ARTICLE

Table S1 A summary of sample type, sampling location, number (N) of sampling points, frequency of sampling, period of sampling, type of treatment and analyses conducted after sampling.

Sample type	Location	N of sampling points	Frequency	Period	Type of treatment	Analyses
groundwater	catchment area of the Velika Gorica well field	10	monthly	from March 2021 to February 2022	–	in-situ
					filtering cooling at 4 °C	water chemistry water stable isotopes
					filtering freezing	nitrate stable isotopes
surface water	Sava River (western part of the Zagreb aquifer)	1	monthly	from March 2021 to February 2022	–	in-situ
					filtering cooling at 4 °C	water chemistry water stable isotopes
					filtering freezing	nitrate stable isotopes
precipitation	within the first sanitary protection zone of the Velika Gorica well field	1	monthly	from March 2021 to February 2022	–	in-situ
					filtering freezing	nitrate stable isotopes
soil water	pedological pit	4	monthly	from March 2021 to February 2022	filtering freezing	nitrate stable isotopes
nitrogen sources	Central part of the Zagreb aquifer	6	once	September 2021	drying and grinding	isotopic composition of total nitrogen

Table S2 Descriptive statistics of 17 parameters (pH, EC, DO, T, Cl^-, NO_3^-, SO_4^{2-}, HCO_3^-, Na^+, Mg^{2+}, K^+, Ca^{2+}, $\delta^{15}N_{NO3}$, $\delta^{18}O_{NO3}$, δ^2H_{H2O}, $\delta^{18}O_{H2O}$ and d-excess) measured in groundwater and Sava River.

