

## Comprehensive analysis of nitrates, sulphates and agrochemicals in leachates from an intensive agriculture area - A case study in Croatia

### Sveobuhvatna analiza nitrata, sulfata i pesticida u procjednim vodama iz intenzivno poljoprivrednog područja - Studija slučaja u Hrvatskoj

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#### ABSTRACT

To better understand the impact of conventional agricultural practices on soil and water resources, two main objectives were established in this study: to measure nitrate ( $\text{NO}_3^-$ ) and sulphate ( $\text{SO}_4^{2-}$ ) concentrations in lysimeters and drainpipes leachates in response to different nitrogen fertilization levels and soil amendments and to identify organic contaminants that could have originated from the long-term use of agrochemicals in historically intensive agricultural area in Croatia. During the two-year study period leachate samples were collected from lysimeters and drainpipes. Research results indicate  $\text{NO}_3^-$  content in both lysimeters and drainpipes increased with rising doses of N fertilizer. The highest concentration of  $\text{SO}_4^{2-}$  was recorded in the treatment with added phosphogypsum, while in all other treatments the concentrations were low. Over 40% of the 287 target substances were detected at least once during the two-year study period but only two substances (IPC/propham and carbosulfan) were found to have concentrations above 0.5  $\mu\text{g/L}$ . Additionally, three priority substances were continuously present in the leachate samples: atrazine, simazine and isoproturon.

**Keywords:** UHPLC-Q-TOF-MS, ion chromatography, water contamination, groundwater, phosphogypsum

#### SAŽETAK

Da bi se bolje razumio utjecaj konvencionalne poljoprivredne prakse na tlo i vodne resurse, u ovom radu uspostavljena su dva glavna cilja: mjerenje koncentracija nitrata ( $\text{NO}_3^-$ ) i sulfata ( $\text{SO}_4^{2-}$ ) u lizimetarskim i drenskim procjednim vodama kao odgovor na gnojidbu različitim razinama dušika te poboljšivača tla te identificirati organske onečišćivače čije je moguće izvorište u dugotrajnoj uporabi pesticida na povijesno intenzivno poljoprivrednom području u Hrvatskoj. Tijekom dvogodišnjeg razdoblja uzorci procjednih voda prikupljeni su iz lizimetara i drenskih cijevi. Rezultati istraživanja pokazuju da se sadržaj  $\text{NO}_3^-$  u lizimetrima i u drenskim cijevima povećavao s porastom doza N gnojiva. Najveća koncentracija  $\text{SO}_4^{2-}$  zabilježena je u tretmanu s dodanim fosfogipsom, dok su u svim ostalim tretmanima koncentracije bile niske. Preko 40% od 287 ciljnih tvari otkriveno je barem jednom tijekom dvogodišnjeg razdoblja ispitivanja, ali utvrđeno je da su samo dvije tvari (IPC/propham i carbosulfan) imale koncentracije iznad 0,5  $\mu\text{g/L}$ . Uz to, tri prioritete tvari bile su kontinuirano prisutne u uzorcima procjednih voda: atrazin, simazin i izoproturon.

**Ključne riječi:** UHPLC-Q-TOF-MS, ionska kromatografija, onečišćenje vode, podzemne vode, fosfogips

## INTRODUCTION

From 1950 to the present, the world's population grew by 1 to 2% annually, and by the end of the century, the world's population could grow to about 10.9 billion people (United Nations, 2019). Coupled with rapid economic growth and urbanization, the agricultural system is under great pressure to increase its efficiency in producing and distributing food for the growing population. Global trends show the decline in arable land from 0.38 ha per person in 1970 to a projected 0.15 ha in 2050 (Alexandratos and Bruinsma, 2012). Additionally, the decrease in freshwater availability, land degradation and climate change are affecting the productivity of agroecosystems worldwide (Dubey et al., 2020).

Intensive agricultural practices rely on the high use of fertilizers and agrochemicals such as herbicides, insecticides, and fungicides to control pests and weeds and to increase crop production. However, their use has resulted in both terrestrial and aquatic ecosystems being highly contaminated with a large amount of substances that often raise toxicological concerns due to their potential negative effects on human health and the environment (Shefali et al., 2021). According to EEA (2018), the main cause of poor groundwater quality status in Europe are nitrates ( $\text{NO}_3^-$ ) and pesticides resulting from agricultural use. In addition, the production of synthetic organic chemicals contributes about 300 million tons per year to the global anthropogenic flux affecting water quality worldwide and should not be disregarded (Schwarzenbach et al., 2006). Furthermore, there are several pathways through which agrochemicals can leave their target area and cause damage to the environment. These pathways are plant uptake, volatilization to the atmosphere, leaching to groundwater, and runoff to surface waters (Blake and Pallet, 2018). Evidence suggests that some of the more persistent chemicals, such as organochlorines and polycyclic aromatic hydrocarbons, can be transported thousands of kilometres from their point of origin via water or air (Macdonald et al., 2020). Following heavy rainfall events, especially after dry periods, water and solutes move within the soil profile

via preferential flow pathways both vertically and laterally to the water table (Makowski et al., 2020; Lin, 2010). To measure the transport and export of applied agrochemicals after a rainfall event, lysimeters are usually installed below the soil surface (Dousset et al., 2016).

In addition, many studies report that high concentrations of various substances, in particular nitrates, sulphates and pesticides from agricultural activities ultimately appear in drinking water (Frollini et al., 2021; Holik et al., 2020; Fingler et al., 2017).

Therefore, it is important to develop methods that allow comprehensive identification, measurement, and monitoring of hazardous substances in aquatic ecosystems that originate from the agricultural sector. This is especially important in the context of pesticide monitoring, considering that over 20,000 different substances and formulations are used daily in the European Union alone (ECHA- European Chemicals Agency, 2018).

In general, LC-MS (Liquid Chromatography-Mass Spectrometry) methods have brought organic micro contaminants into the focus of the wider scientific community as well as regulatory authorities when their presence in the environment became apparent (Krauss et al., 2010). Following the further development and wider application of the scientific method, regulations and directives were initiated worldwide to alleviate the pressure of the chemical industry on the environment. Namely, the EU legislator created mechanisms to control and monitor all potentially hazardous substances used in industry and agriculture, which are essential for environmental protection. Directive 2013/39/EU identifies 45 priority substances and for each sets the environmental quality standards (EQS) expressed by annual mean values (AA) and maximum allowable concentrations (MAC) in surface water, groundwater and biota. Additionally, directive 2006/118/EC sets the groundwater quality standard for the MAC of "the sum of all individual pesticides detected and quantified in the monitoring procedure, including their relevant metabolites, degradation and reaction products"

(2006/118/EC, annex 1, p. 8). Moreover, the Nitrates Directive (91/676/EEC), as well as Croatian regulations (NN 96/19 and NN 125/17), limit the value of nitrates and sulphates in drinking water to 50 mg/L and 250 mg/L, respectively.

