [a]	Testing exceedance of $TV_{(j)}$ [b]	Trend direction	p-value	SST (α = 0.05)	EST (significant if $UL_{95} > TV_{risk}$)
EC (μS/cm)	2018–2022	14	20	1406.30	1875.00	0	0	Descending	5.47E-02	No	c
Cl (mg/L)	2018–2022	14	20	140.60	187.50	0	0	Ascending	7.17E-02	No	
SO4 (mg/L)	2018–2022	12	20	140.60	187.50	0	0	Descending	8.93E-01	No	
NH4 (mgN/L)	2018–2022	14	20	4.32	4.32	0	0	Descending	4.28E-04	Yes	No
Mn (μg/L)	2018–2022	14	20	190.75	190.75	0	0	Descending	5.23E-02	No	c

Note.
[a] Number of quarterly data where $SM_{(j)} > QS_{risk(j)}$ or $TV_{risk(j)}$.
[b] Number of monitoring stations where $AM_{(i,j)} > QS_{(j)}$ or $TV_{(j)}$.
[c] It is not determined according to the *Significant and sustained trend criterion* for GW body of good chemical status.

the ABL for TS. For NH_4 and Total P, the proportion of < LOQ values was higher than 30%, hence, according to criteria defined in Section 2.1.2.3., UL for these substances were estimated by the Preselection method.

High values of the UL estimate obtained for NH_4 and Mn, which exceeds the EU drinking water standards for those substances, gives evidence for reducing conditions in aquifers of the GWB CSGI_29. It is known that chemical composition of groundwater in the Pannonian basin is controlled by natural geochemical processes that influence to high amount of solutes in groundwater (Ujević et al., 2010).

The relevant "reference values (RF)" and "risk-based reference values (RF_{risk})", with reference to the precautionary principle (EU, 2000a; Commission of the European Communities, 2010), were determined for TS applying the "usage criteria", as a relevant drinking water standards (RF) and as 75% of a relevant drinking water standard (RF_{risk}) respectively. Risk-based threshold values (TV_{risk}) of TS, for the purpose of carrying out relevant risk-based classification tests, were determined according to the procedure described in Section 2.1.2.3. (Table S5). Furthermore, in line with the Tier 2 RA procedure for testing the *Prevent GWB status deterioration* objective, described in Section 2.1.2.2., threshold values ($TV_{(j)}$) from the "GQA" test of relevant TS were determined as well.

Trend analysis is the part of SOI_{risk} and $DWPA_{risk}$ tests, therefore an assessment of SST and EST of saline intrusion indicators and of pollutants or indicators of pollution respectively at the MS level was carried out (Table 3). The SOI_{risk} test should reveal the risk of deterioration of the quality of untreated water if there is a significant impact of saline intrusion of poor-quality water from the river or connected geological strata due to significant pumping. The $DWPA_{risk}$ test should detect

Table 3
Assessment of the statistically (SST) and environmentally (EST) significant trends of targeted substances at the level of monitoring stations.

