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# DISSOLVED ORGANIC CARBON CONCENTRATIONS IN DRAINAGE WATERS AND SOILS FROM AGRICULTURAL ECOSYSTEMS

## ZAWARTOŚĆ ROZPUSZCZALNEGO WĘGLA ORGANICZNEGO W WODACH DRENARSKICH I GLEBACH Z EKOSYSTEMÓW ROLNICZYCH

**Abstract:** The two-year field and laboratory experiments were carried out to investigate the influence of soil management, land use, climate conditions and soil properties on dissolved organic carbon (DOC) concentrations in drainage waters and soils. In the field experiment drainage waters were sampled from 12 drainage watersheds (in four research areas characterized by different soil properties each with three research sites – drainage watersheds were chosen each located in area differing in terms of land use and management practices). In the laboratory study pH values (3.5–7.5) typical for Polish soils were simulated in the soils sampled from the four research areas and DOC concentration was determined. It was found that DOC concentration may increase as the result of FYM an NPK fertilizer application, temperature rise and rainfall (during summer), as well as being depended on the soil properties (percentage of particles with a diameter below 0.02 mm, content of phosphorus and pH value). However the influence of individual factors on DOC concentration might be difficult to predict under field conditions due to their overlapping.

Keywords: DOC, drainage waters, soil management, soil properties

Dissolved organic matter (typically measured as dissolved organic carbon and hereafter referred to as DOC) is a ubiquitous component, present in all ecosystems, operationally defined as comprising any organic compound passing through a 0.45  $\mu$ m filter. Some DOC molecules can be identified chemically (such as organic acids, sugars, amino acids, fats, carbohydrates, and proteins), however most of them have no readily identifiable structure, and are known under the collective term "humic substances" [1–3]. The chemical composition of DOC fractions indicates that DOC consists mainly of by-products of organic matter mineralization and of products of microbial synthesis [2, 4]. Although dissolved organic carbon accounts for only a small proportion of the total organic carbon, which it tends to be in equilibrium with, it is recognized as

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a component that influences soil biological activity, affects the transport of metals and organic pollutants as well as cycling of nutrients and contributes to mineral weathering and podzolization [2, 4-7]. With these complex functions the ecological significance of DOC is not only restricted to the soil. It is also environmentally relevant for hydrosphere. Dissolved organic carbon affects the functioning of aquatic ecosystems through its influence on acidity, trace metal transport, light absorbance and photochemical properties, and energy or nutrient supply [1, 3]. In waters, DOC is assumed to be of predominately allochthonous origin, ie derived externally from terrestrial organic matter, and forms a significant component of the global carbon cycle. Numerous studies have shown increasing levels of DOC in the leachates from agricultural catchments. Flow paths of soil water with DOC are mainly determined by the distribution of the soils in relation to the drainage system. The linkage of DOC originated from the soil with the drainage system is temporally dynamic, depended on (i) intrinsic DOC quality parameters (molecular size, chemical structure, spectroscopic properties, and polarity), (ii) soil solution properties (nutrients, salts, ionic strength, pH, metals, organic compounds and microbial degrader community) and (iii) external factors (environmental factors - climate, landscape, hydrology; soil management - tillage, fertilization, liming, field crops; and land use - forest, grassland, arable) [2, 6-8].

In the present study, field and laboratory experiments were carried out to investigate the influence of management practices, land use, climate conditions and soil properties on dissolved organic carbon concentrations in drainage waters and soils.

### Material and methods

The two-year field experiment was carried in four research areas: Osiny (gmina Żyrzyn\*), Ownia (gmina Ryki\*), Majdan Krasieniński (gmina Niemce\*), and Zalesie (gmina Nowodwór\*), situated on the cultivated soils typical for the Lubelskie region and characterized by different soil properties (Table 1). In these areas three research sites as an experimental unit (drainage watersheds with the final drainage wells  $\emptyset$  1 m) were chosen each located in the area differing in terms of land use and management practices (Table 2). Soil samples were collected from 0-30 cm, 30-60 cm and 60-90 cm layers at the beginning of the experiment and analyzed for the following properties: soil pH determined in H<sub>2</sub>O and 1 M KCl according to the potentiometric method, the hydrolytic acidity (Hh) by the Kappen method, full water capacity by the weight method, soil texture according to the Bouyoucos method modified by Casagrande and Prószyński, contents of exchangeable cations by the F-AAS method (atomic absorption spectrometry with flame atomization) after 1 M CH<sub>3</sub>COONH<sub>4</sub> extraction, the content of available P by the colorimetric method, and available K by the F-AAS method, after extraction according of the Egner-Riehm method (DL), the content of available Mg - bythe F-AAS method after 0.0125 M CaCl<sub>2</sub> extraction.