The directives and regulations aim to achieve good chemical quality of waters throughout the EU and protect them from deterioration by setting general requirements and minimum chemical standards for ecological protection.

Ultra-high performance liquid chromatography coupled with quadrupole time-of-flight mass spectrometry (UHPLC-Q-TOF-MS) is an outstanding hybrid method that enables extensive screening and subsequent identification of substances of interest using accurate mass databases and mass spectral libraries containing data of the substances of interest. The development of this method enabled the simultaneous screening of a large amount of different compounds and the detection of specific trace organic chemicals in a single run (Stipaničev et al., 2017).

Moreover, the method with its many advantages (fast and reliable performance and low detection limits of approx. 1 ng/L) has been successfully used in the investigation of the status of many European water sources (Stipaničev et al., 2017; Li et al., 2017; Jakimska et al., 2014) and water sources around the world (Assress et al., 2019; Pochodylo et al., 2017). Therefore, UHPLC-Q-TOF-MS is a widely recognized method for comprehensive environmental monitoring, showing great performance in screening and monitoring in the field of environmental science, where it has been efficiently used for the study of various contaminants such as agrochemicals as well as pharmaceuticals.

This method has, to the best of the author's knowledge, never been used for the purpose of investigating water quality in the intensive agricultural area in Croatia. Therefore, the aim of this study was to comprehensively investigate the status of leachates collected from a historically intensive agricultural cropland in Croatia over the course of two years. In addition to identifying and

quantifying pesticides, potential hazardous substances originating from the use of agrochemicals in the area using the UHPLC-Q-TOF MS method, nitrates ( $\text{NO}_3^-$ ) and sulphates ( $\text{SO}_4^{2-}$ ) originating from fertilizer, as well as soil amendment use were also monitored via ion chromatography method. Special emphasis in the study was given to detection and quantification of pesticides of which some are priority substances listed in Directives 2013/39/EU and 2006/118/EC that could potentially be present in the collected leachate samples. The use of many of these substances are prohibited in the EU (e.g., atrazine, isoproturon, diuron) but is frequently detected in surface and groundwater as well as drinking water across Europe, as reported by Fingler et al. (2017), Herrero-Hernández et al. (2017) and McManus et al. (2017).

## MATERIALS AND METHODS

### *Study location and research layout*

The experimental field was established in Potok near Popovača - Croatia (45°33'N, 16°31'E; Figure 1) on acidic stagnosols (according to WRB- World Reference Soil Base, 2015) with a low organic matter content, where precipitation water periodically stagnates on the illuvial horizon (52-97 cm). Drainpipe system was installed to accelerate water drainage and prevent excessive stagnation within the solum. The recorded mean soil pH (measured in KCl) and organic matter content were 4.84 and 0.59%, respectively, as reported in previous studies (Galić, 2019; Šestak et al., 2019; Šestak et al., 2014; Zgorelec et al., 2013). The study was conducted as a long-term field experiment with ten treatments and four replicates, in which different nitrogen (N) rates of NPK fertilizer were applied: 1. Control (no fertilization), 2.  $\text{N}_0 + \text{P} + \text{K}$ , 3.  $\text{N}_{100} + \text{P} + \text{K}$ , 4.  $\text{N}_{150} + \text{P} + \text{K}$ , 5.  $\text{N}_{200} + \text{P} + \text{K}$ , 6.  $\text{N}_{250} + \text{P} + \text{K}$ , 7.  $\text{N}_{250} + \text{P} + \text{K} + \text{phosphogypsum}$ , 8.  $\text{N}_{250} + \text{P} + \text{K} + \text{zeolitic tuff} + \text{CaCO}_3$ , 9.  $\text{N}_{300} + \text{P} + \text{K}$ , 10. Black fallow - no crops. Phosphorous (P - in form of  $\text{P}_2\text{O}_5$ ) and potassium (K - in form of  $\text{K}_2\text{O}$ ) levels were constant: 120 and 180 kg/ha respectively.

In addition to the NPK fertilization, 12 t/ha of phosphogypsum -  $\text{CaSO}_4 \times 2\text{H}_2\text{O}$  (or 4680 kg/3900 m<sup>2</sup> -

area of 1 treatment) was added in treatment 7 to alleviate soil acidity and 3 t/ha (1170 kg/3900 m<sup>2</sup>) zeolitic tuff and CaCO<sub>3</sub> were added in treatment 8 to mitigate nitrate leaching. In 2015, multiannual phosphogypsum and zeolitic tuff addition to these treatments were replaced by 20 t/ha and 40 t/ha of organic solid mixed animal manure to the 7<sup>th</sup> and 8<sup>th</sup> treatment, respectively (Figure 2). In 2014, the hybrid crop triticale (*x.Triticosecale*) was sown in the field and in 2015 the main crop was maize (*Zea mays* L.). The area of the experimental field was approximately 4.5 ha.

The initial objective of the field experiment was to conduct research on mineral nitrogen fertilization, nitrogen use efficiency and nitrogen leaching, as well as on the overall environmental impact of different management systems, the results of which have been published at various points in the past (Šestak et al., 2018; Mesić et al., 2017; Jurišić et al., 2014; Šestak et al., 2014; Mesić et al., 2007).

In 2014 and 2015, the research objective was expanded to identify organic contaminants (pesticides) in leachate following rainfall events (Figure 3), for the purpose of which the past consumption of pesticides in the experimental field was recorded from 1996 to 2015

(applied quantities are presented in the Results section). Each treatment plot included two drainage pipes (placed at a depth of 120 cm) and one lysimeter (at a depth of 80 cm), from which leachate samples were taken when discharge appeared (Figure 2).

### Sampling campaign

For NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> determination and monitoring, the leachate samples were collected after each rainfall for each treatment parcel separately. The leachate samples designated for organic substances screening analysis were collected from each treatment and combined to obtain an average sample of the particular sampling date.

