QUALITY OF DRAINAGE WATERS OF THE DANUBE CATCHMENT AREA IN THE REPUBLIC OF CROATIA

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Abstract: The research aim was to define the quality of drainage waters on ameliorated soils in the Danube catchment area. Certain pollutants, such as atrazine, chlorotoluron, heavy metals (Pb, Ni, Cd, Zn and Cu) and nitrate nitrogen were monitored within the investigations of the quality of drainage waters.

Investigations were carried out on four amelioration trial fields in the 1991-2000 period. The soils studied were drained Gleyic Podzoluvisol and drained Calcic Gleysol. Pipe drainage was combined with contact hydraulic material - gravel and drainpipes discharged directly into open canals.

The common crop rotation included maize and winter wheat. Weed control in maize was performed by the application of Primextra (6 l/ha), while Dicuran (2 kg/ha) was used for weed control in wheat. Application of total mineral nitrogen varied, ranging from 145 kg/ha to 200 kg/ha. Samples of drainage water were taken following the seasonal dynamics (in spring, autumn and winter). Atrazine and chlorotoluron were determined by gas chromatography, heavy metals by atomic absorption spectrometry, and nitrates by means of the yellow dye complex using phenoldisulfonic acid.

Results of long-term trials on the set locations showed that maximum atrazine concentrations in drainage waters in the non-growing season were below 100 ηg/l, and in the growing season mainly from 100 ηg/l to 500 ηg/l, while the maximum atrazine concentrations exceeded 500 ηg/l in some years. Concentrations of chlorotoluron in drainage waters were similar to those of atrazine. Maximum concentrations of heavy metals in drainage waters were 44μg.dm^{-3} for Pb, 15.0 μg.dm^{-3} for Ni, 4.8 μg.dm^{-3} for Cd, 73 μg.dm^{-3} for Zn, and 42.0 μg.dm^{-3} for Cu. Maximum and average concentrations of NO_3-N were higher than 10 mg/l during all trial years. Lower NO_3-N concentrations were recorded in the non-growing season. Maximum NO_3-N concentrations were determined either in the spring period (after the basic tillage for maize sowing or at the time of spring topdressing of winter wheat and the spring precipitation maximum) or in the autumn period at the time of basic fertilization for winter wheat sowing and the autumn-winter precipitation maximum.

The results on particular pollutants point to the conclusion that the concentrations of atrazine, chlorotoluron and NO_3-N exceeded the allowable MAC value and that the concentrations of heavy metals in drainage waters were lower than MAC, all according to the Rulebook on Health Criteria for Drinking Water in the Republic of Croatia (Official Gazette 64/1994) and the Decree on Hazardous Substances in Running Waters (Official Gazette 78/1998)

Since the issue here concerns hazardous potential pollutants of drainage waters in the narrower sense and waters in the global sense, the problem should be approached in a more serious and comprehensive way so as to encompass the entire catchment area of the Danube.

Keywords: drainage water, atrazine, chlorotoluron, heavy metals, nitrates

GŰTE DER SICKERWÄSSER AUF DEM EINZUGSGEBIET DER DONAU IN DER REPUBLIK KROATIEN

Zusammenfassung: Die Forschung war darauf gezielt, die Güte der Sickerwässer auf den meliorierten Böden im Flussgebiet der Donau festzustellen. In den Untersuchungen der Sickerwassergüte wurden bestimmte Schadstoffe, wie z.B. Atrazin, Chlortoluron, Schwermetalle (Pb, Ni, Cd, Zn i Cu) und Stickstoff in Nitratform beobachtet.

Die Forschungen wurden auf vier meliorierten Versuchsfeldern im Zeitraum von 1991-2000 durchgeführt. Geprüft wurden die Böden melioriertes Gleyic Podzoluvisol und

melioriertes Calcic Gleysol. Die Rohrdrainage erfolgte in Kombination mit hydraulischem Kontaktmaterial Kies und die Rohre mündeten direkt in die offenen Kanäle aus.

