Article

Contaminant Trends in Urban Groundwater: Case Study from Ljubljana (Central Slovenia)

Janja Svetina [1,2,*], Joerg Prestor [1], Brigita Jamnik [3], Primož Auersperger [3] and Mihael Brenčič [1,2]

1   Geological Survey of Slovenia, Dimičeva ulica 14, 1000 Ljubljana, Slovenia; joerg.prestor@geo-zs.si (J.P.); mihael.brencic@ntf.uni-lj.si (M.B.)
2   Faculty of Natural Science and Engineering, University of Ljubljana, Aškerčeva cesta 12, 1000 Ljubljana, Slovenia
3   JP VOKA SNAGA d.o.o., Vodovodna cesta 90, 1000 Ljubljana, Slovenia; brigita.jamnik@vokasnaga.si (B.J.); primoz.auersperger@vokasnaga.si (P.A.)
*   Correspondence: janja.svetina@geo-zs.si

Abstract: Urban areas can significantly alter the quality status of aquifers if appropriate strategies to prevent and detect groundwater contamination are not implemented in time. The prevention of groundwater contamination should be a priority due to its potential long-term impact on the environment and the high cost of remediation. For effective and sustainable groundwater management, it is crucial to proactively monitor a wide range of compounds to prevent their spread, progression and increasing concentrations. This study is one of the few to analyse the trends of various urban groundwater contaminants (nitrate, sulphate, hexavalent chromium, pesticides, PCE and TCE) from a groundwater management perspective. Characteristic trends are assessed using linear regression and the Mann–Kendall method, while significant changes in trends are determined using the Darken and Pettitt tests. The time span of the analysed trends covers the transition period before and after the implementation of the Water Framework Directive (2000/60/EC) and the Groundwater Directive (2000/60/EC). This study confirms the effectiveness of enforcement measures to protect groundwater quality, as evidenced by several statistically significant decreasing trends. On the other hand, this study emphasises the importance of intervention-targeted sampling campaigns and the reporting of raw analytical values according to the ISO 11843 series of standards. This approach is essential to detect upward trends in emerging contaminants at an early stage and prevent them from reaching levels that could negatively impact the economy or even jeopardise the safety of drinking water supplies.

Keywords: groundwater contamination; contaminant trends; groundwater management; urban aquifer; Ljubljansko polje

1. Introduction

Located beneath the city of Ljubljana, the alluvial aquifer of Ljubljansko polje is an important source of drinking water. The groundwater currently meets quality standards and is fed into the drinking water supply system with minimal to no treatment [1]. This is certainly appreciated elsewhere in densely populated regions. Nevertheless, the highly urbanised catchment area poses a major threat to groundwater quality caused by agricultural, industrial and wastewater-related environmental pressures [2], so the pumping regime and recharge zone must be strictly controlled to prevent the potential inflow of contaminated groundwater into the supply system.

The city has a long-standing and sophisticated surveillance and operational groundwater monitoring system, which is managed by three institutions. Although each institution collects its data independently, considerable effort has been made in recent decades to establish a protocol for consolidating this data into a common standardised database. This has provided valuable insight into the spatial and temporal trends in groundwater quality and offered an accurate and up-to-date understanding of changing conditions in the region

for the period between 1992 and 2019. This time span covers the transition period before and after the implementation of the Water Framework Directive (WFD, 2000/60/EC) and the Groundwater Directive (GWD, 2000/60/EC). One of the main environmental objectives of the WFD and the GWD is to achieve the good status of groundwater bodies by the end of 2015, with a conditional extension to 2021 or 2027. Both directives also require that any significant and sustained upward trend in pollutant concentrations be identified and reversed.

Although this article focuses on data from a specific aquifer, it stands out as a rare overview of a pilot case that provides valuable insights into several long-term pollution trends in urban groundwater from a groundwater management perspective. The case serves as an exemplary illustration that highlights both effective practises and potential challenges in managing groundwater pollution in comparable aquifers. This paper also emphasises the crucial role of advanced analytical methods in the early detection of contamination. As the development and progress of water management and protection continue, water quality standards should no longer be the objectives of water management but rather safety thresholds for consumers and ecosystems. The contemporary objective for urban groundwater should be a continuous restoration of quality and protection from emerging contaminants. Any contamination should be kept in a downward trend, and any upward trend of new emerging synthetic organic compounds should be detected and stopped at much lower concentrations than the actual water quality standard, in the range between the limit of detection (LOD) and the limit of quantification (LOQ). The data set presented in this paper considers all available data, regardless of their different sources and time periods, and captures the transition from the era of the "nitrate and atrazine dispersed pollution" paradigm [3–5] to the contemporary challenges posed by "emerging organic synthetic pollutants and multipoint pollution sources" [6–8].

Background and Perspective

It is predicted that by 2050, about 84% of the European population will live in cities and urban areas [9], where groundwater is more at risk due to high population density and intensive land use. Urban hydrogeology has been the subject of several important review articles addressing topical issues from different perspectives [10–14]. The main challenges that urbanisation poses to groundwater are fluctuations in groundwater levels due to changes in land and water use and the deterioration of groundwater quality due to human activities in urban areas, both of which may be exacerbated by the effects of climate change [15–19].

Groundwater recharge in urban areas may decrease as surface sealing impedes natural infiltration [20,21], although other studies suggest that groundwater recharge rates may increase due to reduced evapotranspiration and leaky utility lines, storm sewer systems and stormwater catchments [22,23]. The net effect is difficult to predict as each city has different settings and climatic conditions [24]. Increasing water demand combined with inappropriate groundwater management, such as excessive groundwater extraction, can lead to groundwater depletion, land subsidence, saltwater intrusion in coastal regions and numerous other problems [25–27].

According to the EEA [28], groundwater abstraction accounts for less than a quarter of total water consumption in the EU-27 Member States, but it represents 65% of total water abstraction for public water supply. The relative share of groundwater in total water abstraction increased by 4% between 2000 and 2019. While poor quantitative status was reported for 9% of the total groundwater body area in the EU-27, a much larger proportion, 24% of the groundwater body area, had poor chemical status [28]. Agriculture remains the main source of groundwater contamination, affecting about 19% of the total groundwater body area in the EU-27, followed by abandoned industrial and contaminated sites (5%) and mining activities (3%). Burri et al. [10] provided a thorough overview of potentially contaminating compounds in groundwater based on three major land use categories, namely agriculture, urban areas and industry, which can be further subdivided

in various ways. The study [10] points to the fact that the same compounds can originate from multiple sources and that categories of land use rarely exist in isolation, but often overlap and interact with each other.

Nitrate, for example, remains the main contributor to the poor chemical status of groundwater bodies in the EU-27 region, affecting more than 18% of groundwater bodies by area [29]. It mainly originates from agricultural runoff due to the excessive use of mineral and organic nitrogen fertilisers and animal manure in rural areas [30–35]. However, in urban areas, losses from sewerage systems, industrial wastewater and leachate from landfills can also contribute significantly to contamination [4,10,36,37]. Pesticides, on the other hand, have a negative impact on around 6.5% of groundwater bodies in the EU-27 region [29]. Despite the banning or restriction of some pesticides, which has led to reduced occurrence in groundwater [29], many pesticide-related active substances, together with their by-products such as metabolites, degradation products and reaction products, are still relevant [38–42]. Some unknown degradation products, which are not yet well characterised, could potentially be more critical for the environment than the parent compounds [43,44].

In addition to compounds from agriculture and salt intrusion, e.g., chloride [45–47], some industrial chemicals are frequently detected [29], such as volatile organic compounds [48–52] and heavy metals such as arsenic, nickel and lead [53–56]. The main anthropogenic sources of heavy metals are found in various industrial sectors, e.g., current and former mining activities, metal plating, foundries, smelters, battery manufacture, tanneries, petroleum refining, paint manufacture, pigment manufacture, and the printing and photographic industries [57,58].

In recent decades, emerging organic contaminants (EOCs) from pharmaceutical residues, personal care products, pesticides, veterinary drugs, food additives, nanomaterials, industry and other sources [59–61] have been of particular concern in urban areas [62]. Numerous EOCs are frequently detected at high concentrations across Europe [63] but are not yet formally regulated by European directives, despite their potentially harmful effects on the environment and human health [64,65]. Among the emerging pollutants, microplastics have recently gained attention due to their ubiquity and persistence in the environment, especially as their occurrence, fate and transport processes in groundwater are not yet fully understood [66–69]. The main obstacle to achieving comparable results in existing reports on the significance and distribution of microplastics and other emerging pollutants in natural waters (e.g., perfluorinated compounds, benzotriazoles and certain widely used pharmaceuticals) lies primarily in the challenges of sampling and analytical methods.

While most European countries have been monitoring groundwater quantity since the turn of the 20th century, the monitoring of groundwater quality was uncommon before the 1970s and 80s [70,71]. Long-term monitoring of groundwater quality is valuable for several reasons. These include early detection of contamination, understanding trends and patterns, determining potential risks and evaluating the effectiveness of past management measures. The identification of upward trends is also required in Europe by the Water Framework Directive (2000/60/EC) and the Groundwater Directive (2000/60/EC). Common methods for assessing trends in groundwater quality include traditional statistical approaches, such as parametric methods like linear regression and polynomial regression, and non-parametric methods like the Mann–Kendall test [35,72–74]. However, it is important to note that changes in sampling and laboratory practices can affect the time series of water quality data [73,75].

To restore, protect and preserve urban groundwater resources for future generations, effective and sustainable groundwater management is essential. This is a complex task that plays an important role in maintaining and strengthening urban resilience [12]. It requires the cooperation of science and politics with representatives from industry, agriculture and non-governmental organisations [76,77]. The involvement of the population often only increases once a crisis has already occurred. Therefore, development goals, measures and activities should be discussed by a regional implementation group and be based on a risk

assessment [78]. Continuous efforts to raise awareness of groundwater vulnerability are necessary. Preventing the depletion and quality deterioration of groundwater resources should become a shared priority. This is crucial to mitigating the economic impact of the significant costs required to manage and remediate these resources [79].