		Čp-23	Lg-1	Lg-4	P-3	P-7	Vg-1	Vg-10/2	Vg-4	Vg-5/2	Vg-6	Sava River
pH	*Mean*	7.2	7.3	7.3	7.1	7.2	7.3	7.3	7.1	7.1	7.2	8.1
	Min	7.0	7.0	7.0	6.9	7.0	7.0	7.1	6.9	7.0	7.0	7.8
	Max	7.5	7.7	7.8	7.5	7.5	7.6	7.6	7.4	7.5	7.5	8.7
EC (µs cm^{-1})	*Mean*	782.4	696.0	793.3	787.1	777.7	781.4	688.9	905.4	851.8	808.0	413.7
	Min	748.0	677.0	751.0	757.0	749.0	765.0	675.0	873.0	838.0	775.0	353.0
	Max	804.0	713.0	823.0	799.0	796.0	801.0	706.0	938.0	881.0	862.0	461.0
DO (mgO_2 L^{-1})	*Mean*	7.1	3.4	3.6	8.3	8.1	7.0	6.5	6.7	7.4	6.2	10.5
	Min	6.6	0.6	1.2	7.6	7.3	6.2	6.0	6.1	6.4	5.6	7.1
	Max	7.8	7.3	7.0	9.0	8.7	7.8	7.0	7.6	8.0	7.3	14.2
T (°C)	*Mean*	13.2	13.0	13.0	13.0	13.2	13.3	12.6	14.1	13.5	14.1	13.6
	Min	12.8	12.6	12.7	12.5	12.6	12.8	12.4	13.7	13.3	13.8	7.2
	Max	13.8	13.9	13.3	14.7	13.7	14.1	13.0	15.0	14.2	14.8	25.0
Cl^- (mg L^{-1})	*Mean*	26.2	11.1	28.1	23.7	23.4	27.4	10.1	55.6	26.4	37.2	8.7
	Min	13.4	7.6	22.7	19.3	11.8	21.2	8.4	43.4	20.7	22.2	5.9
	Max	32.2	14.5	33.0	31.8	35.9	32.0	13.1	71.6	31.7	63.4	12.4
NO_3^- (mg L^{-1})	*Mean*	16.2	20.1	15.6	17.1	13.4	15.5	20.3	14.8	25.1	12.7	5.2
	Min	12.6	15.0	7.4	14.6	9.2	13.2	17.5	11.4	19.4	9.0	3.5
	Max	19.4	25.8	19.0	20.0	17.9	18.6	23.0	18.9	31.9	16.7	6.5
SO_4^{2-} (mg L^{-1})	*Mean*	21.2	13.5	23.1	16.8	13.1	23.3	14.0	21.1	19.7	20.7	12.2
	Min	13.4	9.2	17.9	12.1	7.5	16.9	11.6	18.3	15.6	15.2	6.3
	Max	26.6	17.3	26.3	22.3	18.7	27.8	18.2	26.9	24.8	27.9	17.0
HCO_3^- (mg L^{-1})	*Mean*	423.6	407.5	426.7	443.7	451.5	426.0	401.8	445.8	460.8	425.6	-
	Min	378.6	378.6	359.9	397.2	422.0	415.8	359.9	391.0	415.8	397.2	-
	Max	440.6	415.8	453.0	453.0	484.1	440.6	415.8	471.7	477.9	446.8	-
Na^+ (mg L^{-1})	*Mean*	12.6	6.2	11.2	10.4	10.9	11.5	5.6	29.1	13.9	22.2	7.0
	Min	11.7	5.4	7.9	8.5	6.3	9.7	4.8	22.7	12.0	19.3	4.6
	Max	14.6	7.6	15.3	14.0	17.2	15.6	7.2	37.2	17.9	27.9	10.1
Mg^{2+} (mg L^{-1})	*Mean*	24.4	24.2	26.1	26.9	27.3	24.6	25.1	26.2	25.9	23.4	13.6
	Min	22.9	21.7	22.6	23.6	23.9	23.5	23.4	23.6	23.4	19.9	10.4
	Max	26.7	25.8	33.8	35.1	31.2	26.1	32.2	33.1	28.3	29.5	19.8
K^+ (mg L^{-1})	*Mean*	1.8	1.9	1.7	1.5	1.3	1.6	1.7	2.1	4.8	3.7	1.8
	Min	1.6	1.6	1.3	1.2	0.9	1.3	1.5	1.6	4.4	3.0	1.1
	Max	2.3	2.2	2.5	2.3	1.8	2.1	2.2	2.8	5.6	6.0	3.7
Ca^{2+} (mg L^{-1})	*Mean*	109.0	98.5	109.4	109.3	108.4	111.8	101.4	117.7	116.7	107.2	54.4
	Min	105.1	77.6	84.3	100.6	97.5	106.8	95.3	90.5	97.4	97.3	35.7
	Max	118.4	106.8	122.2	119.3	114.7	127.4	128.4	136.4	124.8	115.3	69.1
$\delta^{15}N_{NO3}$ (‰)	*Mean*	10.4	10.9	15.9	8.5	8.6	10.5	9.2	11.2	9.6	12.1	8.8
	Min	3.8	3.8	9.5	3.9	2.6	7.2	5.9	6.6	4.0	7.6	4.4
	Max	17.6	15.6	38.9	14.1	14.5	13.3	13.4	18.3	14.8	16.7	13.1
$\delta^{18}O_{NO3}$ (‰)	*Mean*	0.7	2.7	5.5	0.7	0.7	0.8	0.9	1.9	1.2	1.9	0.9
	Min	-4.0	-3.2	-1.3	-3.5	-6.7	-1.8	-5.1	-3.4	-2.1	-1.8	-0.8

	Max	4.0	8.0	17.6	3.7	4.7	4.6	4.5	5.0	4.3	4.7	3.9
δ^2H_{H2O} (‰)	*Mean*	-60.0	-63.5	-61.0	-59.7	-60.5	-60.7	-64.5	-59.4	-59.7	-58.0	-60.2
	Min	-60.5	-64.1	-61.9	-60.3	-61.5	-61.2	-65.0	-59.7	-60.3	-58.7	-61.8
	Max	-59.7	-62.8	-60.1	-59.0	-59.7	-59.8	-64.1	-59.2	-58.4	-57.5	-59.2
$\delta^{18}O_{H2O}$ (‰)	*Mean*	-8.8	-9.3	-9.0	-8.9	-8.9	-9.0	-9.5	-8.8	-8.8	-8.7	-9.1
	Min	-9.0	-9.5	-9.2	-9.0	-9.1	-9.2	-9.6	-8.9	-8.9	-8.7	-9.4
	Max	-8.7	-9.3	-8.9	-8.8	-8.8	-8.8	-9.4	-8.7	-8.6	-8.6	-8.9
d-excess	*Mean*	10.7	11.2	11.1	11.1	10.9	11.1	11.3	11.1	10.9	11.2	12.7
	Min	10.2	10.4	10.3	10.0	10.1	10.4	10.5	10.3	10.4	10.8	11.7
	Max	11.2	12.2	11.7	11.8	11.7	12.2	11.9	11.7	11.3	11.8	13.6