Figure 4 shows the soil water balance and calculated water surplus and deficit using Thornthwaite and Mather (1957) method for the reference period 1961-1990 and for the two years studied. After the soil reaches the water holding capacity, any excess precipitation is counted as water surplus and is subject to runoff. In 2014, water surplus is present for most of the year, except June and July, and totals 716 mm, while in 2015, excess water totalled 376 mm during the spring and winter months, and a water deficit of 114 mm occurred in July and August. Samples were taken during the period when

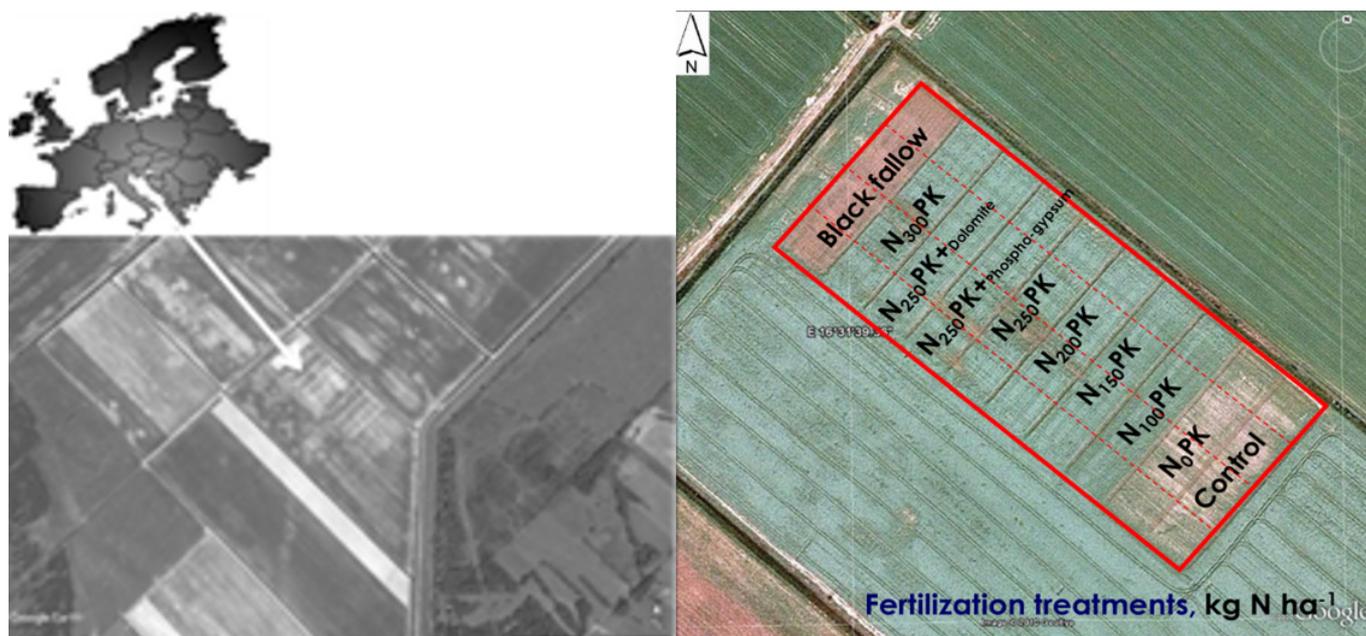


Figure 1. Study location: Potok in Popovača, Croatia

(Source: Google Earth, 2017)

water surplus was present in the soil and water discharge occurred. Consequently, a total of 244 leachate samples for  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  (135 from lysimeters and 109 from drainpipes) analysis, and 16 average samples for organic substances (11 from lysimeters and 5 from drainpipes) analysis were collected during the study period. The

samples were stored in 500 mL polycarbonate bottles in a dark and dry place at 4 °C and filtered through a 0.45  $\mu\text{m}$  (for  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ ) and 0.2  $\mu\text{m}$  PTFE filter (for organic substances) upon entering the laboratory for immediate analysis.

