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Dissolvable organic carbon in groundwater as an indicator of its contamination as a result of many years of on-ground storage of manure

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Abstract. The paper presents results of studies on the effects of long-term storage of cattle manure directly on the ground on the contamination of shallow groundwater with dissolved organic carbon (DOC). The research was carried out from January 2008 to December 2009. It was conducted at the site where cattle manure had been stored for about 20 years. Water samples were collected from three wells located at the site of manure storage and next to it. Moreover, at the same time water from two nearby ditches was sampled. Water samples were analyzed calorimetrically for the concentration of DOC using segmented flow analysis (S.F.A.S.).

The research indicated that long-term manure storage on the ground resulted in significant pollution of groundwater with dissolved organic carbon. Annual average DOC content in groundwater from the monitored units was approximately from 51.0 to approximately 189.0 mg C dm^{-3}. Its concentration in water samples collected on a monthly basis was as high as 597.0 mg C dm^{-3}. The concentration of DOC in the surrounding ditches in the study period ranged from 3.5 mg C dm^{-3} to 12.5 mg C dm^{-3}. Concentration of that element was higher in water from a ditch located in close proximity to manure storage (11.1 mg C dm^{-3}) than in a ditch located further away from that area (6 mg C dm^{-3}).

The research indicates that it is necessary to intensify research towards a better identification of the role of DOC in the movement and accumulation of minerals in the water, and that DOC can be a good indicator of water pollution from agricultural sources.

key words: DOC, groundwater, storage manure

INTRODUCTION

Manure stored directly on the ground poses a great threat to the environment, especially for waters. This threat is usually considered in terms of loss of nitrogen from the fertilizer. However, in the process of mineralization of organic matter during manure storage, in addition to nitrogen, other mineral elements and carbon leak into the environment. They can be once more put into biological circulation or get washed deeper in the soil profile and thus get into the groundwater and surface water. Organic carbon in soil solution and surface water has a form of humic substances of complex chemical structure which include basic components of fertilizer, such as nitrogen and phosphorus. The most labile fraction of organic carbon is dissolved organic carbon (DOC). This is a fraction of carbon defined as all organic substances present in the solution less than 0.45 μm (Aiken, 2002; Silveira, 2005). DOC is a very important component in biogeochemical cycling of elements characterized by high susceptibility to leaching. It is recommended to be used as an indicator of ground water pollution (Gooddy, Hinsby, 2007). It is believed that DOC may be a particularly useful indicator of water pollution from landfills and similar sites which release high loads of organic carbon (Gooddy, Hinsby, 2007). In a typical uncontaminated groundwater DOC concentration is on the level of 1 mg C dm^{-3} (Chomycia et al., 2008). This value can serve as a benchmark in assessing the quality of the water analyzed for that component. The aim of this study is to assess the effects of long term "on-ground" storage of cattle manure on the pollution of shallow ground waters with dissolved organic carbon (DOC).

MATERIAL AND METHODS

The study covered the period from January 2008 to December 2009. It was carried out near Warsaw at the site where manure had been stored on the soil developed from sand over the period of 20 years. By 2007, the use of the storage site consisted of repeated annual cycles of stockpiling and removal of the manure to be used to fertilize crops. In 2008 only a small batch of manure was delivered to the site, and from 2009 its exploitation was stopped. In 2008 and 2009 rainfall amounted to respectively over 840 and

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Table 1. Average monthly rainfall and temperature distribution in the studied period (Szymczak, Klasicka, 2008, 2009).

Years	Rainfall [mm]												
	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	annual sum
2008	113.8	50.5	77.7	58.3	60.6	29.1	127.0	108.5	79.9	22.6	48.6	63.8	840.4
2009	39.4	62.7	82.5	10.4	108.5	184.0	88.0	74.0	26.6	114.3	90.1	65.7	946.2
Years	Temperature [°C]												
	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	annual average
2008	1.2	3.1	3.8	9.4	14.0	18.8	19.5	18.9	12.7	10.2	5.2	1.5	9.8
2009	-3.1	-1.1	2.4	10.7	13.4	16.2	19.9	18.3	14.6	6.4	b.d.	b.d.	9.8

b.d. – no data

946 mm, and average annual air temperature was in each year 9.8 °C (Table 1).