2. Site-Specific Conditions

The Ljubljansko polje aquifer is located in the central part of Slovenia (Figure 1). It extends over an area of about 71 km^2 in the Ljubljanska Kotlina tectonic depression, which was formed by tectonic subsidence in the early Pleistocene [80]. The bedrock consists of impermeable Permian and Carboniferous clay shale, sandstone and siltstone [81–83]. The basin is filled with Pleistocene and Holocene alluvial deposits of the Sava River, which are locally more than 100 m thick and consist mainly of carbonate gravel and sand beds with layers of conglomerate [83–85]. In the western part of the aquifer, there are intermediate layers of clay and clayey gravel above the main aquifer, which reach a thickness of up to 10 metres and serve as a barrier that retains the perched groundwater [83,86].
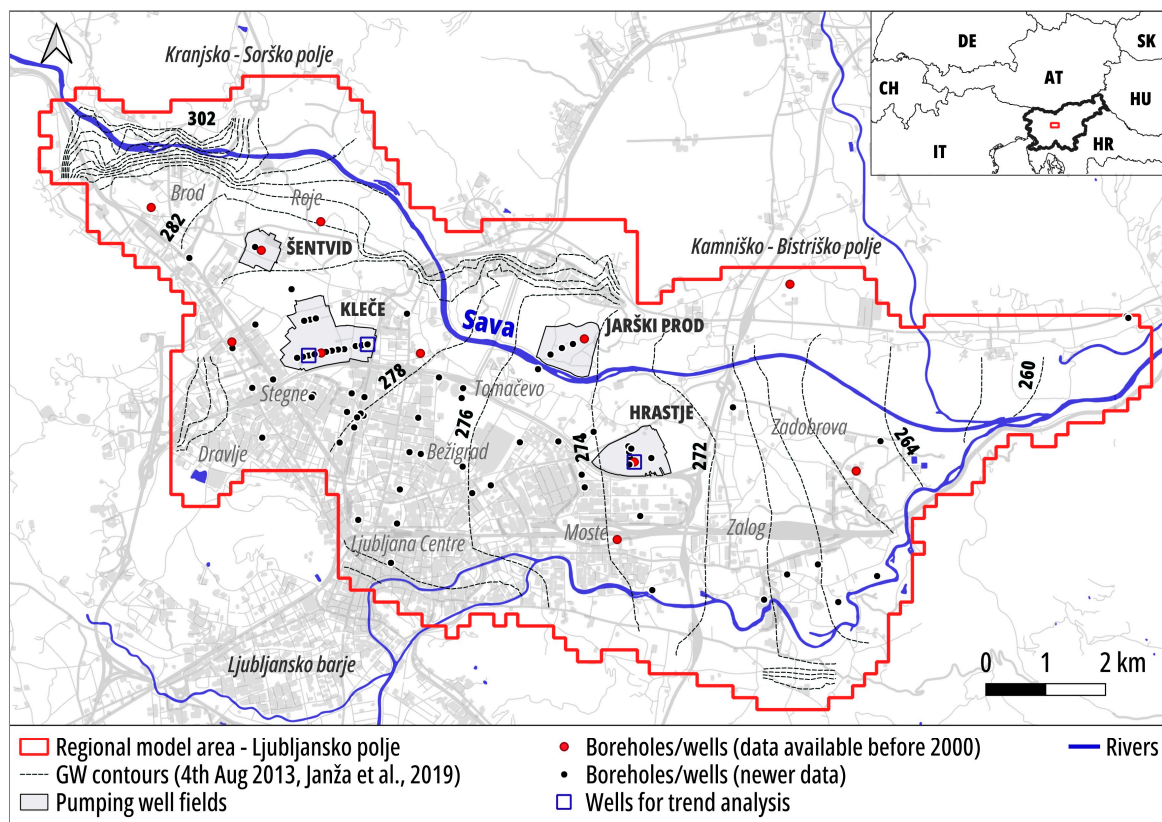

Figure 1. Study area of Ljubljansko polje aquifer (Ljubljana, Slovenia) with groundwater contours from the regional model of 4 August 2013 [87].

The unconfined aquifer is characterised by intergranular porosity. The hydraulic conductivity in the central part of the aquifer is between 1×10^{-2} and 5×10^{-3} m/s, while it is lower at the edges at around 5×10^{-4} m/s [84]. The general direction of groundwater flow is towards the SE, with an average velocity of 10 m/day, although the maximum velocity can locally exceed 20 m/day [2,4]. The groundwater table is on average 20–25 m below the surface. The aquifer interacts strongly with surface water, particularly with the Sava River, which recharges the aquifer in its NW part and drains the eastern part of Ljubljansko polje [2,85]. Precipitation contributes 2.2 m^3/s of water, and infiltration from the Sava River contributes 3.2 m^3/s of water [2,88]. However, the proportion of both sources is influenced by the depth of the observation point and its distance from the Sava River [89].

The adjacent groundwater bodies of Kranjsko—Sorško polje, Kamniško—Bistriško polje and Ljubljansko barje contribute a small share [89] (Figure 1).

About 45% of the Municipality of Ljubljana is covered by water protection zones, especially in the western part of the city, which includes the city centre. The groundwater for the central water supply system of the city is extracted from five well fields located in two aquifers—Ljubljansko polje and Ljubljansko barje. In this paper, our focus is confined to the Ljubljansko polje aquifer, which comprises four well fields (Kleče, Hrastje, Jarški prod and Šentvid) (Figure 1). The abstracted water is mainly intended for drinking water supply (domestic use) and partly for industrial use [2].

In the study area, the occurrence of contaminants is monitored by three institutions—the Slovenian Environment Agency (ARSO) since 1990, the City of Ljubljana (MOL) since 1997 and the local utility company Vodovod Kanalizacija Snaga (VOKA Snaga) since 1992. ARSO is responsible for monitoring at the highest national (state) level. It forms the framework of the national monitoring system, which ensures the representativeness of the data for the country and the higher levels of— the transboundary river basins and the EU community. The next level of monitoring is the level of functional urban areas managed by the local community—MOL. It advocates appropriate spatial planning that also relies on the status and development of groundwater quality and provides spatial regulatory elements for the long-term functionality of the city in relation to its water resources. At the most detailed level, the local public utility company—VOKA Snaga—manages intervention-targeted monitoring to protect wells from potential contamination and to ensure a safe water supply for the community.

3. Methodology

This study is primarily based on the existing database of sampling results from three institutions responsible for monitoring groundwater quality in the study area. This database was originally created as part of the INCOME project (LIFE07) for the period 1992–2011 [90], updated and expanded as part of the AMIIGA project [8] for the period 2011–2016 and additionally updated in 2020 for the period 2016–2019, so that it now documents a total of 283,538 entries. The database contains information on 473 chemical and physico-chemical parameters and 164 monitoring sites in two hydrogeologically connected aquifers, Ljubljansko polje and Ljubljansko barje. The analysed parameters from the database are classified into characteristic groups and subgroups. Data on the presence of microbiological parameters are not included in this database. In general, the microbiological condition of drinking water is good, but this is a broad field that is beyond the scope of this article.

In this study, we used the latest version of the database and focussed specifically on 90 sampling sites in the Ljubljansko polje area (Figure 1). The entries related to Ljubljansko barje were omitted as they are not the focus of this study. The availability of data in the database varies greatly between different time periods, sampling sites and different parameters. In particular, data from the last decade are more numerous than those from the 1990s. We have therefore statistically analysed the occurrence of contaminants with a focus on the last decade, 2010–2019, which is of greatest interest to us with regard to the status of groundwater quality.

Data prior to the year 2000 are only available in the database for 11 sampling sites in the study area (Figure 1). Particular attention was paid to the pumping wells VD Hrastje-1A, VD Kleče-10 and VD Kleče-14, which proved to be the most suitable for analysing trends due to long-term regular sampling (Figure 1). A comprehensive review of existing local studies and a statistical analysis of the available data facilitated the selection of the most critical contaminants in the study area, which were thoroughly analysed from the point of view of the effectiveness of previous groundwater management measures.

Contaminant trends were analysed using the Hype statistical tool (BRGM) [91], which was developed specifically for analysing trends in groundwater quality data [91]. The Hype tool is used in an R environment. If the sampling result (input data) is below the limit of quantification (LOQ) or below the limit of detection (LOD), half of the reported LOQ or

LOD is considered the concentration value, in accordance with the recommendations of the Water Framework Directive (2000/60/EC) and the Groundwater Directive (2006/118/EC). The input data are first tested for normal distribution using the Shapiro–Wilk test, and the quantification rate is calculated. Trends are calculated using linear regression and the Mann–Kendall method, while significant changes in trends are analysed using the Darken [92] and Pettitt [93] tests. All details and equations are described in the user manual [91].

4. Results

Based on the analysis of 50 sampling sites in the study area between 2010 and 2019, the groundwater is generally of good quality. The groundwater temperature is between 10–14 °C, while the pH value is between 6.9 and 7.8. The average electrical conductivity at 20 °C is 490 μS/cm and fluctuates in the range of 300–800 μS/cm. Oxidative conditions prevail in the aquifer, with an average oxygen saturation of 85%. The concentration of total organic carbon (TOC) generally remains below 0.5 mg/L and occasionally reaches peak values of up to 2 mg/L at individual sampling sites. The biochemical oxygen demand (BOD) generally remains below 0.5 mg/L, with occasional peaks of up to 1 mg/L.

At least 332 parameters from different characteristic groups were analysed between 2010 and 2019, with organic compounds accounting for almost 77% (Table 1). The subgroup of pesticides had the largest set of analysed parameters (131), followed by microelements (58) and pharmaceutical residues (51). In addition to the basic groundwater parameters mandated by the Rules on Groundwater Status Monitoring [94], the most frequently analysed inorganic parameters were hexavalent chromium, total chromium, fluorides and bromides. Of 255 different organic compounds, 68 were detected above LOQ at least once in the study area (Table 1).

Table 1. Number of analysed parameters (Np) and individual analyses (Na) conducted between 2010 and 2019 by subgroups (SubGr). Most frequently analysed parameters (MA) and most frequently detected parameters (MD) between 2010 and 2019 by subgroups.

Gr	SubGr	Np	Np > LOQ	Na	Na > LOQ	Na < LOD	MA	MD
IP	MacE	19	11	15,982	12,813	1253	K	K
	MicE	58	50	9468	3412	1127	Cr(VI)	Cr(T)
OP	VHH	32	12	14,552	1697	9047	1,1,1-TCA	PCE
	Pest	131	29	53,571	4113	38,896	MTC	DAT
	PCBs	1	-	12	-	-	-	-
	PAHs	14	1	152	1	45	PAH	Benzene
	PhR	51	13	6369	237	4138	CBZ	CAFF-PROP
	OthOC	23	11	1782	124	1392	2M-2H-BTA	2M-2H-BTA
	OthOC Sum	3	2	976	404	377	AOX	AOX

Notes: Gr: Group; IP: inorganic parameters; OP: organic parameters; SubGr: subgroup; MacE: macroelements; MicE: microelements; VHH: volatile halogenated hydrocarbons; Pest: pesticides; PCBs: polychlorinated biphenyls; PAHs: polycyclic aromatic hydrocarbons; PhR: pharmaceutical residues; OthOC: other organic compounds; OthOC Sum: other organic compounds (sum parameter analysis); Np: number of analysed parameters; Np > LOQ: number of parameters detected above LOQ at least once (2010–2019); Na: number of analyses (2010–2019); Na > LOQ: number of analyses with detected concentrations above LOQ (2010–2019); Na < LOD: number of analyses with concentrations below LOD (2010–2019); MA: most frequently analysed parameter (2010–2019); MD: most frequently detected parameter above LOQ (2010–2019); K: potassium; Cr(VI): hexavalent chromium; Cr(T): total chromium; 1,1,1-TCA: 1,1,1-trichloroethane; PCE: tetrachloroethene; MTC: metolachlor; DAT: desethylatrazine; PAH: polycyclic aromatic hydrocarbon; CBZ: carbamazepine; CAFF-PROP: caffeine–propyphenazone; 2M-2H-BTA: 2-methyl-2H-benzotriazole; AOX: adsorbable organic halides.

The concentrations of most of the analysed parameters in the study area are around the LOQ. Of greater importance for ensuring safe drinking water are the pollutants that occasionally exceed the drinking water standards or show increasing trends at certain sampling sites. Table 2 shows the most prevalent parameters of concern in the study area compared to the EU requirements for water intended for human consumption.

Table 2. The most widespread parameters of concern in the study area between 2010 and 2019 compared to EU requirements for water intended for human consumption.