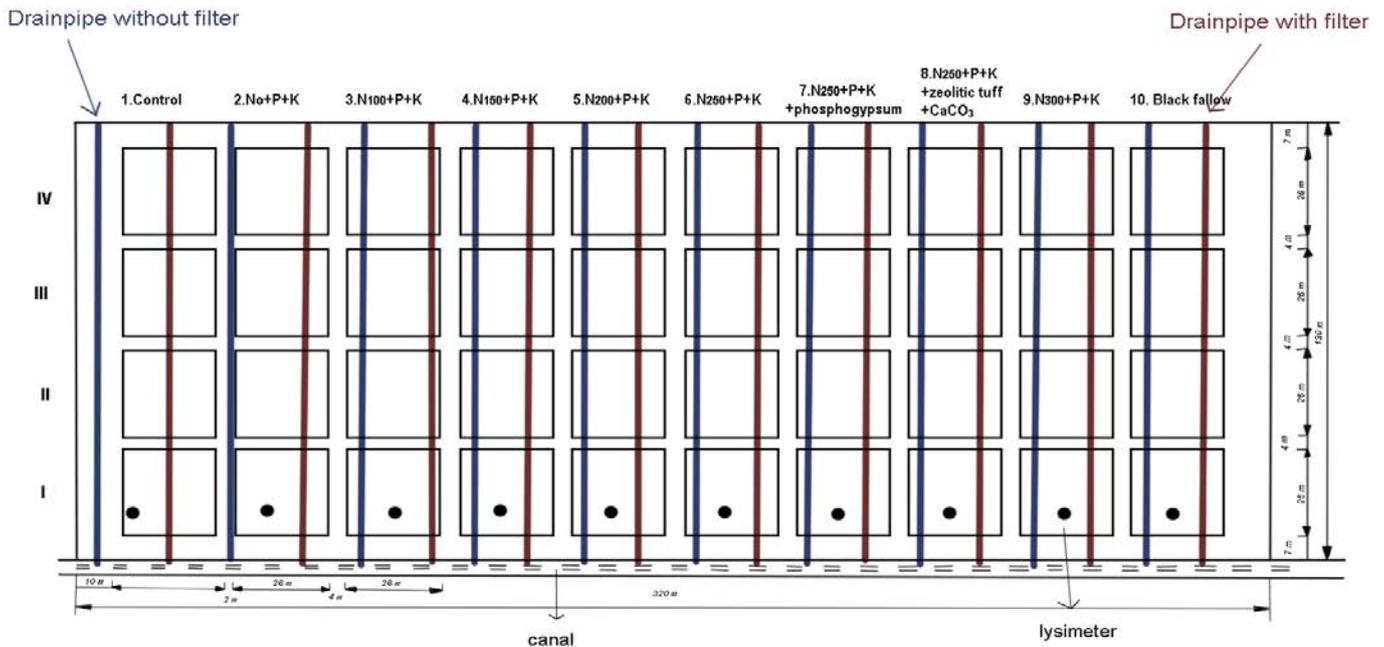


Figure 2. Research layout

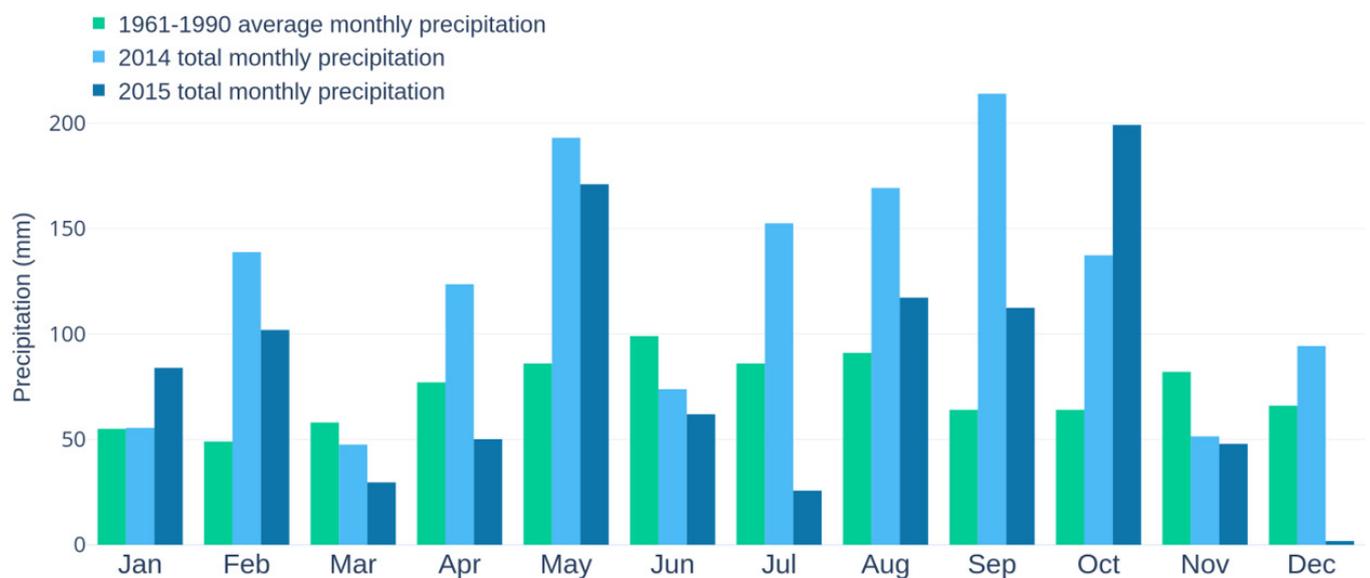
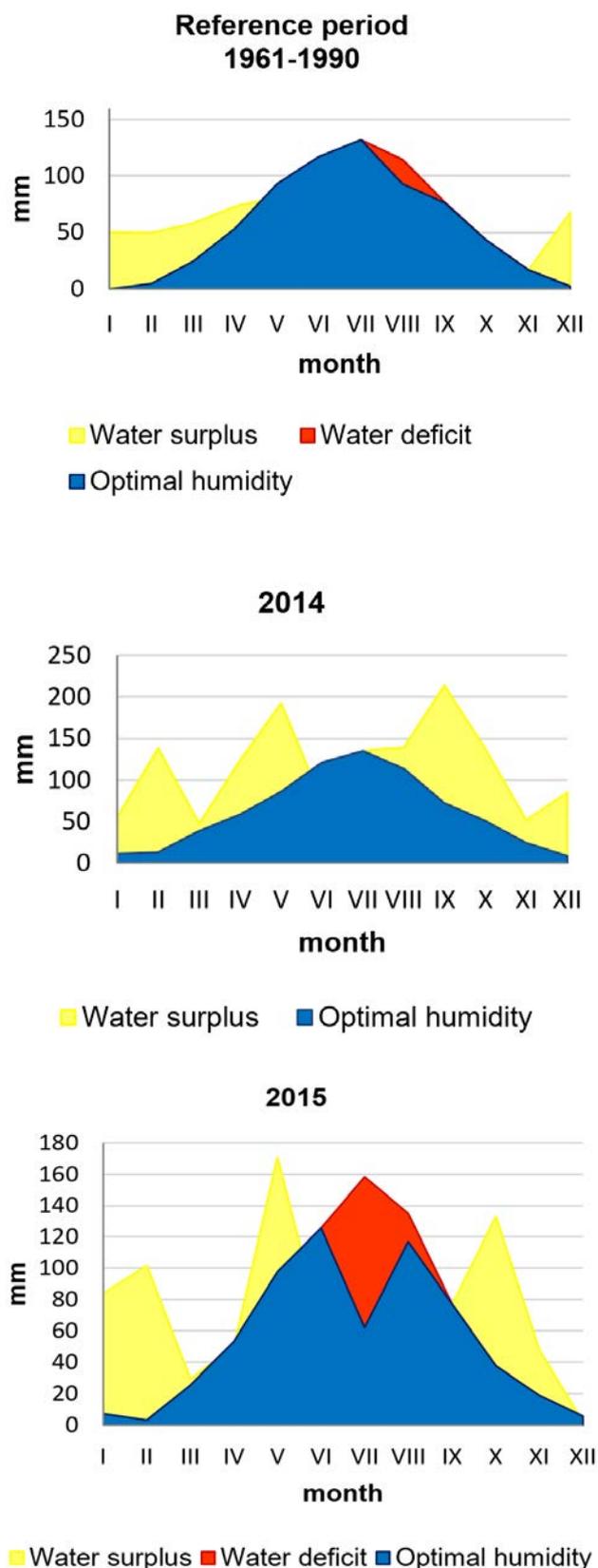


Figure 3. Average precipitation during the reference period and the two investigated years (mm)



**Figure 4.** Soil water balance according to Thornthwaite and Mather method for reference period from 1961-1990 and for the study period

### Laboratory analysis and data processing

The concentrations of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  were determined by suppressed ion chromatography (Dionex ICS-1000 system) using IonPac AS 17-C separation column (4 x 250 mm) at 30 °C, fitted with IonPac AG 17 guard column. The gradient flow analysis was conducted using KOH (10-30-10 mmol in  $\text{H}_2\text{O}$ ) as an eluent solution which was passed through the system at 1 mL/min.

UHPLC-Q-TOF/MS was used for screening and quantification of the organic substances. 1290 UHPLC system, Agilent Technologies, USA (G4226A autosampler, G4220B binary pump and G1316C thermostated column) and RP column ACQUITY UPLC, HSS T3 (150 mm x 2.1 mm, 1.8 mm) was used for the separation of the analytes. The gradient was from 100% water to 100% organic solvent in a 20 min run, and the injection volume was 100  $\mu\text{L}$ . In ESI (+) the mobile phases were 5 mM ammonium formate and 100% MeOH, while in ESI (-) the mobile phases were 1 mM ammonium fluoride and 100% MeOH. Gradient elution with a flow rate of 0.4 mL/min was used. The analytes were detected using a 6550 i-Funnel Q-TOF-LC/MS (Agilent Technologies, USA) in 4 GHz detector rate, with a 40,000 resolving power and b2 ppm accuracy (for a more detailed method description please refer to Stipančević et al., 2017).