Angebaut war die übliche Fruchtfolge der Kulturen Mais und Winterweizen. Als Unkrautschutz im Mais wurde das Mittel Primextra in der Menge von 6 l/ha appliziert, während das Unkraut im Weizen mit Dicuran in der Menge von 2 kg/ha bekämpft wurde. Die Düngung mit dem gesamten Mineralstickstoff erfolgte unterschiedlich, und lag bei 145 kg/ha bis 200 kg/ha. Die Sickerwasserproben wurden nach der bestimmten Saisondynamik (im Frühjahr, Herbst und Winter) entnommen. Atrazin und Chlortoluron bestimmte man mittels der gaschromatographischen Analyse, Schwermetalle durch die Atomabsorptions-Spektrometrie, während Nitrate durch den Komplex der gelben Farbe mit Phenodisulfonsäure ermittelt wurden.

Die Ergebnisse der mehrjährigen Forschungen auf den untersuchten Standorten ergaben, dass die höchsten Konzentrationen des Atrazins in den Sickerwässern außerhab der Vegetationsperiode unter 100 ηg/l lagen, während sie in der Vegetationsperiode meistens in den Bereich von 100 ηg/l bis 500 ηg/l fielen, in den einzelnen Jahren aber die höchsten Atrazinkonzentrationen den Wert von 500 ηg/l überschritten. Die Konzentrationswerte von Chlortoluron lagen in den Sickerwässern den Atrazinkonzentrationen nahe. Die höchsten Schwermetallkonzentrationen in den Sickerwässern war bei Pb von 44µg.dm^{-3}, bei Cd 4,8 µg.dm^{-3}, bei Zn 73 µg.dm^{-3} und bei Cu 42,0 µg.dm^{-3}. Die höchsten und durchschnittlichen Konzentrationen des NO_3-N während aller Forschungsjahre überstiegen 10 mg/l. Niedrigere NO_3-N Konzentrationen konnten außerhalb der Vegetationsperiode verzeichnet werden. Die höchsten NO_3-N Konzetrationen wurden entweder im Frühjahr (nach der Grunddüngung bei der Maissaat oder bei der Nachdüngung des Winterweizens im Frühjahr und beim Herbst/Winter-Maximum an Niederschlägen) oder im Herbst nach der Grunddüngung bei der Winterweizensaat und beim Herbst/Winter-Maximum an Niederschlägen festgestellt.

Aufgrund der festgestellten Werte von einzelnen Schadstoffen ist es zu schließen, dass die Atrazin-, Chlortoluron- und NO_3-N-Konzentrationen den erlaubten Wert nach MAC Bewertung überstiegen und dass die Schwermetallkonzentrationen in den Sickerwässern unter dem erlaubten Wert nach MAC Bewertung lagen, wobei sich die Ermittlungen in Allem auf die Verordnung über die gesundheitliche Unbedenklichkeit des Trinkwassers in der Republik Kroatien (Amtsblatt «NN» 64/1994) und die Verordnung über die Schadstoffe in den fließenden Wässern («NN» 78/1998) stützten.

Da hier die Rede von gefährlichen potenziellen Verunreinigern der Sickerwässer in einer engeren Betrachtung, und der Gewässer in einer globalen Erfassung ist, sollte das Problem seriöser behandelt und das gänzliche Flussgebiet der Donau umfasst werden.

Schlüsselwörter: Sickerwässer, Atrazin, Chlortoluron, Schwermetalle, Nitrate

1. Introduction

Protection of waters in agriculture is a topical scientific and professional problem of local, national and international importance. Pollution of surface and ground waters with nitrates, heavy metals and residues of active pesticide substances periodically occurs in the agroecological conditions of extensive and intensive agricultural production. Nitrates and pesticide residues have been the greatest problem for groundwater quality in the last decade. The soil-water-plant system is faced with the increasing problem of heavy metals, which do not belong to biogenic elements but act only toxically, like for instance cadmium and lead. However, sources of air and water pollution are not always, or exclusively, from agriculture, so an interdisciplinary approach is called for.

The research aim was to define the quality of drainage waters on ameliorated soils in the Danube catchment area. Pollutants, such as atrazine, chlorotoluron, heavy metals (Pb, Ni, Cd, Zn and Cu) and nitrate nitrogen were monitored within the investigations of the quality of drainage waters.