During the study period the samples of ground water were collected for analysis from the site of manure storage, three groundwater sampling wells installed in its vicinity, and two sampling points from nearby ditches (Fig. 1).

Samples of groundwater were collected from sampling wells bored along the direction of the movement of ground water (Fig. 1) at monthly intervals during the whole time of the research. Before the collection of the samples, the level of ground water was measured, and then water was pumped out from the well, and after about ten minutes a sample of newly seeped water was taken for the analysis. The bottom of the wells was at a depth of 2 m below ground level.

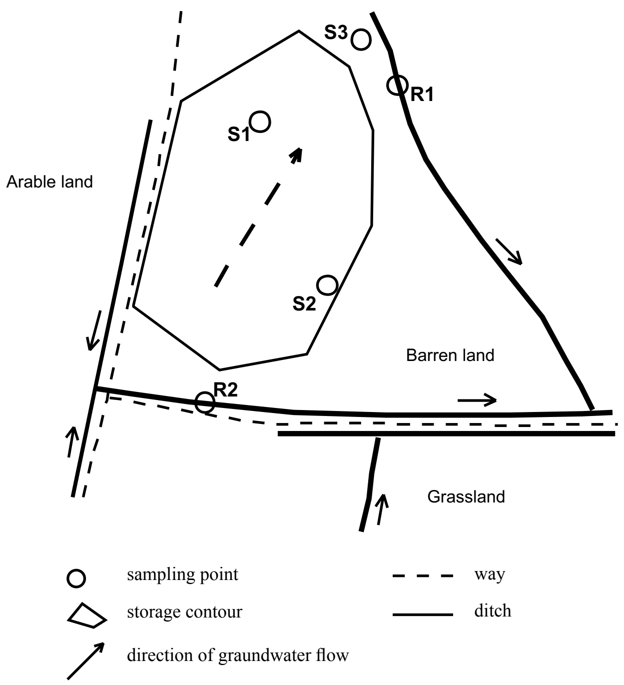


Figure 1. Outline location of FYM storage on the ground together with the sampling points of waters.

DOC concentration in the samples was determined colorimetrically, using a segmented flow of the stream (S.F.A.S.) using the autoanalyser manufactured by "Skalar". The process of determining the DOC, after filtration through a 0.45 µm filter was performed in the following stages (Skalar Methods, catnr. 311-411):

1) Acidification of the samples with sulfuric acid and removing non-organic carbon by the stream of dry nitrogen;
2) Subjecting the samples to UV radiation in the presence of buffered potassium persulfate resulting in the release of carbon dioxide from dissolvable compounds of organic carbon;
3) The dialysis of the sample at the presence of hydroxylamine hydrochloride, during which carbon dioxide passes through a gas-permeable silicone membrane, reducing the pH of phenolphthalein indicator solution which due to the acidification solution gets discoloured in proportion to the concentration of dissolved organic carbon in the sample;
4) The measurement of the intensity of discoloration of the phenolphthalein solution in 30 mm flow cuvette at the wave length of $\lambda = 550$ nm.