Table S3 Correlation matrix of the major anions and cations for sampling site Vg-6 using the Pearson coefficient. All variables are in mg L^{-1}.

	Cl^-	NO_3^-	SO_4^{2-}	HCO_3^-	Na^+	Mg^{2+}	K^+	Ca^{2+}
Cl^-	1.00							
NO_3^-	0.80	1.00						
SO_4^{2-}	0.53	0.44	1.00					
HCO_3^-	-0.31	-0.15	-0.49	1.00				
Na^+	-0.22	-0.39	-0.40	-0.08	1.00			
Mg^{2+}	0.10	0.24	0.00	-0.01	0.63	1.00		
K^+	-0.35	-0.30	-0.25	-0.20	0.84	0.75	1.00	
Ca^{2+}	0.05	-0.25	-0.32	0.09	-0.14	-0.60	-0.49	1.00

Significance at $p < 0.05$

Table S4 Correlation matrix of the major anions and cations for sampling site Vg-5/2 using the Pearson coefficient. All variables are in mg L^{-1}.

	Cl^-	NO_3^-	SO_4^{2-}	HCO_3^-	Na^+	Mg^{2+}	K^+	Ca^{2+}
Cl^-	1.00							
NO_3^-	0.69	1.00						
SO_4^{2-}	0.93	0.51	1.00					
HCO_3^-	0.02	-0.03	-0.01	1.00				
Na^+	-0.43	-0.53	-0.17	0.41	1.00			
Mg^{2+}	0.49	0.36	0.59	-0.09	-0.04	1.00		
K^+	0.15	-0.01	0.39	0.24	0.59	0.77	1.00	
Ca^{2+}	0.61	0.35	0.63	-0.15	-0.21	0.69	0.34	1.00

Significance at $p < 0.05$

Table S5 Correlation matrix of the major anions and cations for sampling site Čp-23 using the Pearson coefficient. All variables are in mg L^{-1}.

	Cl^-	NO_3^-	SO_4^{2-}	HCO_3^-	Na^+	Mg^{2+}	K^+	Ca^{2+}
Cl^-	1.00							
NO_3^-	0.28	1.00						
SO_4^{2-}	0.97	0.26	1.00					
HCO_3^-	0.68	0.03	0.53	1.00				
Na^+	0.12	0.02	-0.07	0.57	1.00			
Mg^{2+}	0.49	0.45	0.43	0.36	0.37	1.00		
K^+	-0.24	0.39	-0.31	-0.32	0.21	0.47	1.00	
Ca^{2+}	0.38	0.19	0.29	0.36	0.29	0.84	0.43	1.00

Significance at $p < 0.05$

Table S6 Correlation matrix of the major anions and cations for sampling site Lg-1 using the Pearson coefficient. All variables are in mg L^{-1}.

	Cl^-	NO_3^-	SO_4^{2-}	HCO_3^-	Na^+	Mg^{2+}	K^+	Ca^{2+}
Cl^-	1.00							
NO_3^-	0.36	1.00						
SO_4^{2-}	0.91	0.28	1.00					
HCO_3^-	0.38	-0.20	0.55	1.00				
Na^+	-0.34	-0.26	-0.24	0.37	1.00			
Mg^{2+}	0.01	0.37	0.07	-0.10	0.38	1.00		
K^+	-0.04	-0.19	-0.03	0.48	0.86	0.49	1.00	
Ca^{2+}	0.29	0.55	0.27	-0.07	-0.37	-0.03	-0.31	1.00

Significance at $p < 0.05$

Table S7 Correlation matrix of the major anions and cations for sampling site Lg-4 using the Pearson coefficient. All variables are in mg L^{-1}.