Wellfield	Observation well	Time period	N quarterly data	Trend direction	p-value	SST (α = 0.05)	EST (significant if UL_{95} exceeds QS_{risk} or TV_{risk})
		EC (μS/cm)					
Jelas	18184	2018–2022	20	Descending	1.24E-01	No	No
St. Jankovci	18281	2018–2022	19	Descending	3.79E-02	Yes	No
		Cl (mg/L)					
Jelas	18184	2018–2022	20	Ascending	4.73E-03	Yes	**Yes** (SOI_{risk})
Trslana	18191	2018–2022	19	Descending	3.92E-05	Yes	No
St. Jankovci	18281	2018–2022	19	Ascending	1.02E-02	Yes	**Yes** (SOI_{risk})
		SO4 (mg/L)					
Jelas	18184	2018–2022	20	Descending	4.35E-01	No	No
Trslana	18191	2018–2022	19	Descending	3.25E-07	Yes	No
St. Jankovci	18281	2018–2022	19	Ascending	5.37E-03	Yes	**Yes** (SOI_{risk})
		NH4 (mgN/L)					
Jelas	18184	2018–2022	20	Descending	1.62E-02	Yes	No
Trslana	18191	2018–2022	19	Descending	4.79E-03	Yes	No
St. Jankovci	18281	2018–2022	19	Descending	3.26E-03	Yes	No
		Total P (mgP/L)					
Jelas	18184	2018–2022	19	Descending	2.40E-04	Yes	No
Trslana	18191	2018–2022	19	Descending	1.06E-02	Yes	No
		Mn (μg/L)					
Jelas	18184	2018–2022	20	Descending	1.72E-02	Yes	No
Trslana	18191	2018–2022	19	Ascending	3.33E-01	No	No
St. Jankovci	18281	2018–2022	19	Ascending	1.50E-02	Yes	No

Table 4
Saline or other intrusions (SOI_{risk})" classification test results.

Wellfield	Observation well	EC (µS/cm) TV_{risk}	Time period	N quarterly data ($AM_{(i,j)}$)	N quarterly data above TV_{risk}	Trend direction	p-value	SST ($\alpha = 0.05$)	EST (significant if UL_{95} exceeds QS_{risk} or TV_{risk})
Otok	18040	1007.73	2018–2022	15	1	it is not relevant according to the test criteria			
Jelas	18184		2018–2022	20	0				
Trslana	18191		2018–2022	15	0				
St. Jankovci	18281		2018–2022	19	0				
Wellfield	**Observation well**	**Cl (mg/L)** TV_{risk}	Time period	N quarterly data ($AM_{(i,j)}$)	N quarterly data above TV_{risk}	Trend direction	p-value	SST ($\alpha = 0.05$)	EST (significant if UL_{95} exceeds QS_{risk} or TV_{risk})
Otok	18040	19.98	2018–2022	15	**15**	criteria for calculating trends are not fulfilled			
Jelas	18184		2018–2022	20	1	it is not relevant according to the test criteria			
Trslana	18191		2018–2022	19	0				
St. Jankovci	18281		2018–2022	19	0				
Wellfield	**Observation well**	**SO4 (mg/L)** TV_{risk}	Time period	N quarterly data ($AM_{(i,j)}$)	N quarterly data above TV_{risk}	Trend direction	p-value	SST ($\alpha = 0.05$)	EST (significant if UL_{95} exceeds QS_{risk} or TV_{risk})
Otok	18040	14.04	2018–2022	15	**11**	criteria for calculating trends are not fulfilled			
Jelas	18184		2018–2022	20	0	it is not relevant according to the test criteria			
Trslana	18191		2018–2022	19	0				
St. Jankovci	18281		2018–2022	19	2				
Wellfield	**Observation well**	**Mn (µg/L)** TV_{risk}	Time period	N quarterly data ($AM_{(i,j)}$)	N quarterly data above TV_{risk}	Trend direction	p-value	SST ($\alpha = 0.05$)	EST (significant if UL_{95} exceeds QS_{risk} or TV_{risk})
Otok	18040	190.75	2018–2022	15	2	it is not relevant according to the test criteria			
Jelas	18184		2018–2022	20	2				
Trslana	18191		2018–2022	19	0				
St. Jankovci	18281		2018–2022	19	0				

whether there have been significant and sustained changes in the untreated groundwater quality at the abstraction point, which might affect an increase of the level of the purification treatment, if any, in the production of drinking water.