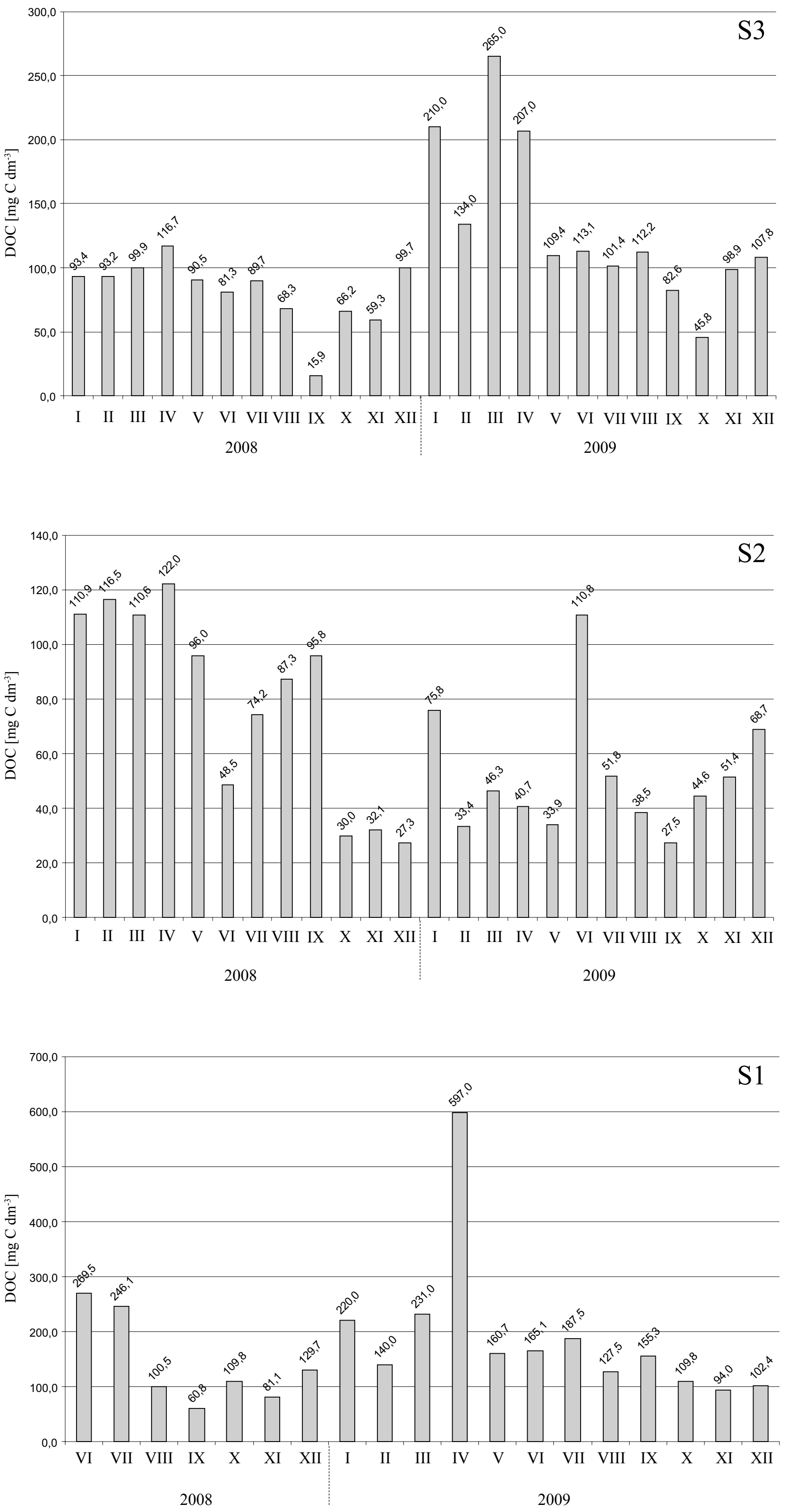
RESULTS AND DISCUSSION

In the result of manure storage directly on the sandy soil there was also a significant enrichment of ground water in DOC in the zone of its impact. This impact varied depending on the year of the research and the localization of a monitoring point. The highest average level of DOC (134.8 mg C dm^{-3} in 2008 and 189.0 mg C dm^{-3} in 2009) was found in ground water from S1 well, located in the main part of the stockpiling site. The lowest average level of DOC was found in sampling well S2, located on the edge of the landfill (Fig. 1). It was 79.3 mg C dm^{-3} in 2008, and 50.7 mg C dm^{-3} in 2009, which was the lowest average level of this component during the whole study period (Table 2). In 2009 a significant increase of groundwater content of DOC (135.1 mg C dm^{-3}) was recorded in the well situated outside the S3 landfill in comparison with 2008 (81.2 mg C dm^{-3}). It can be explained by significant changes in the amount and distribution of precipitation in the years of study, and therefore by a different rate and direction of the spread of this element with groundwater.