Parameter	Unit	Concentration Range in the Study Area (2010–2019)	Occurrence Rate above Quality Standard [1]	Human Consumption (EU) [2]
nitrate	mg/L	2–75	0.1%	50
sulphate	mg/L	5–55		250
chloride	mg/L	2–114		250
hexavalent chromium	µg/L	<3–54		
total chromium	µg/L	<3–54	5.3% *	25 *
atrazine	µg/L	<0.002–0.15	1.3%	0.1 **
desethylatrazine	µg/L	<0.002–0.18	1.4%	0.1
terbuthylazine	µg/L	<0.001–0.023		0.1 **
desethylterbutylazine	µg/L	<0.001–0.017		0.1
sum of pesticides	µg/L	<0.002–0.507	0.2%	0.5
tetrachloroethene	µg/L	<0.05–5.9		10 ***
trichloroethene	µg/L	<0.05–1.0		10 ***
carbamazepine	µg/L	<0.008–0.1		0.25 ****
2-methyl-2H-benzotriazole	µg/L	<0.001–0.047		

Notes: [1] Occurrence rate: the number of results above the EU water quality standard compared to the total number of samples analysed for this parameter, expressed as a percentage. [2] EU: minimum requirements for parametric values used to assess the quality of water intended for human consumption, Annex I [95]. * The parametric value of 25 µg/L for chromium should be met, at the latest, by 12 January 2036. The parametric value for chromium until that date shall be 50 µg/L [95,96]. The occurrence rate is calculated with regard to the new standard of 25 µg/L. If the quality standard is set at 50 µg/L, the occurrence rate of total chromium is 0.6%. ** Atrazine is banned on the national level in Slovenia and on the EU level. In the study area, terbuthylazine is banned in the inner water protection zone. *** The quality standard of 10 µg/L should apply to the sum of the concentrations of tetrachloroethene and trichloroethene. **** The quality standard for carbamazepine is a proposal, in accordance with the Proposal for a Directive amending the Water Framework Directive, the Groundwater Directive and the Environmental Quality Standards Directive [97].

4.1. Inorganic Contaminants

4.1.1. Nitrate

Although the nitrate concentration generally does not exceed the drinking water standard (i.e., 50 mg/L), it is still considered one of the most important and ubiquitous contaminants in Ljubljansko polje. The local background concentration is estimated to be around 6 mg/L [4], while higher concentrations clearly indicate anthropogenic pollution related to either agriculture (i.e., mineral fertilisers and livestock manure) or sewerage losses. Based on a local groundwater transport model covering an area of 58 km^2 [4] (Figure 2a), the total nitrogen load was estimated to be 334.22 tonnes/year, of which 38% arises from the leaking sewerage system and 62% from agriculture [4]. The proportion of each source, however, varies considerably at the local level [4,5]. According to Ogrinc et al. [5], nitrate from atmospheric deposition accounts for around 10% of the nitrate in groundwater.

The mean nitrate concentration in Ljubljansko polje is 16 mg/L (2010–2019) and has decreased significantly since 2005 at a rate of 0.256 mg/L per year [8]. Considering the regulatory measures mandated by the EU Nitrates Directive 91/676/EEC and the Slovenian Nitrates Decree, it is reasonable to presume that the observed reduction in total nitrogen load is primarily due to the reduced use of nitrates in agriculture. Unfortunately, we lack information regarding the use of preparations that could confirm our assumptions. This declining trend is particularly evident in well VD Hrastje 1a (Figure 2b), for which measurements are available over a longer period of time, namely since 1993. The Shapiro–Wilk test indicates a non-normal distribution of the input data for the trend analysis ($p < 0.05$). Both the Mann–Kendall method (-0.242 mg/L/year, $p = 1.4 \times 10^{-29}$) and the linear regression (-0.240 mg/L/year, $p = 1.9 \times 10^{-18}$) show a significant decreasing trend. In contrast, the Darken method shows a statistically significant decreasing trend after 1999 (-0.244 mg/L/year, $p = 3.3 \times 10^{-23}$), while the trend before 1999 was insignificant. In addition, the Petitt test indicates a significant change in the mean value ($p = 7.5 \times 10^{-22}$) in 2010, which decreased from 23.33 mg/L to 20.79 mg/L after the turning point.
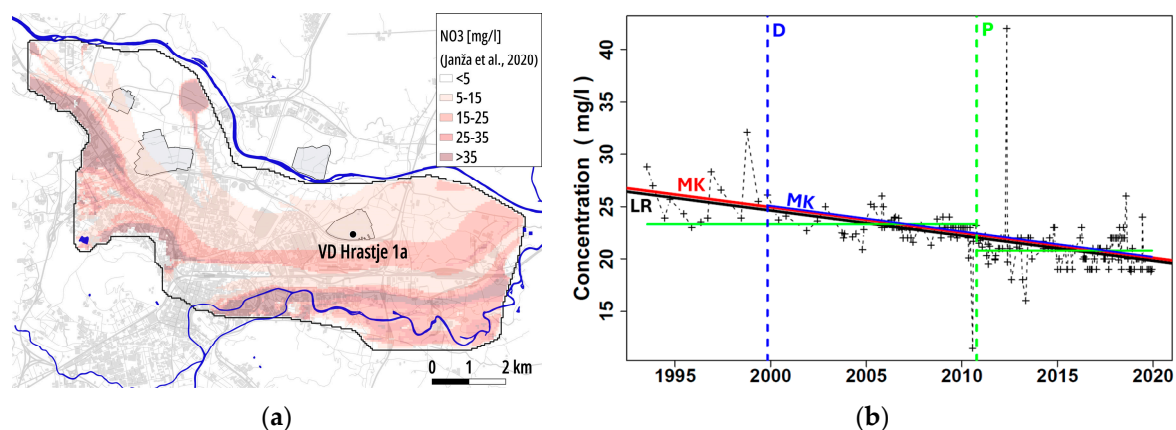
Figure 2. (**a**) The spatial distribution of modelled nitrate concentrations in groundwater of Ljubljansko polje [4]; (**b**) Trend analysis of nitrate concentrations at VD Hrastje 1a: black line—linear regression (LR); red line—Mann–Kendall (MK); blue dashed line—Darken [92] date of trend reversal (D) and blue solid lines—MK trend before/after trend reversal; green dashed line—Pettitt [93] change in mean (P) and green solid lines—mean value before/after the change.

Despite the general decrease in nitrate load, certain areas within the region have recorded an increase in nitrate levels. The analysis of monitoring for the 2010–2019 period indicates that out of 1900 measurements at 71 monitoring sites, the annual mean nitrate value exceeded 20 mg/L at 9 monitoring sites, namely 30 times, and was above 30 mg/L 5 times at 3 monitoring sites. The highest concentrations (>25 mg/L) were observed in the area where two conditions were met, namely a high load from sewerage and agriculture and, at the same time, a low groundwater flow rate and dilution capacity [4]. This is particularly the case at the edge of the aquifer, at the western edge of the Kleče waterworks along Stegne and Dravlje.

4.1.2. Hexavalent Chromium

Groundwater contamination with hexavalent chromium—Cr(VI), identified at the end of 1985, was the first major contamination that led to a temporary halt of water extraction from several wells at the Kleče pumping station [98]. Despite comprehensive research over the past few decades, the main individual sources have not yet been identified. The quantities that could be lost from the sewage system in the normal course of events are not expected to result in concentrations as high as monitoring indicates, implying that the primary sources are uncontrolled [99]. Given that modern technological use of chromium is typically based on closed systems, thereby avoiding direct outflow of wastewater containing chromium, it is assumed that the main source of pollution could be the saturation of soil with chromium at the site of former galvanising plants and "illegal dumps" [98].

Concentrations of Cr(VI) in Kleče waterworks began to decrease only after 1994 and are expected to eventually fall below the LOD. However, the most probable modelled scenarios have shown that at least two pronounced contamination plumes still pose a threat to the Hrastje waterworks [100] (Figure 3a), where concentrations remain relatively high, particularly in the southernmost water wells. 197 sampling results from well VD Hrastje-1a were used for the long-term trend analysis, 96% of which were above the LOQ. The Shapiro–Wilk test indicates a non-normal distribution of the input data ($p < 0.05$). While both the Mann–Kendall method and the linear regression showed statistically significant trends over the entire 26-year period, their values and slopes do not match, which is likely due to the influence of trend reversal. The Darken method, which was used to identify the characteristic change in the trend, proved to be the most reliable ($p = 2 \times 10^{-29}$) with a trend reversal in 2009. The Mann–Kendall trend for the period before 2009 shows a characteristic increasing trend (0.739 µg/L/year, $p = 2.8 \times 10^{-16}$) and a characteristic decreasing trend (-0.277 µg/L/year, $p = 1.3 \times 10^{-15}$) after 2009.

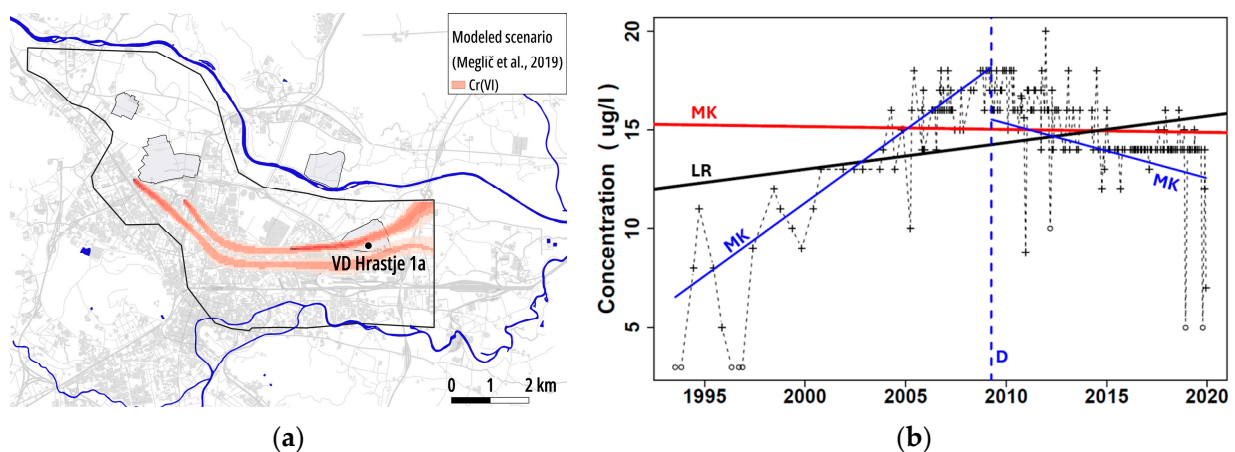**Figure 3.** (**a**) Two pronounced Cr(VI) contamination plumes in the area of Ljubljansko polje—modelled scenario [100]; (**b**) Trend analysis of Cr(VI) concentrations at VD Hrastje 1a: black line—linear regression (LR); red line—Mann–Kendall (MK); blue dashed line—Darken [92] date of trend reversal (D); and blue solid lines—MK trend before/after trend reversal. The plus signs indicate results > LOQ, the circle signs indicate results < LOQ or <LOD.

It is important to note that the decreasing concentration of Cr(VI) in the Hrastje waterworks is not significantly related to the movement of concentrations in the hinterland. On the contrary, in the central part of Ljubljansko polje between Stegne and Hrastje, an increasing trend has been observed in recent years. As part of an investigation-targeted sampling campaign between 2017 and 2022, concentrations of Cr(VI) in the Stegne industrial area were repeatedly above the quality standard for total chromium (i.e., 50 μg/L), which was even exceeded threefold on one occasion. This indicates that we are dealing with continuous sources of chromium that may still be active. The scattered concentrations and the slight downward trend may both be related to sampling uncertainty. Further research is ongoing to address this issue.