<sup>\*</sup> Local Administrative Units - LAU 2

Table 1

Site	Soil type	Maximum water capacity [%]	pH <sub>KCl</sub>	Percentage [%] of fraction	Available forms [mg kg <sup>-1</sup> ]		
				with $\emptyset < 0.02 \text{ mm}$	Р	Mg	K
Osiny	Light loam	35.37	5.53	17.83	233.26	95.75	138.23
Ownia	Sandy loam	27.94	3.98	18.50	94.26	76.75	94.64
Majdan	Silit loam	43.21	4.27	41.66	19.86	66.75	58.32
Zalesie	Sandy loam	35.20	5.38	17.33	37.31	54.00	31.34

The soil properties in the research areas

#### Table 2

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The	research	site	specification

Site	Watershed area [ha]	Livestock $[LU^* \cdot ha^{-1} yr^{-1}]$	FYM 1998–2000 $[Mg \cdot ha^{-1} yr^{-1}]$	NPK fertilization 1998–2000 $[kg \cdot ha^{-1} yr^{-1}]$
Osiny 1	7.2	0	0	240
Osiny 2	11.4	0	0	170
Osiny 3	6.4	0	0	75
Ownia 1	5.0	8.0	48	310
Ownia 2	18.36	2.8	25	220
Ownia 3	28.16	0.5	6	80
Majdan 1	0.4	5.4	53	260
Majdan 2	4.48	1.4	10	175
Majdan 3	15.12	0.8	10	75
Zalesie 1	13.3	1.1	10	240
Zalesie 2	2.76	0.7	6	135
Zalesie 3	17.19	2.2	12	110

\* LU - Livestock Unit

Drainage water samples (1 dm<sup>3</sup> volume) were taken from each drainage watershed four times a year (in the early spring – beginning of the vegetation period, in the early summer – maximum biological activity of agricultural ecosystems, in the late autumn – the end of the vegetation period, and after harvest). All the samples were refrigerated until analysis of DOC concentrations were made (after the removal of inorganic carbon – by acidifying the sample, the DOC concentrations were determined by the conversion of organic carbon to  $CO_2$  by an ultraviolet (UV) digester with detection of  $CO_2$  using an infrared (IR) analyzer).

The net monthly precipitation (Fig. 1) was calculated as the difference between the monthly precipitation and the field reference evapotranspiration – FRE, on the basis of the data obtained from the Institute of Meteorology and Water Management (IMGW),

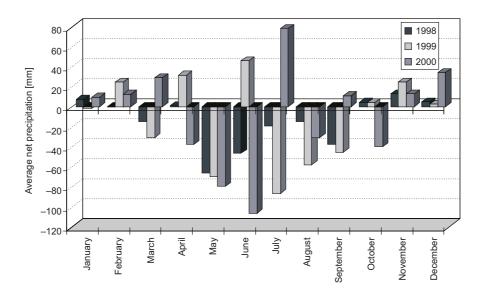


Fig. 1. Average net precipitation in the research areas

the Institute of Soil Science and Plant Cultivation (IUNG) and employing a mathematical model based on the Penman-Monteith equation for the FRE calculation. Areas and system of drainage watersheds were traced with the use of drainage maps from Lubelskie province Boards for Amelioration and Hydraulic Structures (WZMiUW). Data used for the analysis of soil management (rates of fertilizer applied, number of livestock, crop rotation) was gathered during surveys, by interviewing the farmers in the studied area. On the basis of the results characterized the livestock farmed and literature manure application rates were estimated (Table 2).

In the laboratory study pH values (3.5-7.5) typical for Polish soils were simulated in the soils sampled from the four research areas (0-20 cm). The soil materials were sieved (1 mm) and placed in plastic cups (250 g of soil was an experimental unit). The pH values of the soil samples were adjusted to a range 3.5-7.5 using 1 M and 0.1 M HCl as well as 1 M NaOH; 60 % of full water capacity was being maintained during six month-period of the incubation. At the end of the incubation soil samples were collected and analyzed for DOC concentration using an infrared (IR) analyzer.

The data were subjected to the double classification analysis of variance with two factors (site and sampling time in the case of DOC concentrations in drainage waters and area and pH in the case of DOC concentrations in soils), followed by Tukey's honest significance test; for the estimation of missing data Yeat's method was applied. The simple correlation method was used for the estimation of the relationships between DOC, P and N concentrations in drainage waters (field experiment), as well as DOC and  $H^+$  concentrations in soils. In both, the field as well as the laboratory experiments pH values were logarithmically transformed into  $H^+$  concentrations for the statistical purposes.