In other studies located in the vicinity of the study site (in the distance of approximately 1200 m), carried out in 2008/2010 on a meadow experiment – with no natural but only mineral fertilizers being used, it was determined that in the samples of shallow groundwater (n=60), the concentration of DOC was 8.58 mg C dm^{-3} (Burzyńska, 2010). So, by comparison, the concentrations of DOC at and close to the manure stockpiling site were much higher. When considered on a monthly basis the largest concentration of DOC was determined in water taken from well S1 for the spring months of 2009 – April (597.0 mg C dm^{-3}), with PWG (level of groundwater table) -26 cm being also one of the highest (Fig. 3), and March (231.0 mg C dm^{-3}), PWG -11 cm. A similar tendency was observed for well S3 – March (265.0 mg C dm^{-3}), PWG -45 cm. In the case of point S2, situated on the periphery of the site, the largest concentrations of DOC occurred in the first four months of 2008 and June 2009 (Fig. 2). A high variation, both month-to-month and year-to-year, can be explained by a significant variability in the amount and distribution of precipitation in the period of the research (Table 1), which contributed to considerable changes in groundwater level (Fig. 3).

Generally, we can observe (Fig. 2) higher concentration of DOC in winter – spring season, but it was dependent on the location of the monitoring point.

It must be noted that the results of previously conducted studies at the same study site showed that the groundwater occurring within its area was also substantially contaminated with fertilizer components. On average, in the water samples taken from the period of 7 months up to 13 months, depending on the localization of monitoring point were: 2.7–25.9 mg $P\text{-}PO_4$ dm^{-3}, 3.0–73.4 mg $N\text{-}NO_3$ dm^{-3}, 6.7–11.0 mg $N\text{-}NH_4$ dm^{-3}, 175.0–1085.1 mg K dm^{-3}



S1, S2, S3 – see Fig. 1

Figure 2. DOC concentration in water samples from various points at a former FYM on-ground storage site from January 2008 to December 2009.

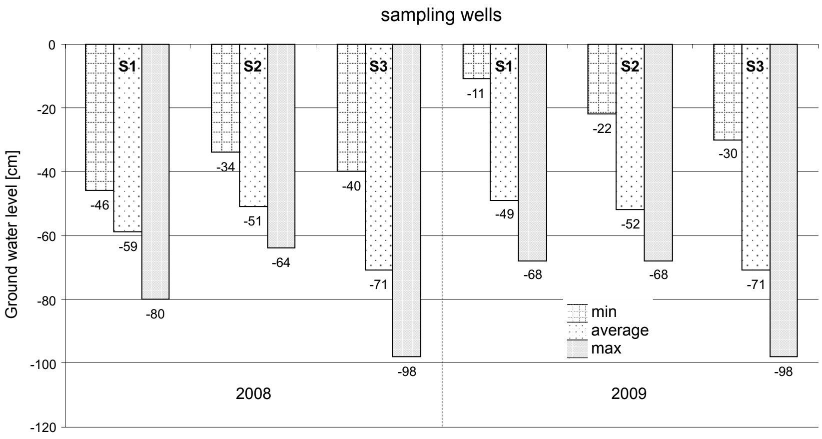


Figure 3. Average level of groundwater table in the sampling wells as measured in 2008 and 2009.