4.1.3. Other Inorganic Contaminants

The inorganic parameters that frequently occur above the limit of quantification (LOQ) include the basic parameters of groundwater that are also present in the natural background, such as chlorides, nitrates and sulphates. Regular monitoring of these parameters is important to detect anomalies or deviations from expected values. The presence of chlorides does not jeopardise the supply of drinking water and does not exceed the quality limits, although local concentrations above 30 mg/L indicate pressures associated with sewage and industrial effluents, road salting and the use of mineral fertilisers such as KCl.

Of particular note is the parameter sulphate, which showed the most significant trend of decreasing concentration. This was determined both by linear regression (-0.42 mg/L/year, $p = 4.1 \times 10^{-34}$) and by the Mann–Kendall method (-0.47 mg/L/year, $p = 2.4 \times 10^{-31}$) (Figure 4a). No trend reversal was observed, but the Pettitt test showed a significant change in the mean value in 2012 ($p = 4.6 \times 10^{-23}$). This decreasing trend can be attributed to the reduction of sulphur dioxide in the atmosphere between 1993 and 2006 (-2.75 μg/m^3/year, $p = 2.5 \times 10^{-5}$), which is due to the decrease in emissions from coal combustion plants before the widespread introduction of natural gas as a fuel source [101] (Figure 4b). According to the Pettitt test, the most significant change in the mean value of sulphur dioxide in the atmosphere occurred in 2004 ($p = 4.4 \times 10^{-5}$).
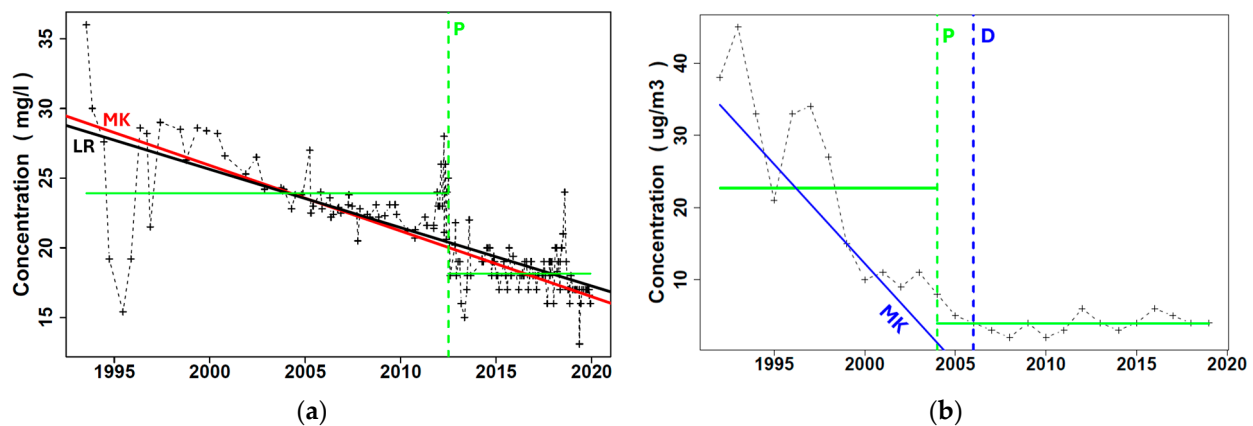
Figure 4. (**a**) Trend analysis of SO$_4$ concentrations in the groundwater at VD Hrastje 1a; (**b**) Trend analysis of SO$_2$ concentrations in the air at the Ljubljana Bežigrad monitoring station [101]: black line—linear regression (LR); red line—Mann–Kendall (MK); blue dashed line—Darken [92] date of trend reversal (D) and blue solid line—MK trend before trend reversal; green dashed line—Pettitt [93] change in mean (P) and green solid lines—mean value before/after the change.

4.2. Organic Contaminants

4.2.1. Pesticides

The widespread use of pesticides was one of the main threats to groundwater resources in Ljubljansko polje at the turn of the century [102]. The presence of atrazine, desethyla-trazine and 2,6-dichlorobenzamide—the degradation products of dichlobenil—regularly endangered well fields, especially Hrastje, as the threshold values for drinking water (i.e., 0.1 μg/L) were repeatedly exceeded [3,102]. Following the ban on the use of phy-topharmaceuticals containing dichlobenil and atrazine in 2002 and 2003, respectively, the water quality in the waterworks improved significantly within two years (Figure 5a,b). A significant downward trend ($p < 0.01$) for atrazine was determined both by linear re-gression (−0.0068 μg/L/year) and by the Mann–Kendall method (−0.0094 μg/L/year) (Figure 5a). The same applies to 2,6-dichlorobenzamide, where the linear regression and the Mann–Kendall method showed a decreasing trend of −0.0021 and −0.0015 μg/L/year, respectively (Figure 5b).

The banned substances were largely replaced by alternative compounds that were recognised as less soluble and mobile in groundwater, such as terbutryn and terbuthy-lazine [102,103]. Although for this reason terbuthylazine was considered significantly less risky for groundwater contamination in 2005 [102] and was still below the LOQ, increasing trends were observed for both compounds—terbuthylazine and especially its more soluble degradation product, desethylterbutylazine—throughout the period 2010–2017 in the Kleče and Šentvid waterworks. In particular, a significant upward trend of 0.0001 μg/L/year ($p < 0.01$) was observed in well VD Kleče 10 using both linear re-gression and the Mann–Kendall method (Figure 5c). In response to the persistent upward trend, the use of terbuthylazine was finally banned in 2016. Subsequent monitoring from 2017–2019 indicated the effectiveness of the measures taken, however, the available data was not yet long enough to confirm a statistically significant trend reversal (Figure 5). The largest waterworks, Kleče, was also characterised by a periodic occurrence of the herbicide metazachlor, with the highest concentration measured in the winter of 2009/10 (approx. 0.6 μg/L) (Figure 5d). After the peak, a significant trend reversal was detected in 2010 using the Darken method ($p = 9.5 \times 10^{-33}$). In addition, the Petitt test shows a significant change in the mean value ($p = 2.3 \times 10^{-31}$) in 2012.
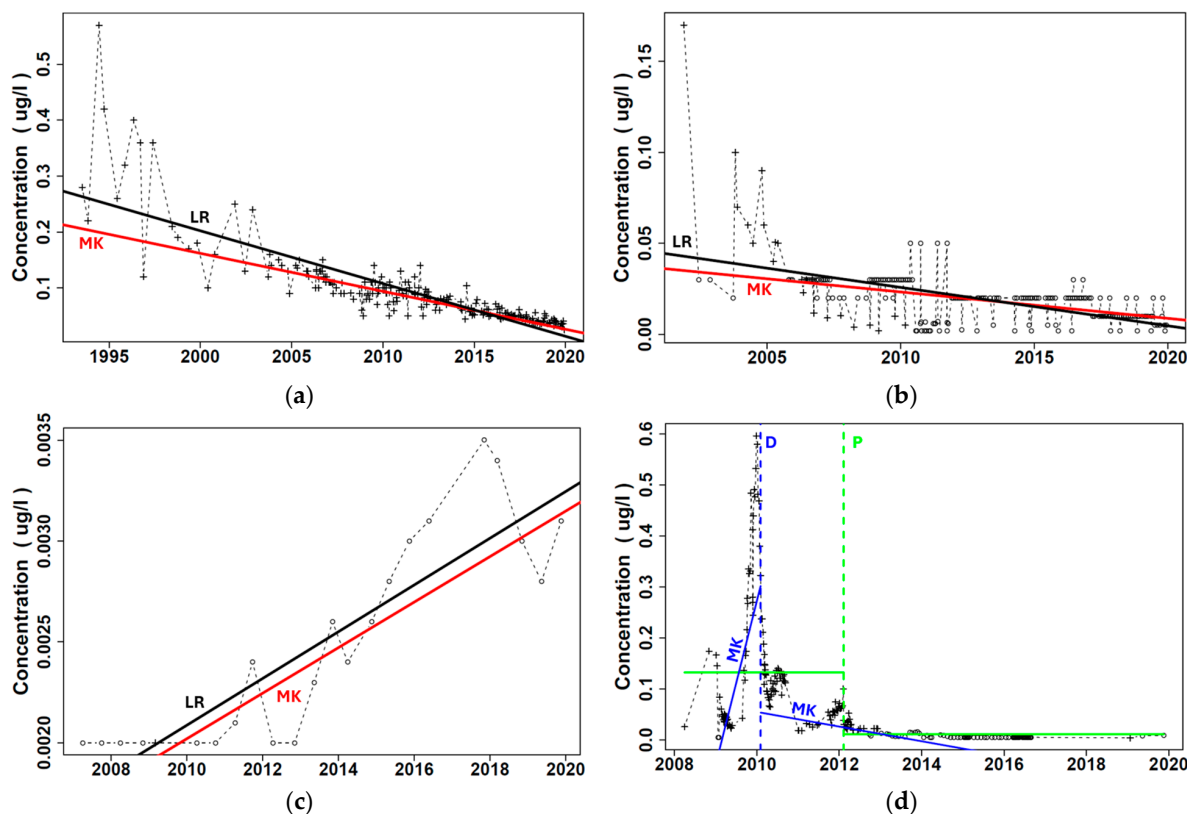
Figure 5. Characteristic trends of (**a**) atrazine at VD Hrastje 1a; (**b**) 2,6-dichlorobenzamide at VD Hrastje 1a; (**c**) desethylterbuthylazine at VD Kleče 10; (**d**) metazachlor at VD Kleče 14: black line—linear regression (LR); red line—Mann–Kendall (MK); blue dashed line—Darken [92] date of trend reversal (D) and blue solid lines—MK trend before/after trend reversal; green dashed line—Pettitt [93] change in mean (P) and green solid lines—mean value before/after change. The plus signs indicate results > LOQ, and the circle signs indicate results < LOQ or <LOD.

Due to long-standing agricultural practises in the hinterland of waterworks, pesticides remain the most frequently analysed compounds among organic pollutants. Of the 131 pesticides analysed between 2010 and 2019, the concentration of 25 different pesticides was detected at least three times above the LOQ, 10 of which are currently banned in the inner water protection zone (VVO I) in Ljubljansko polje (Table 3). The frequency of occurrence with concentrations above the LOQ was by far the highest for desethylatrazine and atrazine (Table 3).

Table 3. Occurrence of pesticides or their degradation products banned in water protection zones.

Parameter (2010–2019)	Na > LOQ	Na	Nmp > LOQ	Nmp
desethylatrazine	1381	1573	73	76
atrazine	1152	1382	71	75
metazachlor	259	1594	17	73
desethylterbutylazine	39	1016	22	68
metolachlor	82	1693	28	76
bentazone	74	555	19	29
terbuthylazine	33	1136	17	74
isoproturon	4	555	4	29
dimethenamid	5	1379	2	76
metalaxyl	7	596	5	29
desisopropylatrazine	1	1161	1	74

Notes: Na > LOQ: Number of analyses with detected concentrations above LOQ; Na: Total number of analyses; Nmp > LOQ: Number of measuring points with detected concentrations above LOQ; Nmp: Total number of measuring points.

To curb the emergence of new pesticides that replace atrazine, a mitigation measure has been in place since 2015 that requires continuous preventive monitoring of drinking water wells to detect the presence of pesticides. If pesticides are detected, the active substance is subject to a specific procedure and added to the list of prohibited substances in the inner water protection zone [104].