The screening included 287 substances used in agricultural industry in Croatia as follows: 113 insecticides, 92 herbicides, 77 fungicides, 2 plant growth regulators, 1 antihelmintic agent, 1 nematicide and 1 defoliant. The search of the spectrum of organic compounds of interest and their quantification was carried out with high resolution (>10000 FWHM, full width half maximum), with accurate mass precision (<1 ppm) and satisfactory sensitivity in full acquisition mode. The sensitivity of the method was estimated by determining the limits of detection (LOD), limits of quantification (LOQ) and minimum detection limits (MDL) for each substance. The list of individual LODs, LOQs, MDLs, and the respective final concentrations for all 287 substances can be found in the raw data table available upon request from the authors.

One-way ANOVA and Tukey HSD test at  $P < 0.05$  were used to determine the statistically significant differences between the ten different fertilization treatments and  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  concentrations. The analysis was performed in the R 3.6.2 environment (R core team, 2020) using ggplot (v2\_3.2.1), emmeans (v1.4.4) and multcompView (v0.1-8) packages. All other calculations were performed in Microsoft Excel 2010.

## RESULTS AND DISCUSSION

### *Concentration of nitrates and sulphates in leachate samples*

During the two-year research period the concentrations of  $\text{NO}_3^-$  varied from 0 mg/L minimum to 265 mg/L maximum in lysimeter, and from 0 to 182 mg/L in drainpipe leachates (Table 1). Highest overall concentrations were observed in drainpipes, which were installed deeper within the solum, thus confirming that nitrates do not bond with soil particles and are leached to groundwater. The highest average concentrations of  $\text{NO}_3^-$  in the two-year period for each treatment were also measured in drainpipe leachates (112 mg/L, Table 2).

Concentrations of  $\text{SO}_4^{2-}$  varied from 1.47 to 302 mg/L in lysimeter, and from 0 to 173 mg/L in drainpipe leachates. As expected, the maximum average concentrations were recorded in treatment 7 with added phosphogypsum (190 mg/L in lysimeters and 111 mg/L in drainpipes), while the average concentrations on all other treatments were low ( $< 20$  mg/L, Table 2).

Similar research had been conducted by Otero et al. (2009), where the  $\text{NO}_3^-$  concentrations in groundwater of an intensive agricultural area in Spain had been investigated, and by Schilling and Walter (2001), who investigated the  $\text{SO}_4^{2-}$  concentrations in groundwater of a 5221 km<sup>2</sup> large watershed in a predominately agricultural area of Iowa, USA.

They found concentration levels from 10 to 529 mg/L of  $\text{NO}_3^-$ , with 127 mg/L on average in the 2005-2006 period, which is higher than in the presented study, and 10 to 52 mg/L of  $\text{SO}_4^{2-}$ , and an average of 20.7 mg/L, which is in accordance with the presented study in all treatments, excluding the 7<sup>th</sup> treatment, which was treated with phosphogypsum.

Moreover, Table 2 shows that the average  $\text{NO}_3^-$  concentrations in treatments 5-9 exceed the MAC value of 50 mg/L for drinking water (NN 125/17). However, because of the added  $\text{CaCO}_3$  in treatment 8, the concentration in lysimeter leachates decreased, possibly because carbonates promote  $\text{NO}_3^-$  adsorption on soil particles, as confirmed by Prasad et al. (2018) on different soils. This confirms that with the addition of  $\text{CaCO}_3$  to the soil, the leaching of  $\text{NO}_3^-$  could be mitigated to a certain extent, which would depend primarily on the amount of applied N fertilization.

The effect of different N fertilization levels and added soil amendments on concentrations of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  are presented in Figure 5. The results suggest that the rising N fertilization rates do have an effect on  $\text{NO}_3^-$  concentrations.

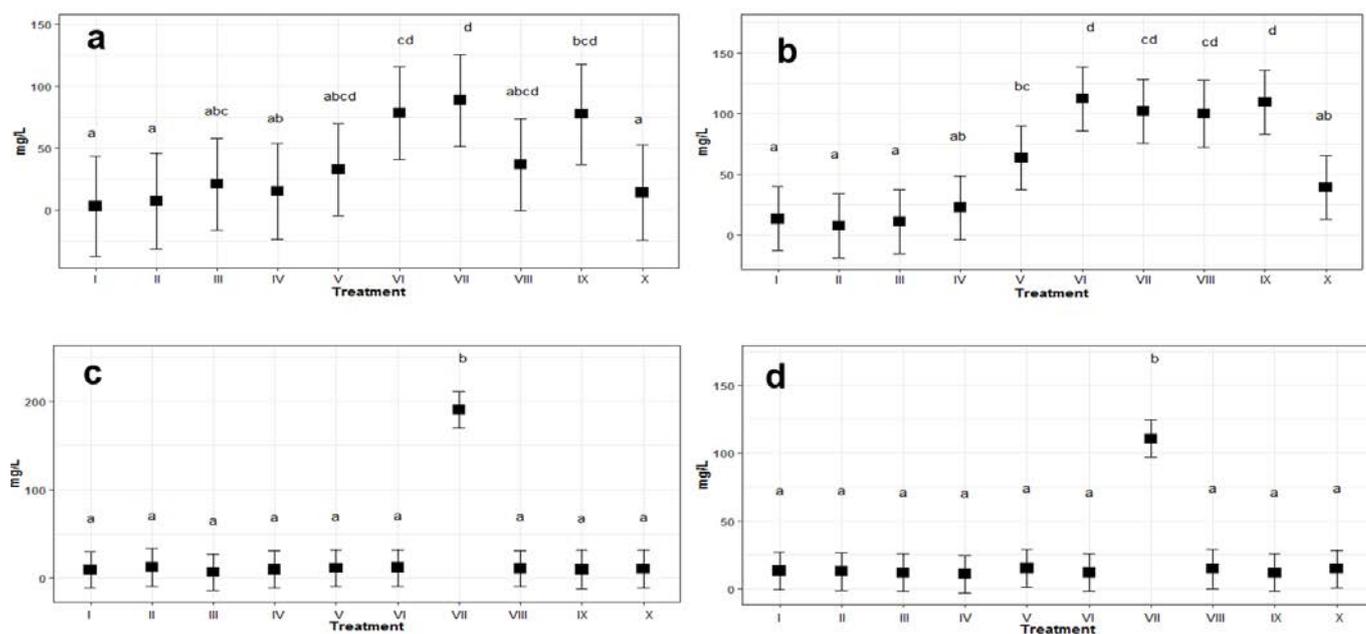
**Table 1.** Descriptive statistics for  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  concentrations in leachates over the two-year study period