2. Material and methods

Investigations were carried out on four amelioration trial fields in the 1991-2000 period. The soils studied were drained Gleyic Podzoluvisol and drained Calcic Gleysol. Pipe drainage was combined with contact hydraulic material - gravel and drainpipes discharged directly into open canals. Drainpipes have the following characteristics: spacing of 15 m, 20 m, 25 m and 30 m, length 95 m, diameter 65 mm, average slope 3‰ and average depth 1 m, and they discharge directly into canals.

The common crop rotation included maize and winter wheat. The same agricultural engineering practices were applied to all amelioration trial fields in each trial year. Weed control in maize was performed by the application of Primextra (6 l/ha), while Dicuran (2 kg/ha) was used for weed control in wheat. Application of total mineral nitrogen varied, ranging from 145 kg/ha to 200 kg/ha.

Samples of drainage water were taken following seasonal dynamics (in spring, autumn and winter).

Qualitative and quantitative analyses of atrazine in drainage water were done by capillary gas chromatography, heavy metals by atomic absorption spectrometry, and nitrates by means of the yellow dye complex using phenoldisulfonic acid.

3. Soil characteristics

Before the trial was set up, the area was utilised as a pasture, which was in association with swamp vegetation (Salix sp., Juncus sp., etc.). Major characteristics of ameliorated Gleyic Podzoluvisol are presented in Table 1 (average values). Soil profile layering is: Ap-Bt, g-Gso-Gr. Depth to the impervious layer amounts to 1.3 m. Excess soil moistening prior to drainage was caused by ground and surface waters.

Table 1. Major characteristics of ameliorated Gleyic Podzoluvisol

Horizons	Depth (cm)	Content of soil particles %		Porosity %	Capacity %		Permeability (m/day)	pH	
		Silt	Clay		Water	Air		H_2O	KCl
Ap	0-35	47	46	48	44	4	0.011	6.7	5.3
Bt,g	35-75	45	48	49	45	4	0.010	6.5	5.2
Gso	75-115	55	39	46	42	4	0.011	7.9	7.1
Gr	115-130	63	25	49	45	4		8.1	7.2

The soil is of silty clayey texture to the depth of 0.75 m. The clay content of this soil section is in the range of 46-48%, and the silt content is 45-47%. The soil depth of 0.75-1.15 m is of lighter texture. The silt component preponderates in soil texture (55%), while the clay content decreases (34%). Soil texture at depths over 1.15 m is silty loamy. The soil is porous, with the total pore volume of 48-49%. Soil water capacity is 42-45%. Air capacity is low - 4%. Vertical hydraulic conductivity is very low (0.011 m/day).

4. Weather characteristics

Weather characteristics are presented in terms of the quantity of annual precipitation (mm) and mean annual air temperature (^oC) in Table 2.

During the ten-year trial period, the total annual precipitation ranged between 745 mm (1994) and 999 mm (1998). Air temperatures ranged from 10.3 ^0C (1996) to 12.9 ^0C (2000).

Table 2. Total annual precipitation (mm) and mean annual air temperature (^oC)

Year	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000
P (mm)	900	837	948	745	929	924	809	999	980	748
T (^0C)	10.5	12.6	10.8	11.2	11.5	10.3	10.6	11.1	11.8	12.4
Kf	85.7	66.4	87.8	66.5	80.8	89.7	76.3	90.0	83.1	60.3

Based on Lang's rain factor, the climate of the Danube catchment area in the Republics of Croatia has been defined as semihumid (1992, 1994,1997 and 2000) to humid (in all other years) while based on the mean annual air temperature, the climate is generally classified as temperate warm climate (8-12 ^{o}C).

5. Results and discussion

Research results on atrazine and chlorotoluron, heavy metal and nitrate concentrations in drainage water are presented in Tables 3,4 and 5.

5.1. Atrazine and chlorotoluron concentrations in drainage water

Research results on atrazine and chlorotoluron concentrations in drainage water are presented in Table 3.