4.2.2. Volatile Halogenated Hydrocarbons

Short-term elevated concentrations of volatile halogenated hydrocarbons from unknown pollution sources have occurred occasionally and randomly in the past, with the most serious pollution being caused by tetrachloroethene (PCE) and trichloroethene (TCE). The average annual concentration of PCE exceeded the normative limit for drinking water of 2 μg/L (Figure 6), which meant that the aquifer did not fulfil the requirements for achieving good chemical status in 2003 [102]. The highest concentrations were detected at the Hrastje well field at 3.5–6.9 μg/L. Despite generally decreasing concentrations (-0.053 μg/L/year, $p = 6.3 \times 10^{-10}$), especially between 2010–2015, a new upward trend was observed after the trend reversal in 2015 (0.025 μg/L/year, $p = 2.6 \times 10^{-3}$). On the other hand, the Petitt test shows a significant change in the mean value ($p = 1.3 \times 10^{-14}$) in 2012.
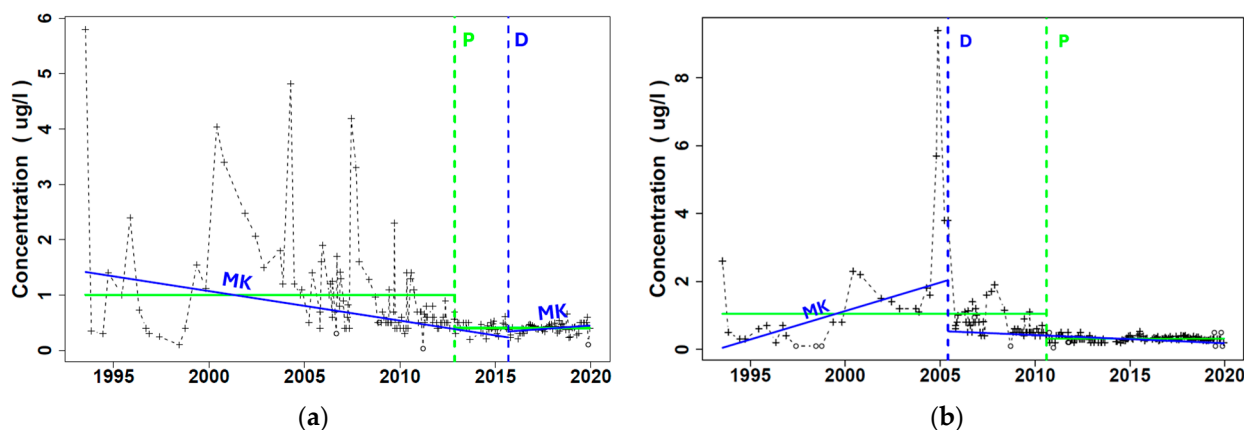

Figure 6. Characteristic trends at VD Hrastje 1a: (**a**) tetrachloroethene (PCE) and (**b**) trichloroethene (TCE). Blue dashed line—Darken [92] date of trend reversal (D) and blue solid lines—Mann–Kendall (MK) trend before/after trend reversal; green dashed line—Pettitt [93] change in mean (P) and green solid lines—mean value before/after change. The plus signs indicate results > LOQ, and the circle signs indicate results < LOQ or <LOD.

In 2004, severe localised pollution with TCE was detected as a uniform sharp contamination peak about 2.5 km southwest of the Hrastje waterworks with maximum concentrations of over 700 μg/L [102,105]. The pollution gradually covered the southern part of the Hrastje waterworks (Figure 6) and exceeded the already high background concentrations of PCE and TCE. After the uniform peak of the TCE concentration in VD Hrastje 1a, the TCE concentration started to decrease by 0.024 μg/L/year ($p = 5.0 \times 10^{-17}$) after a trend reversal in 2005. According to the Pettitt test, there was a significant change in the mean value of the TCE concentration in 2010 ($p = 1.3 \times 10^{-19}$), and after 2010, only threshold values were found (Figure 6). This indicates that pollution was released from several pulse-like contaminant inputs. The downward trend could also be a consequence of the state Decree on the Area of the Ljubljansko Polje Aquifer and Its Hydrographic Reserves at Risk from Plant Protection Products and Volatile Chlorinated Hydrocarbons, which came into force in 2003.

Of the 33 volatile halogenated hydrocarbons analysed between 2010 and 2019, 14 exceeded the LOQ at least once, but concentrations remained relatively low. PCE and TCE continued to dominate the frequency of occurrence above the LOQ, followed by trichloroethane and trichloromethane. Between 2012 and 2017, new, increasing trends in

TCE and PCE were observed at two sampling points located in the direct hinterland of the Hrastje waterworks, emphasising the importance of continuous monitoring to detect deterioration in quality and take immediate action if necessary.

4.2.3. Pharmaceutical Residues and Other Synthetic Organic Pollutants

The presence of endocrine disruptors, pharmaceutical residues and other chemicals from personal care products in the groundwater of Ljubljansko polje has become a subject of research in the last decade [6–8]. Back in 2009, Ljubljansko polje was not overloaded with characteristic pharmaceutical residues such as caffeine, carbamazepine, and propyphenazone, but traces of contaminants were already observed, including the detection of carbamazepine in the Hrastje well field [6]. Between 2010 and 2019, out of 51 pharmaceutical compounds analysed, only 13 were quantifiable, with salicylic acid being the most frequently detected (62% of analyses), followed by caffeine (17%), sulfamethoxazole, theophylline, propyphenazone and carbamazepine. In terms of prevalence across sampling sites, caffeine, salicylic acid, carbamazepine and propyphenazone predominated.

Due to its properties, carbamazepine was considered one of the most serious emerging contaminants between 2010 and 2019 [7]. It was typically found in scattered concentrations, indicating diffuse pollution in the area. In 2017, the highest values between 10 and 50 ng/L were found in the shallow perched aquifer in the NW part of Ljubljansko polje, as well as in the most SW part. Due to the lack of time series data at the most relevant sampling sites, it was not possible to examine any trends. Given that the contamination plume extends south of the waterworks, it is unlikely that carbamazepine will pose a significant threat to water quality in the well fields. However, to prevent further increases in carbamazepine concentrations, it is critical to reduce the losses from the sewerage system, which is believed to be the primary source of contamination.

Among the 23 synthetic organic pollutants analysed between 2010 and 2019, 11 were found above the LOQ. Above all, nonylphenols, phthalates, bisphenol A and 2-methyl-2H-benzotriazole were detected most frequently. In 2017, particularly high concentrations of 2-methyl-2H-benzotriazole (up to 47 ng/L) were observed at the western edge of the aquifer, where perched groundwater is present. Its primary source is the entire urban area, including losses from the sewage system.

Recent targeted sampling conducted between 2022 and 2024 revealed characteristic increasing trends of 1H-benzotriazole, 4-methyl-1H-benzotriazole and 5-methyl-1H-benzotriazole in the central part of Ljubljansko polje. This poses a potential threat to the Hrastje waterworks and is the reason for the ongoing research efforts. These parameters were not monitored in the target period of 2010–2019 due to the lack of precise equipment required to accurately detect these compounds. The same applies to the occurrence of PFAS, which remains uncertain due to unavailable data. Based on the annual reports on the compliance of drinking water in the supply areas managed by the public company Vodovod Kanalizacija Snaga, PFAS does not appear to pose a significant threat to the safety of the water supply. However, it should be noted that trace amounts of these compounds can be detected, usually close to the detection limit of the test methods.

Because emerging pollutants occur in markedly low concentrations or in trace amounts, they are difficult to evaluate statistically in terms of reliability of results and probability of prediction. For this reason, some sampling results in the study area [3,8] have started to be reported in accordance with ISO 11843-2:2000 [106]. Table 4 shows an example where both the analytical raw value and its uncertainty are given. If the measured value does not exceed the critical value, which, for example corresponds to the limit of detection (LOD) set at LOD = 0.0100 µg/L, the notation < LOD = 0.0100 µg/L is given, with the measured raw value in brackets. This approach is quite demanding and requires a dedicated effort from the laboratory, but it allows the prediction of temporal and spatial trends of emerging pollutants even before the concentrations become quantifiable. This is particularly valuable for drinking water supply systems, as they need to take action before the pollutant concentrations become characteristic or exceed the LOD or LOQ.

Table 4. An example of reporting raw analytical values in accordance with the ISO 11843 standard in the area of Ljubljansko polje [7,8].

Concentration Value Level	Original Value [μg/L]	Numerical Value [μg/L]
Conc. > LOQ	0.078 (>LOQ = 0.033)	0.078
LOQ > Conc. > LOD	<LOQ = 0.033 & >LOD = 0.010 (0.0215)	0.0215
Conc. < LOQ	<LOQ = 0.033 (0.017)	0.017
Conc. < LOD	<LOD = 0.0100 (0.00758)	0.00758

Note: Original value = the result presented in the laboratory report.

5. Discussion

The surveillance and operational monitoring of groundwater quality in the functional urban area of Ljubljana have proven effective in ensuring comprehensive control of groundwater resources and the safety of drinking water supply. In recent years, groundwater monitoring at the local level has been greatly modernised through frequent, targeted sampling campaigns, the introduction of passive sampling and the reporting of raw analytical values in accordance with the ISO 11843 series of standards [7,8], which has enabled the very early detection of several unfavourable upward trends (e.g., desethylterbutylazine). By consolidating data from different institutions, an important step was taken to simplify the interpretation of monitoring results and improve groundwater management. However, the main disadvantage of long data sets is the potential scarcity and inconsistency of data [72], as well as the impact of changes in sampling protocols and laboratory methods on the comparability of data [72,73]. Some studies suggest that changes in sampling and laboratory practises may have a greater impact on the data than actual environmental changes [73,75]. Our data set shows that data prior to the year 2000 are significantly sparser and more scattered, and that extreme values occured more frequently.

In general, the data set revealed that quite a large number of the analysed parameters were only reported as a qualitative result, i.e., below the LOQ or below the LOD, without a quantitative value. If the parameter was never quantified at the measurement site, it could be concluded that no such contamination was present. According to the risk-based approach, this parameter would only be of concern if there is a reliable identification of a detectable or quantifiable concentration or if there is a clear indication that substances are leaking into the environment and are expected to be present in groundwater sooner or later. However, with the continuous advances in analytical methods, the limits of detection and quantification are gradually being lowered. As a result, current advanced analyses can reveal contaminant levels and trends that were previously unquantifiable. It is important to note that the absence of quantifiable contaminants in previous analyses does not necessarily mean that they were not present in the past. Therefore, it is necessary that the data is always linked to LOQ and LOD information. To ensure the accuracy, reliability and reproducibility of the data collected at each sampling point, it is also essential to keep a detailed record of the sampling conditions. This record enables the direct comparison of successive samplings and can improve the representativeness of the data series.

After a thorough review of local studies and analysis of available data, we identified the most critical contaminants in the study area to investigate the characteristic trends. Our analysis revealed that none of the input data sets followed a normal distribution, as shown by the Shapiro–Wilk test. Long-term trends were assessed using both the non-parametric Mann–Kendall test and parametric linear regression. In cases where consistent trends were observed over a longer period of time (e.g., decreasing nitrate and sulphate levels and increasing desethylterbutylazine levels), the two methods yielded very similar slopes with minimal differences in trend assessment. However, in cases where a significant trend reversal was observed, such as with hexavalent chromium, the differences between the two methods were more pronounced. This clearly demonstrates how the techniques that detect monotonic trends can be considerably affected by trend reversal [72]. A slightly smaller amount of data prior to the year 2000 showed no significant effect on trend assessment, but

the Mann–Kendall method appeared to be less influenced by outliers within the data set, which is also consistent with the conclusions of Oliva et al. [72].