	Valid N	Mean	Min	Max	St.dev.	Cv (%)
$\text{NO}_3^-$ (mg/L)						
Lysimeters	133	38.15	nd	264.67	56.18	147.29
Drainpipes	109	57.79	nd	182.20	51.27	88.71
$\text{SO}_4^{2-}$ (mg/L)						
Lysimeters	135	28.59	1.47	301.94	61.09	213.66
Drainpipes	109	22.88	nd	172.95	33.30	145.54

nd-not detected

**Table 2.** Average  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  concentrations in lysimeters and drainpipes during the two-year study period

	$\text{NO}_3^-$ (mg/L)		$\text{SO}_4^{2-}$ (mg/L)	
	Lysimeters	Drainpipes	Lysimeters	Drainpipes
1. Control	3.20	13.42	8.91	13.35
2. $\text{N}_0 + \text{P} + \text{K}$	7.60	7.75	11.96	12.84
3. $\text{N}_{100} + \text{P} + \text{K}$	21.17	11.07	6.37	11.85
4. $\text{N}_{150} + \text{P} + \text{K}$	15.51	22.74	9.53	10.93
5. $\text{N}_{200} + \text{P} + \text{K}$	32.96	63.72	10.96	15.13
6. $\text{N}_{250} + \text{P} + \text{K}$	78.49	112.22	11.26	12.06
7. $\text{N}_{250} + \text{P} + \text{K} + \text{phosphogypsum}$	88.80	102.18	190.37	110.61
8. $\text{N}_{250} + \text{P} + \text{K} + \text{zeolitic tuff} + \text{CaCO}_3$	36.86	99.81	10.43	14.67
9. $\text{N}_{300} + \text{P} + \text{K}$	77.64	109.32	9.35	11.83
10. Black fallow	14.38	39.49	10.16	14.76

**Figure 5.** Concentrations of  $\text{NO}_3^-$  from lysimeter (a) and drainpipe (b) and  $\text{SO}_4^{2-}$  from lysimeter (c) and drainpipe (d) leachates during the two-year investigation period. Boxes represent least square mean values for each of ten treatments. Error bars indicate 95% confidence intervals. Means sharing a letter are not significantly different ( $P < 0.05$ )

Treatments 6 to 9 in lysimeter leachates and 5 to 9 in drainpipe leachates showed significantly higher concentrations when compared to control. The difference between N fertilization treatments between treatments 1 to 4 (with N fertilization rates from 0 to 150 kg/ha) and 5 to 9 (with fertilization rates 150-300 kg/ha) is more pronounced in drainpipe leachates. This suggests that  $\text{NO}_3^-$  concentrations fluctuate more in the application zone of the soil (closer to the lysimeters depth), and that concentrations depend more on the crop management used in the field. Therefore, deeper within the solum the true  $\text{NO}_3^-$  leaching potential is more pronounced, and as recommended by the Croatian legislature, N fertilization rates should not exceed 150 kg N/ha (as is recommended by NN 15/2013 for some crops, including triticale).

Moreover, one-way ANOVA results suggest that the addition of phosphogypsum had an effect on  $\text{SO}_4^{2-}$  concentrations, which resulted in its increase in both lysimeter and drainpipe leachates. However, the observed concentrations did not exceed the prescribed MAC value of 250 mg/L on any occasion.

Following its dissociation in water, phosphogypsum increases  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  ions in soil (Vyshpolsky et al., 2008), which are then available for plant uptake and are leached from the surface (Mesić et al., 2016). In a study by Mesić et al. (2007), it was found that the elevated  $\text{SO}_4^{2-}$  concentrations in leachates were caused primarily by phosphogypsum.

#### ***Overall presence of agrochemicals in leachate samples***

Of the 287 target substances, 123 were detected in lysimeter water (43%) and 136 (47%) in drainpipe water at least once during the two-year study period. During this time, only two substances (IPC/propham and carbosulfan) were found to have concentrations above 0.5  $\mu\text{g/L}$  (quality standard for groundwater by the European commission - 2006/118/EC). Both were found in drainpipe leachates.

Total concentrations of detected compounds on eight sampling dates ranged from 304 to 850 ng/L in lysimeter samples and from 109 to 2726 ng/L in drainpipe

samples (raw data table available upon request from the authors). In both cases, the period when the highest total concentrations were detected was December 2015, which is likely due to the fact that the soil is bare and evapotranspiration is the lowest during this time, resulting in the water and any compounds dissolved in it moving more easily and quickly to the depths of the solum.

In 2014, nicosulfuron had the highest total concentration in both lysimeter and drainpipe samples at 247 ng/L and 446 ng/L, respectively (Table 3). Nicosulfuron is an N-sulfonylurea post-emergence herbicide used to control annual and perennial grass weeds in maize crops (Lewis et al., 2016). It is characterized by rapid degradation in the environment, is mobile in soil, and is also considered a high leaching risk to groundwater due to its low sorption rates in soil (Cueff et al., 2020; Azcarate et al., 2015). Possibly due to its high mobility, concentrations found in leachate samples from deeper layers (i.e. drainpipes) within the soil were higher than concentrations from shallower layers. Additionally, since it was not applied to the experimental field prior to May 2015 (Table 4), the high concentrations recorded in March and May 2014 could potentially be explained by application to one of the surrounding fields and subsequent migration via runoff and/or spray drift, followed by relocation within the soil profile via both lateral and vertical preferential flows following the rainfall events in February and April of that year.

In 2015, bupirimate had the highest concentration in the lysimeter samples at 105 ng/L, while in the drainpipe samples it was carbosulfan at 1270 ng/L, both detected in December. Since both bupirimate (fungicide) and carbosulfan (insecticide) are considered to have low mobility in soil as well as low leachability (EFSA, 2010; EFSA, 2009), their presence could possibly be reflecting recent application in the broader agricultural area, as there was no record of their use in the experimental field.