	Cl^-	NO_3^-	SO_4^{2-}	HCO_3^-	Na^+	Mg^{2+}	K^+	Ca^{2+}
Cl^-	1.00							
NO_3^-	0.07	1.00						
SO_4^{2-}	0.88	-0.18	1.00					
HCO_3^-	0.16	0.57	-0.14	1.00				
Na^+	0.02	0.44	-0.44	0.60	1.00			
Mg^{2+}	0.07	0.13	-0.15	0.26	0.51	1.00		
K^+	0.14	0.45	-0.29	0.60	0.87	0.81	1.00	
Ca^{2+}	0.35	0.35	0.31	0.06	-0.12	-0.51	-0.22	1.00

Significance at $p < 0.05$

Table S8 Correlation matrix of the major anions and cations for sampling site P-3 using the Pearson coefficient. All variables are in mg L^{-1}.

	Cl^-	NO_3^-	SO_4^{2-}	HCO_3^-	Na^+	Mg^{2+}	K^+	Ca^{2+}
Cl^-	1.00							
NO_3^-	0.21	1.00						
SO_4^{2-}	0.94	0.01	1.00					
HCO_3^-	0.09	-0.21	0.32	1.00				
Na^+	0.10	-0.59	0.36	0.32	1.00			
Mg^{2+}	-0.08	-0.21	0.06	0.00	0.62	1.00		
K^+	0.40	-0.24	0.48	-0.02	0.69	0.81	1.00	
Ca^{2+}	0.46	0.05	0.49	0.07	-0.03	-0.12	0.01	1.00

Table S9 Correlation matrix of the major anions and cations for sampling site Vg-1 using the Pearson coefficient. All variables are in mg L^{-1}.

	Cl^-	NO_3^-	SO_4^{2-}	HCO_3^-	Na^+	Mg^{2+}	K^+	Ca^{2+}
Cl^-	1.00							
NO_3^-	-0.14	1.00						
SO_4^{2-}	0.99	-0.16	1.00					
HCO_3^-	-0.35	0.13	-0.37	1.00				
Na^+	-0.56	-0.15	-0.56	0.58	1.00			
Mg^{2+}	-0.04	-0.08	0.07	0.04	0.39	1.00		
K^+	-0.01	0.25	-0.07	0.15	0.44	0.35	1.00	
Ca^{2+}	-0.63	-0.15	-0.61	0.35	0.94	0.49	0.49	1.00

Significance at $p < 0.05$

Table S10 Correlation matrix of the major anions and cations for sampling site P-7 using the Pearson coefficient. All variables are in mg L^{-1}.

	Cl^-	NO_3^-	SO_4^{2-}	HCO_3^-	Na^+	Mg^{2+}	K^+	Ca^{2+}
Cl^-	1.00							
NO_3^-	0.89	1.00						
SO_4^{2-}	0.99	0.91	1.00					
HCO_3^-	-0.52	-0.49	-0.52	1.00				
Na^+	0.85	0.89	0.87	-0.45	1.00			
Mg^{2+}	0.10	0.25	0.23	0.07	0.15	1.00		
K^+	0.89	0.89	0.90	-0.50	0.92	0.26	1.00	
Ca^{2+}	0.44	0.49	0.47	-0.10	0.28	0.69	0.58	1.00

Significance at $p < 0.05$

Table S11 Correlation matrix of the major anions and cations for sampling site Vg-10/2 using the Pearson coefficient. All variables are in mg L^{-1}.

	Cl^-	NO_3^-	SO_4^{2-}	HCO_3^-	Na^+	Mg^{2+}	K^+	Ca^{2+}
Cl^-	1.00							
NO_3^-	0.79	1.00						
SO_4^{2-}	0.96	0.87	1.00					
HCO_3^-	0.29	0.35	0.22	1.00				
Na^+	-0.26	-0.45	-0.30	0.26	1.00			
Mg^{2+}	-0.09	-0.05	-0.03	0.16	0.74	1.00		
K^+	-0.20	-0.15	-0.16	0.27	0.84	0.84	1.00	
Ca^{2+}	-0.25	-0.48	-0.35	0.17	0.55	-0.13	0.26	1.00

Significance at $p < 0.05$

Table S12 Correlation matrix of the major anions and cations for sampling site Vg-4 using the Pearson coefficient. All variables are in mg L^{-1}.