To detect a trend reversal, i.e., a shift from an upward trend to a downward trend or vice versa, the Darken test proved to be the most suitable. This method, which is based on recognising a change of sign in the slope, is already integrated into the statistical tool Hype [91] and described in the Common Implementation Strategy for the Water Framework Directive and the Floods Directive [107]. On the other hand, the Pettitt test, although widely used, proved to be less reliable for detecting a trend reversal point, as already stated by Frollini et al. [73]. In almost all analysed data sets, the Pettitt test showed apparently significant shifts that were not related to the actual trend reversal, i.e., the change in the sign of the slope, but rather to the smaller changes in the data set, such as the changes in the mean value and the data scatter.

The time span of the long-term contaminant trends in the study area covers the transition period before and after the implementation of the Water Framework Directive and the Groundwater Directive in 2000. While the period between 1992 and 2005 was characterised by higher pollutant concentrations (e.g., nitrate, sulphate, atrazine) or even increasing trends (e.g., hexavalent chromium, trichloroethene), the situation began to improve towards 2010. Statistically significant changes in the mean value of pollutant concentrations based on the Pettitt test can be observed between 2010 and 2012. The greatest improvements can be seen for some pesticides, such as metazachlor and 2,6-dichlorobenzamides, which occur around the LOQ, while nitrates and hexavalent chromium, for example, are still well above natural background concentrations. Although occasional peaks in pollutant concentrations still occur locally, the general groundwater status improved between 2010 and 2019. This confirms the effectiveness of enforcing measures to protect groundwater quality—not only directives at the EU level but also regulations at the national or even municipal level.

An excellent example of good practice was the ban on atrazine and, in the inner water protection zone, the ban on dichlobenil-based pesticides, which successfully reduced the infiltration of pollutants into the aquifer and significantly improved the safety of drinking water supplies. Such positive effects are not necessarily self-evident in other regions [35,108] and depend on many factors, such as the historical use of pollutants, the initial status of the groundwater and the properties of the aquifer. A proactive approach to integrated agriculture is still required throughout the hinterland of the waterworks in the study area. It is also particularly important to control emerging pollutants in the wastewater system, which is becoming a critical source of the mass flow of pollutants.

As we approach the end of the period set by the European directives as the final deadline for achieving good groundwater status, it is assumed that pollutant concentrations are under control and below water quality standards. Compliance with the quality standards alone should no longer be sufficient as the primary objective of groundwater management, because as soon as the pollutant exceeds the quality standard, it is already considered problematic. Instead, the quality of urban groundwater should be continuously improved and protected from new emerging contaminants. Any contamination should be kept in a downward trend, and any upward trend should be detected at much lower concentrations than the current water quality standard, preferably in the range between LOD and LOQ.

6. Conclusions

Based on the existing database, a comprehensive analysis of the long-term data on the groundwater quality of the Ljubljansko polje aquifer was carried out. The analysis revealed predominantly favourable conditions and good groundwater quality status in the study area. Many contaminants that were highly prevalent in the 1990s (e.g., nitrate, sulphate, atrazine, etc.) show statistically significant decreasing trends. In contrast, the prevalence of emerging organic compounds has increased over the last decade. Although many of these compounds do not exceed the LOQ, their detection has become possible thanks to modernised groundwater sampling techniques and advanced analytical methods,

which have revealed several previously unquantifiable contaminant levels and trends. Such advanced monitoring enables the immediate introduction of appropriate measures to counteract contamination before it poses a significant risk to drinking water supplies. This is also in line with the EU Water Framework Directive (WFD, 2000/60/EC), which emphasises the principle of "prevent and limit". With the increasing use of various new substances and the advancing technology of chemical analysis and scanning capabilities, we expect that the risk-based approach will play an important role in reducing the amount or proportion of non-numerical results below the LOQ and LOD. We anticipate that the quality and precision of sampling will be more important than the number of samples, as sampling itself will become more technically and logistically demanding and it will be hardly possible to process large quantities of samples.

References

1. Krajnc, M.; Gacin, M.; Krsnik, P.; Sodja, E.; Kolenc, A. Groundwater Quality in Slovenia Assessed upon the Results of National Groundwater Monitoring. *Eur. Water* **2007**, *19*, 37–46.

2. Janža, M. A Decision Support System for Emergency Response to Groundwater Resource Pollution in an Urban Area (Ljubljana, Slovenia). *Environ. Earth Sci.* **2015**, *73*, 3763–3774. [CrossRef]

3. Auersperger, P.; Lah, K.; Kus, J.; Marsel, J. High Precision Procedure for Determination of Selected Herbicides and Their Degradation Products in Drinking Water by Solid-Phase Extraction and Gas Chromatography-Mass Spectrometry. *J. Chromatogr. A* **2005**, *1088*, 234–241. [CrossRef]

4. Janža, M.; Prestor, J.; Pestotnik, S.; Jamnik, B. Nitrogen Mass Balance and Pressure Impact Model Applied to an Urban Aquifer. *Water* **2020**, *12*, 1171. [CrossRef]

5. Ogrinc, N.; Tamše, S.; Zavadlav, S.; Vrzel, J.; Jin, L. Evaluation of Geochemical Processes and Nitrate Pollution Sources at the Ljubljansko Polje Aquifer (Slovenia): A Stable Isotope Perspective. *Sci. Total Environ.* **2019**, *646*, 1588–1600. [CrossRef]

6. Jamnik, B.; Auersperger, P.; Urbanc, J.; Lah, K.; Prestor, J. Pharmaceuticals as Indicators of Anthropogenic Influence on the Groundwater of Ljubljansko Polje and Ljubljansko Barje Aquifers. *Geologija* **2009**, *52*, 241–248.

7. Prestor, J.; Cerar, S.; Svetina, J.; Meglič, P. *Analysis of the Occurence of New Emerging Pollutants in the Groundwater of Ljubljansko Polje*; Geological Survey of Slovenia: Ljubljana, Slovenia, 2020. (In Slovene)

8. Cerar, S.; Prestor, J.; Meglič, P.; Svetina, J.D. *T2.2.5—Presentations of Statistical and Environmental Trends and Long-Term Forecasts, Version 2: Part 2*; Project AMIIGA, Interreg Central Europe: Ljubljana, Slovenia, 2019.

9. United Nations. *World Urbanization Prospects: The 2007 Revision*; Population Division of the Department of Economic and Soicial Affairs of the United Nations Secretariat: New York, NY, USA, 2008.

10. Burri, N.M.; Weatherl, R.; Moeck, C.; Schirmer, M. A Review of Threats to Groundwater Quality in the Anthropocene. *Sci. Total Environ.* **2019**, *684*, 136–154. [CrossRef]

11. Vázquez-Suñé, E.; Sánchez-Vila, X.; Carrera, J. Introductory Review of Specific Factors Influencing Urban Groundwater, an Emerging Branch of Hydrogeology, with Reference to Barcelona, Spain. *Hydrogeol. J.* **2005**, *13*, 522–533. [CrossRef]

12. la Vigna, F. Review: Urban Groundwater Issues and Resource Management, and Their Roles in the Resilience of Cities. *Hydrogeol. J.* **2022**, *30*, 1657–1683. [CrossRef]

13. Schirmer, M.; Leschik, S.; Musolff, A. Current Research in Urban Hydrogeology—A Review. *Adv. Water Resour.* **2013**, *51*, 280–291. [CrossRef]

14. Lerner, D.N. Identifying and Quantifying Urban Recharge: A Review. *Hydrogeol. J.* **2002**, *10*, 143–152. [CrossRef]

15. Barbieri, M.; Barberio, M.D.; Banzato, F.; Billi, A.; Boschetti, T.; Franchini, S.; Gori, F.; Petitta, M. Climate Change and Its Effect on Groundwater Quality. *Environ. Geochem. Health* **2021**, *45*, 1133–1144. [CrossRef]

16. Earman, S.; Dettinger, M. Potential Impacts of Climate Change on Groundwater Resources—A Global Review. *J. Water Clim. Change* **2011**, *2*, 213–229. [CrossRef]

17. Stigter, T.Y.; Miller, J.; Chen, J.; Re, V. Groundwater and Climate Change: Threats and Opportunities. *Hydrogeol. J.* **2022**, *31*, 7–10. [CrossRef]

18. Kløve, B.; Ala-Aho, P.; Bertrand, G.; Gurdak, J.J.; Kupfersberger, H.; Kværner, J.; Muotka, T.; Mykrä, H.; Preda, E.; Rossi, P.; et al. Climate Change Impacts on Groundwater and Dependent Ecosystems. *J. Hydrol.* **2014**, *518*, 250–266. [CrossRef]

19. Amanambu, A.C.; Obarein, O.A.; Mossa, J.; Li, L.; Ayeni, S.S.; Balogun, O.; Oyebamiji, A.; Ochege, F.U. Groundwater System and Climate Change: Present Status and Future Considerations. *J. Hydrol.* **2020**, *589*, 125163. [CrossRef]

20. Grischek, T.; Nestler, W. Urban Groundwater in Dresen, Germany. *Hydrogeol. J.* **1996**, *4*, 48–63. [CrossRef]

21. Rose, S.; Peters, N.E. Effects of Urbanization on Streamflow in the Atlanta Area (Georgia, USA): A Comparative Hydrological Approach. *Hydrol. Process* **2001**, *15*, 1441–1457. [CrossRef]

22. Barron, O.V.; Donn, M.J.; Barr, A.D. Urbanisation and Shallow Groundwater: Predicting Changes in Catchment Hydrological Responses. *Water Resour. Manag.* **2013**, *27*, 95–115. [CrossRef]

23. Passarello, M.C.; Sharp, J.M.; Pierce, S.A. Estimating Urban-Induced Artificial Recharge: A Case Study for Austin, TX. *Environ. Eng. Geosci.* **2012**, *18*, 25–36. [CrossRef]

24. Minnig, M.; Moeck, C.; Radny, D.; Schirmer, M. Impact of Urbanization on Groundwater Recharge Rates in Dübendorf, Switzerland. *J. Hydrol.* **2018**, *563*, 1135–1146. [CrossRef]

25. Molle, F.; López-Gunn, E.; van Steenbergen, F. The Local and National Politics of Groundwater Overexploitation. *Water Altern.* **2018**, *11*, 445–457.