Trend analysis was performed on chemical data that fulfil spatial and temporal regularisation criteria, for MS located in the immediate vicinity of the active wellfields, Jelas and Trslana and near the reserve wellfields, Otok and St. Jankovci (Fig. S2). MS used in conducting both tests were selected following criteria for carrying out chemical status classification tests from the CIS guidance document No. 18 (Commission of the European Communities, 2009), which define that the possible anthropogenic impact on the quality of untreated (raw) water used for human consumption should be assessed at the locations of pumping wells and/or monitoring stations set within the radius of influence of pumping wells. Following the criteria for conducting SOI_{risk} and $DWPA_{risk}$ tests, a respective risk-based threshold values (Table S5) were used in trend assessment analysis.

Results from the previous research (Brkić et al., 2016; Nakić et al., 2020) demonstrate that elevated concentrations of chloride and sulphate in groundwater of the GWB CSGI_29 may be due to intrusion of the low water quality from the Sava River, which is in direct hydraulic connection with shallow aquifers. However, the risk intensity map of the GWB CSGI_29 (Fig. 12) and the existing conceptual model of the GWB CSGI_29 (Fig. S2) did not confirm these results with a high level of confidence. For the purposes of implementing risk-based classification tests, a conservative approach was applied, by assuming that high concentration of chemical substances indicative for saline intrusion may appear in groundwater because of the cumulative effect of intrusion and percolation of the pollution from the surface. Therefore, both tests were applied for those substances.

Table 3 indicate on EST of saline intrusion indicators for Jelas and St. Jankovci wellfields, however, they were not used in the interpretation of SOI_{risk} test results (Table 4), considering criteria for conducting the "Saline or other intrusions" tests for assessing groundwater chemical status (Commission of the European Communities, 2009) and criteria for conducting the SOI_{risk} test from Section 2.1.2.3., on the basis of which EST are not determined unless the most (min. 50%) of quartal arithmetic mean values of TS, intrusion indicators, are higher than respective risk-based TV_{GW}.

Similarly, for the Otok wellfield more than 50% of quartal arithmetic mean values of chlorides and sulphates are higher than respective risk-based TV_{GW}, however, the temporal regularisation criterion for data aggregation at the level of individual MS, described in Section 2.1.2.1. and shown in Fig. 2, is not fulfilled and EST of TS could not be assessed. It means the low confidence of the SOI_{risk} test results in general, indicating that Tier 3 monitoring-based RA should be applied (Fig. 1). It particularly refers to further data collection on pressures, chemical status and local hydrogeological characteristics to refine the existing conceptual model with the aim to review test results.

Risk-based threshold values (TV_{risk}) of TS, applied for the purpose of carrying out $DWPA_{risk}$ and GQA_{risk} tests are significantly higher compared to TV_{risk} values applied for the SOI_{risk} test (Table S5), which affects RA results. The results of the $DWPA_{risk}$ test show that the quartal arithmetic mean values of pollutants or indicators of pollution were lower than the respective risk-based TV_{GW} at all MS (Table S6). The GQA_{risk} test results indicate only a small number of MS where the respective TV_{risk} were occasionally exceeded (Table S7), however not to such an extent that the test results would indicate that there is a risk of not meeting environmental objectives related to protection of groundwater quality.

There are many limitations of the current groundwater monitoring program of the GWB CSGI_29, which are expressed through, for example, high data variability and high proportions of <LOQ values in data set of chemical substances. Therefore, results of application of the tiered approach to RA did not unequivocally confirm that this GWB is not at risk of not meeting environmental objectives defined by the

Article 4 of the WFD, with a high confidence level. In compliance with the use of relevant criteria and classification tests presented in Section 2.1.2., the re-assessment of the risk related to protection of human health and groundwater quality in the future requires a development of high-resolution conceptual model of the GWB CSGI_29, with the purpose to enable revision of the actual monitoring program, possibly drilling new observation wells and carry out regular monitoring of all relevant parameters set by EU regulations and guidelines.