Table 3. Maximum atrazine and chlorotoluron concentrations in drainage water in and out of the growing season, (ng.dm^{-3})

Atrazine		Chlorotoluron	
Out of growing season	In growing season	Out of growing season	In growing season
75	478	67	486

It can be seen from Table 3 that atrazine and chlorotoluron concentrations in drainage water differed in and out of the growing season. This was certainly influenced by the date of atrazine application, quantity and distribution of rainfall and the quantity of drainage discharge. Maximum values of atrazine and chlorotoluron exceeded the tolerated value of 100 ng.dm^{-3} in the growing season whereas lower values were recorded out of the growing season. Maximum atrazine and chlorotoluron concentrations exceeded 500 ng.dm^{-3} in some years. Gaynor et al. (1992) reported that atrazine was lost during the growing season in more cases than at other times. Atrazine concentration decreased with later drainage discharges. Namely, atrazine is very water-soluble and is readily transported with filtered soil waters (Albanis et al. 1988).

The results obtained so far allow the conclusion that concentrations of atrazine and chlorotoluron in drainage waters are influenced by several factors, such as the time of application of protective agents, climatic conditions (amount and distribution of precipitation, or the intensity and duration of drainage discharge, temperature, and decomposition of active pesticide substances) etc. Atrazine and chlorotoluron are pollutants and drainage waters cannot be classified as the 1st and 2nd category waters.

5.2. Heavy metals in drainage water

Research results on heavy metal concentrations in drainage water are presented in Table 4.

Table 4. Maximum concentrations of heavy metals in drainage water (µg.dm^{-3})

Pb	Ni	Cd	Zn	Cu
44	15,0	4,8	73	42
*MAC 50 µg.dm^{-3}	MAC 50 µg.dm^{-3}	MAC 5 µg.dm^{-3}	MAC 100 µg.dm^{-3}	MAC 100 µg.dm^{-3}

*MAC- According to the Rulebook on Health Criteria for Drinking Water in the Republic of Croatia (Official Gazette 64/1994).

Results of maximum concentrations of heavy metals in drainage water recorded in the ten-year trial period did not indicate pollution, which is in agreement with the results obtained by Moore et al. (1981a and 1981b), Đumija et al. (1989) and Čoga et al. (1998), but according to Vidaček et al. (1994), the concentration of heavy metals in drainage water depends on the time of taking water samples. According to Bear and Verryjit (1987), variations in the quantity and percentage of leached Zn and Cd depend mostly on precipitation, as well as on the quantity and speed of drain water, which has an appreciable influence on the physical transport of heavy metals.

The available data point to the conclusion that there were differences between the investigation years, which were due to the hydrological conditions, kinds of crops grown, agricultural management procedures applied and air cleanliness.

5.3. Concentration of nitrate nitrogen in drainage water

Results on the nitrate concentration in drainage water are presented in Table 5.

Table 5. Maximum and average concentrations of NO_3-N in drainage water ($mg.dm^{-3}$)

Maximum	Average
32.1	12.7
MAC 10 $mg.dm^{-3}$	

It can be seen from Table 5 that maximum and average concentrations of NO_3-N during all trial years exceeded the concentration of 10 mg/l, which is the maximal admission concentration of nitrates in water (according to the Rulebook on Health Criteria for Drinking Water in the Republic of Croatia (Official Gazette 64/1994) and the Decree on Hazardous Substances in Running Waters (Official Gazette 78/1998). The maximum NO_3-N concentrations in all years were determined in the spring or in the autumn, after sowing and basic tillage or topdressing, which generally coincided with primary or secondary precipitation maxima, while lower NO_3-N concentrations were recorded out of the growing season. Translocation, that is, leaching of NO_3-N depends primarily on the soil water-permeability and its water content, namely on the soil type and its structure

Similar results for drainage water were obtained in a three-year study done by Jani and Klaghofer (1975) in Petzenkirchen (Lower Austria). They determined an average NO_3-N concentration of 14. 3 mg/l. Foerster (1984) estimated an average concentration of NO_3-N in drainage water of 24.5 mg/l – 38.3 mg/l in northwestern Germany. Šoškić et al. (1987) recorded an average NO_3-N concentration of 9.4 mg/l – 12.9 mg/l on agricultural areas of the pilot farm "Ježevo" (Upper Sava Valley). Šimunić et.al (1996) and Klačić et al. (1998) recorded an average NO_3-N concentration lower than 10 mg/l, and the maximum concentration up to 30 mg/l

The foregoing points to the conclusion that drainage water nitrates exceeded the maximal admission concentration in one part of the year, constituting a hazard to open watercourses.