26. Bierkens, M.F.P.; Wada, Y. Non-Renewable Groundwater Use and Groundwater Depletion: A Review. *Environ. Res. Lett.* **2019**, *14*, 063002. [CrossRef]

27. Jago-on, K.A.B.; Kaneko, S.; Fujikura, R.; Fujiwara, A.; Imai, T.; Matsumoto, T.; Zhang, J.; Tanikawa, H.; Tanaka, K.; Lee, B.; et al. Urbanization and Subsurface Environmental Issues: An Attempt at DPSIR Model Application in Asian Cities. *Sci. Total Environ.* **2009**, *407*, 3089–3104. [CrossRef] [PubMed]

28. EEA. *Europe's Groundwater—A Key Resource under Pressure*; EEA: Copenhagen, Denmark, 2022.

29. EEA. *European Waters—Assessment of Status and Pressures 2018*; EEA: Copenhagen, Denmark, 2018.

30. Tzilivakis, J.; Warner, D.J.; Green, A.; Lewis, K.A. A Broad-Scale Spatial Analysis of the Environmental Benefits of Fertiliser Closed Periods Implemented under the Nitrates Directive in Europe. *J. Environ. Manag.* **2021**, *299*, 113674. [CrossRef] [PubMed]

31. Mititelu-Ionuș, O.; Simulescu, D.; Popescu, S.M. Environmental Assessment of Agricultural Activities and Groundwater Nitrate Pollution Susceptibility: A Regional Case Study (Southwestern Romania). *Environ. Monit. Assess.* **2019**, *191*, 501. [CrossRef] [PubMed]

32. Velthof, G.L.; Lesschen, J.P.; Webb, J.; Pietrzak, S.; Miatkowski, Z.; Pinto, M.; Kros, J.; Oenema, O. The Impact of the Nitrates Directive on Nitrogen Emissions from Agriculture in the EU-27 during 2000–2008. *Sci. Total Environ.* **2014**, *468–469*, 1225–1233. [CrossRef] [PubMed]

33. Weber, G.; Honecker, U.; Kubiniok, J. Nitrate Dynamics in Springs and Headwater Streams with Agricultural Catchments in Southwestern Germany. *Sci. Total Environ.* **2020**, *722*, 137858. [CrossRef]

34. Oenema, O.; Witzke, H.P.; Klimont, Z.; Lesschen, J.P.; Velthof, G.L. Integrated Assessment of Promising Measures to Decrease Nitrogen Losses from Agriculture in EU-27. *Agric. Ecosyst. Environ.* **2009**, *133*, 280–288. [CrossRef]

35. Ducci, D.; della Morte, R.; Mottola, A.; Onorati, G.; Pugliano, G. Nitrate Trends in Groundwater of the Campania Region (Southern Italy). *Environ. Sci. Pollut. Res.* **2019**, *26*, 2120–2131. [CrossRef]

36. Wakida, F.T.; Lerner, D.N. Non-Agricultural Sources of Groundwater Nitrate: A Review and Case Study. *Water Res.* **2005**, *39*, 3–16. [CrossRef]

37. Kuczyńska, A.; Jarnuszewski, G.; Nowakowska, M.; Wexler, S.K.; Wiśniowski, Z.; Burczyk, P.; Durkowski, T.; Woźnicka, M. Identifying Causes of Poor Water Quality in a Polish Agricultural Catchment for Designing Effective and Targeted Mitigation Measures. *Sci. Total Environ.* **2021**, *765*, 144125. [CrossRef]

38. Sjerps, R.M.A.; Kooij, P.J.F.; van Loon, A.; van Wezel, A.P. Occurrence of Pesticides in Dutch Drinking Water Sources. *Chemosphere* **2019**, *235*, 510–518. [CrossRef] [PubMed]

39. Suciu, N.; Farolfi, C.; Zambito Marsala, R.; Russo, E.; de Crema, M.; Peroncini, E.; Tomei, F.; Antolini, G.; Marcaccio, M.; Marletto, V.; et al. Evaluation of Groundwater Contamination Sources by Plant Protection Products in Hilly Vineyards of Northern Italy. *Sci. Total Environ.* **2020**, *749*, 141495. [CrossRef] [PubMed]

40. di Lorenzo, T.; Cifoni, M.; Fiasca, B.; di Cioccio, A.; Galassi, D.M.P. Ecological Risk Assessment of Pesticide Mixtures in the Alluvial Aquifers of Central Italy: Toward More Realistic Scenarios for Risk Mitigation. *Sci. Total Environ.* **2018**, *644*, 161–172. [CrossRef]

41. Hakoun, V.; Orban, P.; Dassargues, A.; Brouyère, S. Factors Controlling Spatial and Temporal Patterns of Multiple Pesticide Compounds in Groundwater (Hesbaye Chalk Aquifer, Belgium). *Environ. Pollut.* **2017**, *223*, 185–199. [CrossRef]

42. Fonseca, E.; Renau-Pruñonosa, A.; Ibáñez, M.; Gracia-Lor, E.; Estrela, T.; Jiménez, S.; Pérez-Martín, M.Á.; González, F.; Hernández, F.; Morell, I. Investigation of Pesticides and Their Transformation Products in the Júcar River Hydrographical Basin (Spain) by Wide-Scope High-Resolution Mass Spectrometry Screening. *Environ. Res.* **2019**, *177*, 108570. [CrossRef] [PubMed]

43. Fenner, K.; Canonica, S.; Wackett, L.P.; Elsner, M. Evaluating Pesticide Degradation in the Environment: Blind Spots and Emerging Opportunities. *Science* **2013**, *341*, 752–758. [CrossRef] [PubMed]

44. Escher, B.I.; Fenner, K. Recent Advances in Environmental Risk Assessment of Transformation Products. *Environ. Sci. Technol.* **2011**, *45*, 3835–3847. [CrossRef]

45. Giménez-Forcada, E.; Bencini, A.; Pranzini, G. Hydrogeochemical Considerations about the Origin of Groundwater Salinization in Some Coastal Plains of Elba Island (Tuscany, Italy). *Environ. Geochem. Health* **2010**, *32*, 243–257. [CrossRef]

46. Delsman, J.R.; van Baaren, E.S.; Siemon, B.; Dabekaussen, W.; Karaoulis, M.C.; Pauw, P.S.; Vermaas, T.; Bootsma, H.; de Louw, P.G.B.; Gunnink, J.L.; et al. Large-Scale, Probabilistic Salinity Mapping Using Airborne Electromagnetics for Groundwater Management in Zeeland, the Netherlands. *Environ. Res. Lett.* **2018**, *13*, 084011. [CrossRef]

47. Corniello, A.; Ducci, D. Hydrogeochemical Characterization of the Urban Coastal Aquifers of Napoli (Southern Italy): An Overview. *Acque Sotter. Ital. J. Groundw.* **2019**, *8*, 11–19. [CrossRef]

48. Czinnerova, M.; Nguyen, N.H.A.; Nemecek, J.; Mackenzie, K.; Boothman, C.; Lloyd, J.; Laszlo, T.; Spanek, R.; Cernik, M.; Sevcu, A. In Situ Pilot Application of NZVI Embedded in Activated Carbon for Remediation of Chlorinated Ethene-Contaminated Groundwater: Effect on Microbial Communities. *Environ. Sci. Eur.* **2020**, *32*, 154. [CrossRef]

49. Zanini, A.; Ghirardi, M.; Emiliani, R. A Multidisciplinary Approach to Evaluate the Effectiveness of Natural Attenuation at a Contaminated Site. *Hydrology* **2021**, *8*, 101. [CrossRef]

50. Bulatović, S.; Ilić, M.; Šolević Knudsen, T.; Milić, J.; Pucarević, M.; Jovančićević, B.; Vrvić, M.M. Evaluation of Potential Human Health Risks from Exposure to Volatile Organic Compounds in Contaminated Urban Groundwater in the Sava River Aquifer, Belgrade, Serbia. *Environ. Geochem. Health* **2022**, *44*, 3451–3472. [CrossRef] [PubMed]

51. Niculae, A.; Vasile, G.G.; Ene, C.; Cruceru, L.V. The Study of Groundwater Contamination with Volatile Organic Micropollutants (Trichloroethylene) in Northern Bucharest. *Rev. Chim.* **2018**, *69*, 6–9. [CrossRef]

52. Alberti, L.; Colombo, L.; Formentin, G. Null-Space Monte Carlo Particle Tracking to Assess Groundwater PCE (Tetrachloroethene) Diffuse Pollution in North-Eastern Milan Functional Urban Area. *Sci. Total Environ.* **2018**, *621*, 326–339. [CrossRef] [PubMed]

53. Åhlgren, K.; Sjöberg, V.; Allard, B.; Bäckström, M. Groundwater Chemistry Affected by Trace Elements (As, Mo, Ni, U and V) from a Burning Alum Shale Waste Deposit, Kvarntorp, Sweden. *Environ. Sci. Pollut. Res.* **2021**, *28*, 30219–30241. [CrossRef] [PubMed]

54. Dokou, Z.; Kourgialas, N.N.; Karatzas, G.P. Assessing Groundwater Quality in Greece Based on Spatial and Temporal Analysis. *Environ. Monit. Assess.* **2015**, *187*, 774. [CrossRef]

55. Sacchi, E.; Bergamini, M.; Lazzari, E.; Musacchio, A.; Mor, J.R.; Pugliaro, E. Natural Background Levels of Potentially Toxic Elements in Groundwater from a Former Asbestos Mine in Serpentinite (Balangero, North Italy). *Water* **2021**, *13*, 735. [CrossRef]

56. Salvo, A.; la Torre, G.L.; Mangano, V.; Casale, K.E.; Bartolomeo, G.; Santini, A.; Granata, T.; Dugo, G. Toxic Inorganic Pollutants in Foods from Agricultural Producing Areas of Southern Italy: Level and Risk Assessment. *Ecotoxicol. Environ. Saf.* **2018**, *148*, 114–124. [CrossRef]

57. Fernández-Luqueño, F.; López-Valdez, F.; Gamero, P.; Luna, S. Heavy Metal Pollution in Drinking Water-a Global Risk for Human Health: A Review. *Afr. J. Environ. Sci. Technol.* **2013**, *7*, 567–584.

58. Panagos, P.; van Liedekerke, M.; Yigini, Y.; Montanarella, L. Contaminated Sites in Europe: Review of the Current Situation Based on Data Collected through a European Network. *J. Environ. Public. Health* **2013**, *2013*, 158764. [CrossRef]

59. Koroša, A.; Brenčič, M.; Mali, N. Estimating the Transport Parameters of Propyphenazone, Caffeine and Carbamazepine by Means of a Tracer Experiment in a Coarse-Gravel Unsaturated Zone. *Water Res.* **2020**, *175*, 115680. [CrossRef]

60. Stuart, M.; Lapworth, D.; Crane, E.; Hart, A. Review of Risk from Potential Emerging Contaminants in UK Groundwater. *Sci. Total Environ.* **2012**, *416*, 1–21. [CrossRef] [PubMed]

61. Kuczyńska, A. Presence of Pharmaceutical Compounds in Groundwater with Respect to Land Use in the Vicinity of Sampling Sites. *Geologos* **2019**, *25*, 231–240. [CrossRef]

62. Lapworth, D.J.; Lopez, B.; Laabs, V.; Kozel, R.; Wolter, R.; Ward, R.; Vargas Amelin, E.; Besien, T.; Claessens, J.; Delloye, F.; et al. Developing a Groundwater Watch List for Substances of Emerging Concern: A European Perspective. *Environ. Res. Lett.* **2019**, *14*, 035004. [CrossRef]

63. Bunting, S.Y.; Lapworth, D.J.; Crane, E.J.; Grima-Olmedo, J.; Koroša, A.; Kuczyńska, A.; Mali, N.; Rosenqvist, L.; van Vliet, M.E.; Togola, A.; et al. Emerging Organic Compounds in European Groundwater. *Environ. Pollut.* **2021**, *269*, 115945. [CrossRef]

64. Pereira, L.C.; de Souza, A.O.; Bernardes, M.F.F.; Pazin, M.; Tasso, M.J.; Pereira, P.H.; Dorta, D.J. A Perspective on the Potential Risks of Emerging Contaminants to Human and Environmental Health. *Environ. Sci. Pollut. Res.* **2015**, *22*, 13800–13823. [CrossRef]

65. Pal, A.; He, Y.; Jekel, M.; Reinhard, M.; Gin, K.Y.H. Emerging Contaminants of Public Health Significance as Water Quality Indicator Compounds in the Urban Water Cycle. *Environ. Int.* **2014**, *71*, 46–62. [CrossRef]

66. Viaroli, S.; Lancia, M.; Re, V. Microplastics Contamination of Groundwater: Current Evidence and Future Perspectives. A Review. *Sci. Total Environ.* **2022**, *824*, 153851. [CrossRef] [PubMed]

67. Moeck, C.; Davies, G.; Krause, S.; Schneidewind, U. Microplastics and Nanoplastics in Agriculture—A Potential Source of Soil and Groundwater Contamination? *Grundwasser* **2023**, *28*, 23–35. [CrossRef]

68. Severini, E.; Ducci, L.; Sutti, A.; Robottom, S.; Sutti, S.; Celico, F. River–Groundwater Interaction and Recharge Effects on Microplastics Contamination of Groundwater in Confined Alluvial Aquifers. *Water* **2022**, *14*, 1913. [CrossRef]

69. Belkhiri, A.H.; Carre, F.; Quiot, F. State of Knowledge and Future Research Needs on Microplastics in Groundwater. *J. Water Health* **2022**, *20*, 1479–1496. [CrossRef] [PubMed]

70. Koreimann, C.; Grath, J.; Winkler, G.; Nagy, W.; Vogel, W.R. *Groundwater Monitoring in Europe*; EEA: Copenhagen, Denmark, 1996.