	Cl^-	NO_3^-	SO_4^{2-}	HCO_3^-	Na^+	Mg^{2+}	K^+	Ca^{2+}
Cl^-	1.00							
NO_3^-	-0.19	1.00						
SO_4^{2-}	0.81	-0.35	1.00					
HCO_3^-	0.39	0.12	0.05	1.00				
Na^+	0.44	-0.28	0.19	0.20	1.00			
Mg^{2+}	-0.23	-0.24	-0.16	0.09	0.56	1.00		
K^+	0.24	-0.17	0.24	0.18	0.62	0.77	1.00	
Ca^{2+}	0.55	-0.13	0.28	-0.04	0.24	-0.48	-0.21	1.00

Significance at $p < 0.05$

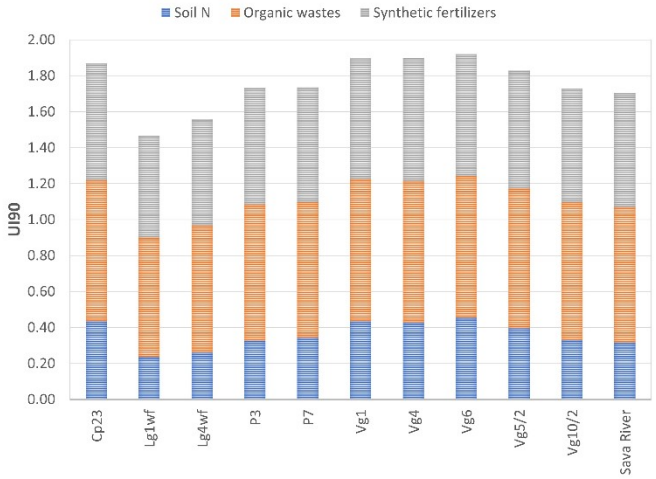

Fig. S1 Stacked column chart of the uncertainty analysis per sampling site.

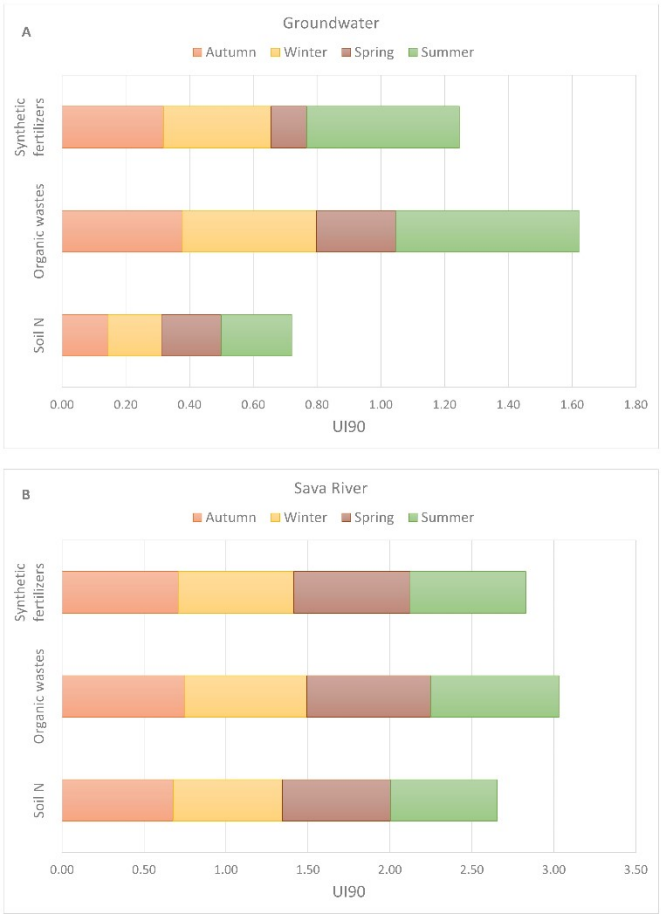

Figure S2 Stacked bar chart of the uncertainty analysis per season for groundwater (A) and Sava River (B).