4. Conclusions

The tiered approach to assessment of risk of not meeting environmental objectives of the Water Framework Directive (WFD) related to protection of human health and groundwater itself is straightforward to use and represents the upgrade of the existing risk screening tools derived in the context of the Common Implementation Strategy (CIS) of the WFD. It combines the Tier 1, semi-quantitative GIS mapping-based risk screening, with the Tier 2, quantitative monitoring-based risk assessment (RA), aiming to characterize data uncertainty and to assess a confidence level of meeting risk-based criteria for good GWB chemical status related to protection of groundwater and human health. This approach has been successfully tested in the case study of the groundwater body "Eastern Slavonia - Sava River Basin" (GWB CSGI_29), representing the relevant aquifer types in the Pannonian region of Croatia.

The Tier 1, GIS mapping-based risk screening, carried out by aggregating hazard and vulnerability indices point counting systems into log risk intensity index values showing the spatial distribution of the risk intensity, is sensitive and dependent on the realistic evaluation of number, type, distribution and reliability of the available data used to estimate parameters and factors applied in vulnerability mapping and/or classified hazard mapping parametric methods. Specifically, the values of parameters used for the calculation of the hazard indices in the process of developing a classified hazard map greatly depend on uncertainties and variability of the data from the pressures and impacts analysis. In cases where the amount of potentially toxic substances released to the environment is not known, then a geospatial data of natural systems can be applied to calculate the corresponding discrete values of the ranking factor (Q_n), by attributing the ranks of quantity of potentially toxic substances from hazards released to groundwater to corresponding values of relevant physical parameters, for example to permeability, of hydrogeological units of the aquifer system.

The Tier 2, monitoring-based risk assessment, is based on the use of appropriate criteria and risk-based classification tests in combination with the confidence assessment of the risk of not meeting environmental objectives of the WFD related to the protection of the groundwater and human health. To make a risk assessment with the highest possible confidence level, a spatial representativity of monitoring stations at the GWB level as well as the high percentage of limit of quantification (LOQ) or limit of detection (LOD) values in groundwater concentration data set should be considered. Spatial and temporal criteria for aggregating data at the level of monitoring station and/or at the level of corresponding GWB need to be fulfilled to assess the monitoring network homogeneity and possibility of using each monitoring station and targeted substance that contributes to the risk of not meeting environmental objectives respectively. To address the prediction uncertainty in trend analysis inherent to data variability, it is recommended to use: a) LOESS non-parametric regression, as a data smoothing method to avoid the jagged appearance of the trend line, and b) 95% confidence intervals around extrapolated regression line to reduce the impact of variability of arithmetic or spatial mean of groundwater concentration data. The baseline condition for an application of the risk-based classification tests for drinking water protected areas (DWPA) and groundwater stems from an upgrade of the existing procedure for derivation of threshold values for groundwater status assessment. Precautionary principles, set by the relevant EU CIS guidance documents, were implemented in the procedure for defining relevant reference values. In addition, model-based objective methods were proposed for determination of ambient background concentrations for naturally occurring substances.

To assure a sound implementation of the proposed tiered approach to RA from this paper, a high-quality data sets derived from a high-resolution conceptual model of GWB is to be collected and thoroughly analysed. High proportions of values $<$ LOQ or $<$ LOD in data set and/or significant data variations around the central value greatly affect the confidence assessment of both Tier 1, GIS mapping-based risk assessment and Tier 2, monitoring-based risk assessment. The critical issue in this process is to implement data from monitoring programs, designed to ensure the representativity of the monitoring stations at the level of homogeneous GWB or sub-body.

CRediT authorship contribution statement

Zoran Nakić: Writing – original draft, Methodology, Investigation, Conceptualization. **Dario Perković:** Writing – original draft, Methodology, Formal analysis, Data curation, Conceptualization. **Zoran Kovač:** Writing – review & editing, Visualization, Methodology, Formal analysis, Data curation. **Borna-Ivan Balaž:** Writing – review & editing, Visualization, Formal analysis, Data curation.

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Appendix A. Supplementary data

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Data availability

Croatian Waters is owner of the data. We are not allowed to distribute data.

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