#### ***Detection and quantification of priority substances***

Three compounds listed as priority substances with prescribed environmental quality standards (EQS) were

detected and measured during the study period: atrazine, simazine and isoproturon. Table 5 shows their average annual concentrations in leachates from lysimeters and drainpipes in the studied period in relation to these standards. In 2014, the average annual concentration (AA) of atrazine in lysimeters was 1 ng/L and 0.89 ng/L in drainpipes, and simazine and isoproturon were not detected. The AA concentrations of atrazine, simazine and isoproturon in lysimeters in 2015 were 5, 9 and 0.64 ng/L, respectively. In drainpipes the concentrations were 0.65, 4 and 2 ng/L.

Despite their long-standing ban in the EU, atrazine and simazine have been continuously present in the water samples across Europe (Goessens et al., 2022; Bijlsma et al., 2021; Silva et al., 2015), as well as in the

studied area in Potok, although largely below MAC values. Silva et al. (2015) reported up to 35 µg/L of AA of atrazine and up to 4 µg/L of simazine in surface rivers in the greater agriculture area of Portugal in the period from 2002-2004. More recently, Goessens et al. (2022) found maximum concentration of 39 ng/L of atrazine and 4 ng/L of simazine in a 2019 monitoring campaign of amphibian breeding ponds of Flanders, Belgium. Concentrations were well below MAC but still present in the environment. These findings are consistent with a study by Jablonowski et al. (2009) which observed the persistence of atrazine and simazine in soil and found that the overall persistence of atrazine in the soil might lead to leaching to groundwater reserves even 22 years after its usage in the field.

**Table 3.** Total number of substances measured per sampling date and minimum and maximum concentrations detected in lysimeter and drainpipe samples (ng/L)

# of measured substances			Min	Max	Mean
			Lysimeters		
2014	14-Mar	11	0.24 (Mexacarbate)	246 (Nicosulfuron)	33
	14-May	16	0.12 (DEET/Diethyltoluamide)	247 (Nicosulfuron)	20
	14-Jun	34	0.16 (Fenthion)	57 (Uniconazole)	9
	14-Sep	55	0.07 (Ametryne)	70 (Diethofencarb)	9
	14-Oct	42	0.21 (Methabenzthiazuron)	62 (Fenbuconazole)	12
	14-Nov	38	0.23 (Fenthion)	159 (Fenbuconazole)	15
2015	15-Jun	60	0.43 (Malaaxon)	83 (Spiromesifen)	9
	15-Dec	61	0.38 (Malaaxon)	105 (Bupirimate)	14
			Drainpipes		
2014	14-Mar	21	0.17(Ametryne)	446 (Nicosulfuron)	27
	14-May	12	0.38 (Methabenzthiazuron)	232 (Nicosulfuron)	31
	14-Jun	70	0.16 (Ametryne)	159 (Uniconazole)	12
	14-Sep	10	0.02 (Ametryne)	70 (Fenbuconazole)	11
	14-Oct	49	0.42 (Methabenzthiazuron)	378 (Phoxim)	24
2015	15-Jun	51	1.15 (Atrazine)	510 (IPC*/Propham)	29
	15-Oct	43	0.60 (Oxamyl)	143 (Carbosulfan)	20
	15-Dec	53	0.42 (Oxamyl)	1270 (Carbosulfan)	51

\* IPC - Isopropyl phenylcarbamate

**Table 4.** Time of application of active substances and measured concentration during the monitoring period in leachates

Active substance	Formula and CAS number	Product	Time of application	Applied Amount	Sampling time	Measured concentration (ng/L)			
						L	D		
Chlortoluron	C <sub>10</sub> H <sub>13</sub> ClN <sub>2</sub> O 15545-48-9	Dicuran Forte	Mar-06	1.5 kg/ha	Mar-14	nd	nd		
			Mar-08	1.5 kg/ha	May-14	nd	nd		
					Jun-14	nd	1		
						Sep-14	10	nd	
				Tena	Mar-08	1.5 kg/ha	Oct/Nov-14	19 (Oct)/5 (Nov)	
			Jun-15				nd	nd	
			Oct-15				n/a	nd	
					Dec-15	30	nd		
Clomazone	C <sub>12</sub> H <sub>14</sub> ClNO <sub>2</sub> 81777-89-1	Clon	Apr-11	0.4 L/ha	Mar-14	nd	nd		
					May-14	nd	nd		
					Jun-14	3	9		
					Sep-14	3	2		
					Oct/Nov-14	nd	5		
					Jun-15	nd	nd		
					Oct-15	n/a	nd		
Dec-15	3	nd							
Cyproconazole	C <sub>15</sub> H <sub>18</sub> ClN <sub>3</sub> O 94361-06-5	Artea	May-06	0.5 kg/ha	Mar-14	nd	nd		
					May-14	nd	nd		
					Jun-14	36	112		
							Sep-14	9	nd
					Apr-10	0.5 L/ha	Oct/Nov-14	4	nd
							Jun-15	4	nd
					Apr-12	0.5 L/ha	Oct-15	n/a	nd
				Dec-15	nd	nd			
Dimethachlor	C <sub>13</sub> H <sub>18</sub> ClNO <sub>2</sub> 50563-36-5	Teridox	Aug-08	2.7 L/ha	Mar-14	nd	2		
					May-14	nd	nd		
					Jun-14	nd	nd		
					Sep-14	2	nd		
					Oct/Nov-14	3	nd		
					Jun-15	nd	nd		
					Oct-15	n/a	nd		
Dec-15	2	nd							

Table 4. Continued

Active substance	Formula and CAS number	Product	Time of application	Applied Amount	Sampling time	Measured concentration (ng/L)	
						L	D
Isoproturon	C <sub>12</sub> H <sub>18</sub> N <sub>2</sub> O 34123-59-6	Cougar	Mar-97	1.4 L/ha	Mar-14	nd	nd
					May-14	nd	nd
					Jun-14	nd	nd
					Sep-14	nd	nd
					Oct/Nov-14	nd	nd
					Jun-15	1	2
					Oct-15	n/a	nd
					Dec-15	nd	3
Nicosulfuron	C <sub>15</sub> H <sub>18</sub> N <sub>6</sub> O <sub>6</sub> S 111991-09-4	Samson Extra	May-15	0.7 L/ha	Mar-14	246	446
					May-14	247	232
					Jun-14	nd	4
					Sep-14	7	nd
					Oct/Nov-14	1	2
					Jun-15	2	2
					Oct-15	n/a	11
Dec-15	59	4					
Oxasulfuron	C <sub>17</sub> H <sub>18</sub> N <sub>4</sub> O <sub>6</sub> S 144651-06-9	Dynam	Jun-02	0.1 kg/ha	Mar-14	nd	nd
					May-14	5	nd
					Jun-14	nd	1
			2005* *(month unknown)	100 g/ha	Sep-14	nd	nd
					Oct/Nov-14	nd	nd
					Jun-15	nd	1
					Oct-15	n/a	nd
Dec-15	nd	1					
Propiconazole	C <sub>15</sub> H <sub>17</sub> Cl <sub>2</sub> N <sub>3</sub> O <sub>2</sub> 60207-90-1	Artea	May-06	0.5 kg/ha	Mar-14	nd	nd
					May-14	nd	nd
					Jun-14	3	9
		Artea	Apr-10	0.5 L/ha	Sep-14	nd	nd
					Oct/Nov-14	16	3
					Jun-15	nd	nd
Palis C	May-10	2 L/ha	Oct-15	n/a	nd		
Artea	Apr-12	0.5 L/ha	Dec-15	nd	nd		