### **Results and discussion**

Dissolved organic carbon concentrations in drainage waters are shown in Table 3 and reflects the balance between a wide variety of competing processes that produce and consume DOC.

Table 3

Site	autumn 1998	spring 1999	summer 1999	autumn 1999	spring 2000	summer 2000	after harvest 2000	$\overline{\mathbf{X}}$
Osiny 1	4.95	5.52	5.76	4.87	6.66	*	8.60	6.20 abc**
Osiny 2	8.24	7.67	7.03	6.39	8.70		10.70	8.27 bc
Osiny 3	7.08	8.13	10.04		8.25		9.24	8.63 bc
Ownia 1	5.06	8.21	28.78	22.97	8.98			14.95 d
Ownia 2	14.67	4.11	5.49	_	4.76		_	7.33 abc
Ownia 3	4.54	4.92	9.99		4.12			5.96 abc
Majdan 1	7.66	4.68	4.09	6.84	3.37	4.05	4.72	5.06 a
Majdan 2	4.03	6.19	7.78	_			_	5.70 abc
Majdan 3	—	3.17	8.76	_	2.76	6.46	_	4.96 ab
Zalesie 1	5.40	6.94	4.80	3.65	4.30	4.50	2.59	4.60 a
Zalesie 2	6.75	8.84	12.20	5.28	12.44		_	9.25 c
Zalesie 3	7.58	15.80	9.20	3.23	5.89	11.27	4.46	8.20 bc
X	6.68 a	7.02 a	9.49 b	6.95 a	6.23 a	8.29 ab	7.32 ab	7.43

DOC concentrations [mg dm<sup>-3</sup>] in drainage waters

\* Mark (---) indicates lack of water in the drainage well;

\*\* Different letters following the figures indicate belonging to homogenic groups in variance analysis.

Dissolved organic C export from the drained sites increased significantly under conditions of the over-application of FYM (farmyard manure) along with mineral fertilizers (Ownia 1). The high value of DOC observed in this watershed can also be related to the short duration between FYM application and sampling time. Much of the organic carbon added with organic amendments is degraded and transformed by microbial activity within 4–5 weeks [9]. The immediate impact of the organic material application on the increase in DOC level in soil could take place either directly, due to the addition of soluble organic compounds already present in the applied manure (organic carbon in the water extract of FYM represents about 6 % of the total organic carbon content), or indirectly by changing soil properties such as pH, nitrogen and phosphorus content and microbial activity, which might induce the dissolution of indigenous soil organic matter [4, 6, 9–12]. It ought to be stressed that since the DOC losses in drainage waters increased in the soils amended with high doses of FYM and DOC is a primary source of N and P (significant correlations between DOC and concentrations of P-PO<sub>4</sub> – r = 0.84 and N-NH<sub>4</sub><sup>+</sup> – r = 0.84 – Fig. 2, A-B), they may be the cause of accelerating the water eutrophication in the Ownia 1 watershed.

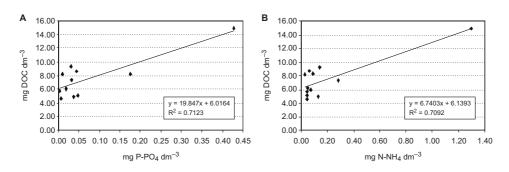


Fig. 2. Relationship between DOC and concentrations of P-PO4 (A) and N-NH4 (B) in drainage waters

In the case of Osiny sites 1–3 (treated only with mineral fertilizers, without manuring), DOC concentrations in leachates were generally above average value, suggesting that other factors, such as mineral fertilization or field crops may have been important in controlling DOC transfer. Increased crop dry matter productivity, which is proportional to N application, leads to greater returns of organic matter to the soil via plant residues and rhizodeposition. The high doses of phosphorus fertilizers (Osiny 1), applied before the experiment began, may have been responsible for a decline in DOC concentration due to the reduction in DOC sorption and in consequence its intensive leaching. It should be underlined that under agroecosystems with superiority of arable cropping (Osiny 2, 3), the soil is more often tilled, which favors DOC formation to a higher extent than under grassland superiority (Osiny 1) [7, 8, 13].

Hydrology and temperature could also play an important role in both production and mobilization of DOC in the studied agricultural soils. DOC outflow from the drained sites was similar for all sampling time, except for the peaks in concentration that coincided with high rainfall (summer 1999), which were most pronounced for sites with high doses of manure (Table 1). The formation of water-soluble organic materials could be increased through the positive influence of moisture and temperature on microbial activity, DOC deposition (rainfall in the temperate zone contains dissolved organic carbon concentrations in the range of  $0.82-2.00 \text{ mg C dm}^{-3}$ ) or through the rewetting effect after dry periods (the greater draw down of water tables in summer, increasing the depth of the oxidation zone and production of DOC; a rising water table, that intersects high DOC concentrations in the upper soil layer, enlarges vertical transport of DOC) [8, 14–16].