On the basis of the results obtained, the authors maintain that fertilizer application should be adjusted to the plant development phases and to weather conditions, that is, fertilizers should be, if possible, applied at several times and at lower rates. This may reduce nitrate leaching, and result in less polluted drainage waters and more efficient (less costly) plant production.

6. References

Albanis, T.A., Pomonis, P.J., Sdoukos, A.T. (1988): *Movement of Methyl Parathion, Lindane and Atrazine Through Lysimeters in Field Conditions*, Toxicological and Environmental Chemistry, Vol. 17, pp 35-45.

American Public Health Association (1992): *Standard methods for the examination of water and wastewater*. 18th Edition, APHA-AWWA-WPCF, Washington.

Bear J., Verryjit, A. (1990): *Modeling Groundwater Flow and Pollution with computer programs for sample cases*, D. Reidel Publishing company, Dordrecht-Boston-Lancaster-Tokyo, p. 414.

Čoga, L., Vidaček, Ž., Poljak, M., Kovačević V. (1998): *Cadmium and Lead in the system drained Soil-Plant-Water in the Drava-Danube catchment area*. 16th World Congress of Soil Science, Volume I, No. 113 (summaries), Montpellier.

Đumija, Lj., Manitašević, J. (1989): *Determination of heavy metals and inorganic pollutants in water of canals on experimental field "Ježevo"*, Agrohemija (Beograd), No. 1-3: 69-77.

Förster, P. (1984): *Stoffgehalte in Drän- und im Grundwasser und Stoffanstiege in einem*

Sandboden Nordwestdeutschlands bei Mineraldüngung und bei zusätzlicher Gütledüngung, Kali - Briefe (Büntehof) 17/5, 373-405.

Gaynor, J.D., MacTavish, D.C., Findlay, W.I. (1992): *Surface and Subsurface Transport of Atrazine and Alachlor From A Brookston Clay Loam under Continuous Corn Production*, Archives of Environmental Contamination & Toxicology, 23, 240-245.

Jani, V., Klaghofer E. (1975): Auswirkung der Mineraldüngung auf Oberflächen und Dränwasser, Sonderdruck aus Veröffentlichungen der Landwirtschaftlich-Chemischen Bundesversuchsanstalt, Linz.

Klačić, Ž., Petošić, D., Čoga, L. (1998): *Nitrogen Leaching in Different Pipe Drainage Distances*, Poljoprivredna znanstvena smotra, Vol. 63, Br.4, 331-338, Zagreb.

Moore, J. W., Sutherland, D.J. (1981a): *Distribution of Heavy Metals and Radionuclides in Sediments*, Water and Fish in an Area of Great Bear Lake Contaminated with Mine Wastes, Arch. Environm. Contam. Toxical, 10: 329.

Moore, J. W. (1981b): *Influence of Water Movements and other Factors on Distribution and Transport of Heavy Metals in a Shallow Bay (Canada)*, Arch. Environm. Contam. Toxical, 10: 715.

Šimunić, I., Tomić, F., Marušić, J. (1996): *Dränabfluß und Stickstoffaustrag bei den verschidenen Systemen der Detailenentwässerung*. XVIIIth Conference of the Danube Countries -on Hydrological Forecasting and Hydrological Bases of Water Management, Volume 19/2, E 31-37, Graz.

Šoškić, M., Đumija, LJ., Manitašević, J., Pavlić, F. (1987): *Quantity of nitrogen in drainage water in dependence on different systems of detailed drainage*, Agrohemija br. 4, Beograd.

Vidaček, Ž., Drevenkar, V.,Husnjak, S.,Sraka, M., Karavidović P. (1994): *Nitrates, pesticides and heavy metals in drained soils and water in the area of catchment basin rivers Karašica and Vučica*, Agriculture and Water (Proceedings of Workshop), 211-222, Bizovačke Toplice (Croatia).