71. Voigt, H.-J.; Jenn, F.; Nitsche, C. European Strategies of Groundwater Monitoring for Different Aims. *Baltica* **2008**, *21*, 63–70.

72. Oliva, F.; Vegas, E.; Civit, S.; Garrido, T.; Fraile, J.; Munné, A. Trend Assessment for Groundwater Pollutants: A Brief Review and Some Remarks. In *Handbook of Environmental Chemistry*; Springer Science and Business Media Deutschland GmbH: Berlin/Heidelberg, Germany, 2015; Volume 43, pp. 25–62.

73. Frollini, E.; Preziosi, E.; Calace, N.; Guerra, M.; Guyennon, N.; Marcaccio, M.; Menichetti, S.; Romano, E.; Ghergo, S. Groundwater Quality Trend and Trend Reversal Assessment in the European Water Framework Directive Context: An Example with Nitrates in Italy. *Environ. Sci. Pollut. Res.* **2021**, *28*, 22092–22104. [CrossRef]

74. Lopez, B.; Baran, N.; Bourgine, B. An Innovative Procedure to Assess Multi-Scale Temporal Trends in Groundwater Quality: Example of the Nitrate in the Seine-Normandy Basin, France. *J. Hydrol.* **2015**, *522*, 1–10. [CrossRef]

75. Wahlin, K.; Grimvall, A. Uncertainty in Water Quality Data and Its Implications for Trend Detection: Lessons from Swedish Environmental Data. *Environ. Sci. Policy* **2008**, *11*, 115–124. [CrossRef]

76. Balderacchi, M.; Benoit, P.; Cambier, P.; Eklo, O.M.; Gargini, A.; Gemitzi, A.; Gurel, M.; Kløve, B.; Nakic, Z.; Predaa, E.; et al. Groundwater Pollution and Quality Monitoring Approaches at the European Level. *Crit. Rev. Environ. Sci. Technol.* **2013**, *43*, 323–408. [CrossRef]

77. Quevauviller, P. Science-Policy Interfacing in the Context of the WFD Implementation. *J. Soils Sediments* **2006**, *6*, 259–261. [CrossRef]

78. Vasin, S.; Gzyl, G.; Bellotti, M.; Colombo, L.; Ghirardi, M.; Gjetvaj, G.; Kohout, P.; Prestor, J.; Rollwagen, S. Developing Groundwater Contaminant Remediation Strategies for Seven Regional Aquifers. *Proc. Inst. Civil. Eng. Water Manag.* **2022**, *176*, 291–302. [CrossRef]

79. Talabi, A.O.; Kayode, T.J. Groundwater Pollution and Remediation. *J. Water Resour. Prot.* **2019**, *11*, 1–19. [CrossRef]

80. Premru, U. *Tectonics and Tectogenesis of Slovenia*; Geological Survey of Slovenia: Ljubljana, Slovenia, 2005. (In Slovene)

81. Kolar-Jurkovšek, T.; Jurkovšek, B. Late Carboniferous Flora of Castle Hill in Ljubljana (Slovenia). *Geologija* **2007**, *50*, 9–18. [CrossRef]

82. Premru, U. *Basic Geological Map of SFRY. Interpreter for List Ljubljana: L 33-66*; Zvezni Geološki Zavod Beograd: Beograd, Serbia, 1983. (In Slovene)

83. Žlebnik, L. Pleistocene Deposits of the Kranj, Sora and Ljubljana Fields. *Geologija* **1971**, *14*, 5–51. (In Slovene)

84. Bračič Železnik, B.; Pintar, M.; Urbanc, J. Natural Conditions of the Aquifer. In *Groundwater of Ljubljansko Polje = Podtalnica Ljubljanskega Polja*; Perko, D., Ed.; Založba ZRC: Ljubljana, Slovenia, 2005; 258p. (In Slovene)

85. Vizintin, G.; Souvent, P.; Veselič, M.; Cencur Curk, B. Determination of Urban Groundwater Pollution in Alluvial Aquifer Using Linked Process Models Considering Urban Water Cycle. *J. Hydrol.* **2009**, *377*, 261–273. [CrossRef]

86. Šram, D.; Brenčič, M.; Lapanje, A.; Janža, M. Perched Aquifers Spatial Model: A Case Study for Ljubljansko Polje (Central Slovenia). *Geologija* **2012**, *55*, 107–116. [CrossRef]

87. Janža, M.; Meglič, P.; Prestor, J.; Jamnik, B.; Pestotnik, S.D. *T2.2.3—Report on the Improved Transport and Surface-Groundwater Interactions Model, Version 2*; Project AMIIGA, Interreg Central Europe: Ljubljana, Slovenia, 2019.

88. Janža, M.; Meglič, P.; Šram, D. *Numerical Hydrological Modeling*; Project INCOME Action Report; Geological Survey of Slovenia: Ljubljana, Slovenia, 2011.

89. Vrzel, J.; Solomon, D.K.; Blažeka, Ž.; Ogrinc, N. The Study of the Interactions between Groundwater and Sava River Water in the Ljubljansko Polje Aquifer System (Slovenia). *J. Hydrol.* **2018**, *556*, 384–396. [CrossRef]

90. Hribernik, K.; Šinigoj, J.; Krivic, M.; Podboj, M. *Establishment and Maintenance of Database System*; Project INCOME Report; Geological Survey of Slovenia: Ljubljana, Slovenia, 2012.

91. Croiset, N.; Lopez, B. *HYPE: Tool for the Statistical Analysis of Time Series of Groundwater Quality—User Manual*; BRGM: Orléans, France, 2013. Available online: https://www.brgm.fr/en/software/hype-tool-characterising-evaluating-trends-temporal-evolution-groundwater-quality (accessed on 1 March 2024). (In French)

92. Darken, P.F. Testing for Changes in Trend in Water Quality Data. Ph.D. Thesis, Faculty of Virginia Polytechnic Institute and State University, Blacksburg, VA, USA, 1999.

93. Pettitt, A.N. A Non-Parametric Approach to the Change-Point Problem. *J. R. Stat. Soc. Ser. C Appl. Stat.* **1979**, *28*, 126–135. [CrossRef]

94. MOP. *Rules on Groundwater Status Monitoring*; Official Gazette RS, no. 13/21 in 44/22—ZVO-2; MOP: Ljubljana, Slovenia, 2021.

95. European Parliament; the Council of the European Union. *Directive (EU) 2020/2184 on the Quality of Water Intended for Human Consumption*; European Union: Brussels, Belgium, 2020.

96. MOP. *Rules on Drinking Water*; Official Gazette of the Republic of Slovenia, no. 19/04, 35/04, 26/06, 92/06, 25/09, 74/15, 51/17 and 61/23; MOP: Ljubljana, Slovenia, 2023.

97. Directorate-General for Environment (DG ENV). *Proposal for a Directive Amending the Water Framework Directive, the Groundwater Directive and the Environmental Quality Standards Directive*; DG ENV: Brussels, Belgium, 2022.

98. Brilly, M.; Jamnik, B.; Drobne, D. Chromium Contamination of the Ljubljansko Polje Aquifer. *RMZ—Mater. Geoenviron.* **2003**, *50*, 71–74.

99. Jamnik, B.; Janža, M.; Smrekar, A.; Breg Valjavec, M.; Cerar, S.; Cosma, C.; Hribernik, K.; Krivic, M.; Meglič, P.; Pestotnik, S.; et al. *Care for Drinking Water = Skrb Za Pitno Vodo*; Kladnik, D., Topole, M., Eds.; Založba ZRC: Ljubljana, Slovenia, 2014. (In Slovene)

100. Meglič, P.; Janža, M.; Prestor, J.; Pestotnik, S.; Jamnik, B.D. *T2.2.7—Report on the Results of the Most Probable Scenarios Threatening Groundwater, Version 2*; Project AMIIGA, Interreg Central Europe: Ljubljana, Slovenia, 2019.

101. ARSO Air Quality Annual Reports. Available online: http://www.arso.gov.si/zrak/kakovost%20zraka/poro%C4%8Dila%20in%20publikacije/kakovost_letna.html (accessed on 14 February 2024). (In Slovene)

102. Auersperger, P.; Jamnik, B.; Krajnc, M. Groundwater Load = Obremenjenost Podzemne Vode. In *Groundwater of Ljubljansko Polje = Podtalnica Ljubljanskega Polja*; Perko, D., Ed.; Založba ZRC: Ljubljana, Slovenia, 2005; 258p. (In Slovene)

103. Tasca, A.L.; Puccini, M.; Fletcher, A. Terbuthylazine and Desethylterbuthylazine: Recent Occurrence, Mobility and Removal Techniques. *Chemosphere* **2018**, *202*, 94–104. [CrossRef] [PubMed]

104. Republic of Slovenia List of Phytopharmaceuticals That Are Prohibited for Use in the Inner Water Protection Zones. Available online: https://spletni2.furs.gov.si/FFS/REGSR/FFS_RegSeznVVO.asp?top=1 (accessed on 6 February 2024). (In Slovene)

105. Schüth, C.; Piepenbrink, M.; Cosma, C.; Janža, M. Contaminant Fingerprinting Using Stable Isotopes and Multilevel Sampling with Passive Samplers = Prstni Odtisi Onesnaževal z Uporabo Stabilnih Izotopov in Večnivojskim Vzorčenjem s Pasivnimi Vzorčevalniki. In *Care for Drinking Water = Skrb za Pitno Vodo*; Kladnik, D., Topole, M., Eds.; Založba ZRC: Ljubljana, Slovenia, 2014; pp. 54–59. (In Slovene)

106. *ISO 11843-2:2000*; Capability of Detection, Part 2: Methodology in the Linear Calibration Case. ISO: Geneve, Switzerland, 2000.

107. Gourcy, L.; Lopez, B. Common Implementation Strategy for the Water Framework Directive and the Floods Directive: Technical Report. on Groundwater Quality Trend and Trend Reversal Assessment. 2019. Available online: https://circabc.europa.eu/sd/a/7a9bdbc8-5b2c-4c16-8832-404b31bd0735/GW_Trend_technical_report_final.pdf (accessed on 1 March 2024).

108. Urresti-Estala, B.; Gavilán, P.J.; Pérez, I.V.; Cantos, F.C. Assessment of Hydrochemical Trends in the Highly Anthropised Guadalhorce River Basin (Southern Spain) in Terms of Compliance with the European Groundwater Directive for 2015. *Environ. Sci. Pollut. Res.* **2016**, *23*, 15990–16005. [CrossRef] [PubMed]