Water percolating through soil surface horizons is considerably enriched in DOC, but then other factors control whether these high DOC concentrations actually reach the ground or surface waters. Encapsulation of OM, flocculation of clay particles, adsorption of mineral particles around organic particles, or stable aggregate formation as well as promoting water retention will reduce DOC leaching [1, 2, 8, 17]. The degree of interaction between soils and waters depends on the soil properties, such as pH or phosphorus content. It is known that the sorption capacities of several mineral phases for organic matter increase with decreasing P content and pH [18, 19]. This seems to explain the comparatively low concentration of DOC in waters from watersheds Majdan 1–3, intensively fertilized and characterized by the soil with a high (41.66 %) percentage of particles with a diameter below 0.02 mm, very low content of phosphorus and pH < 4.5 (Table 3).

The effect of pH values on DOC content in the soils sampled from the studied sites, was also noticed in the laboratory experiment (Table 4). Although a significant correlation between  $H^+$  and DOC concentrations was not observed, which, according to Pietri and Brookes [20], might have been connected with different origin of analyzed soils, an increase in pH above 7.0 or decrease below 4.0 resulted in the dissolution of organic matter (Table 4). Higher solubility of organic matter in alkaline soils is attributed to increased deprotonation of the hydroxyl groups and a change in the microbial community, whereas in acidic soils the dissolution of organic complexes containing polyvalent cations and the advancing saturation of exchange sites are the main factors elevating DOC contents [2, 5, 19].

Table 4

Area	pH						
	3.5	4	5	6	7	7.5	Х
Osiny	65.78	58.25	54.93	57.93	81.75	99.80	69.74
Ownia	59.63	50.88	47.70	48.28	59.82	54.88	53.53
Majdan	66.10	60.13	40.80	38.68	47.13	71.83	54.11
Zalesie	79.68	64.93	69.23	84.65	98.35	103.60	83.40
$\overline{\mathbf{X}}$	67.79	58.54	53.16	57.38	71.76	82.53	65.20

DOC concentrations [mg kg<sup>-1</sup>] in soils

LSD<sub>0.05</sub> for areas (1) - 10.87; for pH (2) - 14.80; for 1  $\times$  2 - 37.29

# Conclusions

The experiments showed that biotic and abiotic factors are likely to control the dynamics of dissolved organic carbon in analyzed drainage waters. It seems that the increase in DOC concentrations in water draining from watersheds is dependent mainly on the over-application of FYM and NPK fertilizers, rise in rainfall and temperature, as well as properties of the soil (percentage of particles with a diameter below 0.02 mm, content of phosphorus and pH). It was found that in both acidic and alkaline soils DOC leaching is liable to increase. However, there do not appear to have been any regular trends in chemical and environmental factors, soil management or land use affecting all analyzed watersheds. Therefore, the influence of them on DOC concentration may be difficult to predict under field conditions.

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#### ZAWARTOŚĆ ROZPUSZCZALNEGO WĘGLA ORGANICZNEGO W WODACH DRENARSKICH I GLEBACH Z EKOSYSTEMÓW ROLNICZYCH

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Abstrakt: Celem przeprowadzonego dwuletniego doświadczenia polowego i laboratoryjnego było zbadanie wpływu użytkowania gleby, użytkowania gruntów, warunków klimatycznych i właściwości gleb na zawartość rozpuszczalnego węgla organicznego (DOC) w wodach drenarskich i glebach. W doświadczeniu polowym pobierano wody drenarskie z 12 działów drenarskich (w każdym z czterech obszarów badawczych, charakteryzujących się zróżnicowanymi właściwościami glebowymi, wytypowano po trzy obiekty badawcze – działy drenarskie, zlokalizowane na zróżnicowanych pod względem użytkowaniu gruntów i zabiegów agrotechnicznych terenach). W doświadczeniu laboratoryjnym w glebach pobranych z czterech obszarów

badawczych symulowano wartości pH typowe dla polskich gleb i oznaczano zawartość DOC. Stwierdzono, że zawartość DOC może się zwiększać w wyniku stosowania obornika i nawozów NPK, wzrostu temperatury i opadów (podczas lata), jak również jest uzależniona od właściwości gleby (udziału frakcji o średnicy 0,02 mm, zawartości fosforu oraz pH). Jednak w warunkach polowych wpływ poszczególnych czynników na zawartość DOC może być trudny do przewidzenia z uwagi na ich nakładanie się.

Słowa kluczowe: DOC (rozpuszczalny węgiel organiczny), wody drenarskie, użytkowanie gleby, właściwości gleby