**Table 4.** Continued

Active substance	Formula and CAS number	Product	Time of application	Applied Amount	Sampling time	Measured concentration (ng/L)	
						L	D
Prosulfocarb	C <sub>14</sub> H <sub>21</sub> NO <sub>5</sub> 52888-80-9	Filon	Nov-11	3 L/ha	Mar-14	nd	nd
					May-14	nd	nd
					Jun-14	2	4
					Sep-14	2	nd
					Oct/Nov-14	nd	3
					Jun-15	2	7
					Oct-15	n/a	nd
					Dec-15	2	7

L - lysimeter; D - drainpipe; n/a - data not available because in Oct-15 the analysis was performed only for samples from drainpipes; nd- not detected. Detailed formulations of individual products are available in the FIS database of Croatian Ministry of Agriculture at: <https://fis.mps.hr/trazilicaszb/>

**Table 5.** Environmental quality standards and detected concentrations of atrazine, simazine and isoproturon (ng/L)

Name of substance	AA-EQS In-land surface waters	MAC- EQS Inland surface waters	MAC - EQS groundwater	AA 2014 lysimeter (n=6)	AA 2014 drainpipe (n=5)	AA 2015 lysimeter (n=2)	AA 2015 drainpipe (n=3)	Max* lysimeter (2014-2015)	Max* drainpipe (2014-2015)
Atrazine	600	2000	100	1	0.89	5	0.65	7	1
Simazine	1000	4000	100	nd	nd	9	4	10	7
Isoproturon	300	1000	100	nd	nd	0.64	2	1	3

AA: annual average; MAC: maximum allowable concentration; EQS: environmental quality standard; nd: not detected.

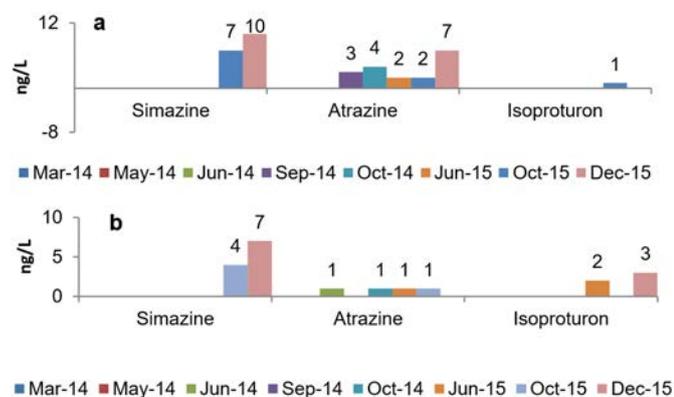
\*maximum concentration detected in the two-year investigation period

Therefore, it is not surprising that these compounds are detected throughout the study period, thus confirming their longevity in the environment. Similarly, isoproturon was occasionally present in the samples; however, its ban was not enforced in the EU until 2016 - two years before the sampling campaign. According to records, it was last used in the study field in 1997. Unlike atrazine and simazine, it does not persist in soil (Walker et al., 2001) and is generally considered to rapidly mineralize largely via microbial degradation in agricultural soils (Sørensen and Aamand, 2003). Therefore, the concentrations, although low, were unexpected in this study. However, as Paijens et al. (2021) reported lower concentrations of isoproturon in Paris's urban area following its ban in France in 2017 (from 0.01-0.06 µg/L in 2013 to <0.01 µg/L in 2018-2019 period), the same trend could be expected for the post-ban period in Croatia.

Overall, the maximum concentrations of atrazine and simazine in 2014-2015 were higher in lysimeter leachates, while the maximum concentration of isoproturon was detected in drainpipe leachates (Figure 6). It is also evident from Figure 6 that the highest concentrations of these compounds were measured in December 2015, similar to the total substances concentrations found in the samples throughout the study period. Again, this could be linked to low evapotranspiration and bare soil that allow water with dissolved compounds to move more freely within the solum.

Although concentrations do not exceed the prescribed EQS in individual cases, the samples collected at depths of 80 and 120 cm cannot be categorized as either surface or groundwater, making it difficult to discuss their compliance to the EQS standards. However, their continuous presence and measured concentrations could

indicate that these compounds remain in the environment for a longer period of time, especially considering that atrazine and simazine have not been authorized for use in Croatia since 2004.



**Figure 6.** Simazine, atrazine and isoproturon in lysimeter (a) and drainpipe (b) leachates (ng/L)

## CONCLUSION

The research findings indicate that a significant amount of nitrates, agrochemicals and, on occasion, sulphates, are present in the environment, which may prove to be a risk to surface and groundwater as well as food safety and other environmental factors. The results suggest that the rising N fertilization rates affect  $\text{NO}_3^-$  concentrations, which exceed the MAC value of 50 mg/L for treatments with >150 kg N/ha. It is therefore recommended that N fertilization rates do not exceed this threshold in order to avoid groundwater leaching. The measured  $\text{SO}_4^{2-}$  concentrations were higher only in the treatment with added phosphogypsum, but did not exceed the MAC value of 250 mg/L on any occasion.

Moreover, over 40% of the 287 detectable substances have been identified and their cumulative effects on soil, water and biota are still unknown. Some of the detected substances such as carbosulfan, bupirimate and nicosulfuron were detected at higher concentrations although there has been no record of their application in the experimental field. This could possibly be due to spray drift and/or runoff. The priority substances atrazine, simazine and isoproturon were regularly detected throughout the two-year study period, although their concentrations did not exceed the EQS of the

EU legislation. Extreme concentrations of particular compounds found in the samples throughout the study period could indicate the potential for percolation to groundwater and contamination of the greater freshwater ecosystem of the area. It is therefore necessary to use agrochemicals rationally and monitor water, soil and air health to ensure food safety and sustainability of all future agricultural production. This study has highlighted the need for further monitoring of organic contaminants originating from Croatian agriculture and, hopefully, raised awareness of pesticide contamination of freshwater sources around the world.

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