(Pietrzak, Nawalany, 2009). The most polluted was water from the well situated in the centre of the stockpile. The content of nitrate nitrogen, ammonium nitrogen, phosphate phosphorus and potassium exceeded the limits accepted in the ruling by the Minister for the Environment of July 23, 2008 (Rozporządzenie Ministra..., 2008) for groundwater of class V.

In watercourses situated in the vicinity of the research area (Fig. 1), average annual concentrations of DOC from the ditches were respectively 6.6 mg C dm^{-3} and 10.5 mg C dm^{3} in different years. The content of DOC in surface water from the nearest ditches was much smaller than in water from sampling wells (Fig. 2). Those contents were close to the amounts of dissolvable organic carbon measured in soil solutions by other researchers (Kalbitz et al., 2001; Łabętowicz, 1995). In nearby watercourses, the highest level of DOC was determined in the initial months of the year (February – 18.3 mg C dm^{-3}, March – 20.3 mg C dm^{-3}), while the smallest in September 1.2 mg C dm^{-3} (Table 2).

Table 2. The average content of DOC in groundwater and surface water in 2008 and 2009 in monitoring points.

Monitoring point	Year	Number of samples	DOC content [mg C dm^{-3}] in ground and surface water			
			mean	SD	max	min
S1	2008	7	134.8	92.8	269.5	6.8
	2009	12	189.0	129.5	597.0	94.0
S2	2008	12	79.3	35.8	122.0	27.3
	2009	13	50.7	22.8	110.8	27.5
S3	2008	12	81.2	26.2	116.7	15.9
	2009	13	135.1	60.8	265.0	45.8
R1	2008	9	9.7	4.2	18.3	5.6
	2009	8	12.5	5.7	20.3	5.1
R2	2008	8	3.5	1.5	5.6	2.0
	2009	12	8.5	7.5	20.2	1.2

S – wells
R – ditches
SD – standard deviation

Intensity of the transformation of organic matter from organic fertilizers, and thus dispersion processes of carbon compounds, can be to a large extent conditioned by basic conditions of soil-water and meteorological factors. One of the factors which can contribute to an increased carbon transformation in the soil, and thus to the presence of larger amounts of soluble organic compounds in soil is water outflow from the soil profile and fluctuations in groundwater table (Kalbitz et al., 2001; Wolt, 1994; Trojanowski, 1973). Groundwater level is presented on the chart (Fig. 3). Despite significant seasonal fluctuations in groundwater and DOC content (Fig. 2), no statistically significant correlation coefficients were obtained between the level of ground water and the concentration of DOC in the water. It could be caused by the time lag of the impact of PWG on the mobilization of dissolvable organic carbon from the soil. A similar view is expressed by Zsolnay (2001), who points also to the fact that soluble form of organic matter, despite constituting a relatively small part (<1%) of the total amount of carbon in the soil, is extremely mobile and can be an excellent indicator of changes of organic carbon in soils.

Our results indicate that the impact of agricultural practices and of livestock production, in particular, on pollution of groundwater with dissolved organic carbon may be very large. It is also confirmed by the results of other, more comprehensive studies carried out on dairy farms in the US. It was shown there that the average concentrations of DOC in ground water were (Chomycia et al., 2008):

- next to ponds for storage of liquid manure – 27.5 (13.0–55.0) mg C dm^{-3},
- in paddocks for animals – 16.9 (8.0–30.0) mg C dm^{-3},
- on fields fertilized with manure – 7.6 (4.0–15.0) mg C dm^{-3},
- at drainage pipe outlets to the drainage channel 10.0 (5.0–12.0) mg C dm^{-3}.

The lack of unequivocal results defining the role of dissolved organic carbon in the movement and accumulation of minerals in the water prompted this study aimed at a better identification of this phenomenon

CONCLUSIONS

1. Long-term storage of manure directly on the ground causes significant pollution of soil and groundwater with soluble organic carbon.

2. Fluctuations in the groundwater level are not unequivocally related to the seasonal variations of dissolvable organic carbon.

3. Although dissolved organic carbon is not yet an official indicator of water quality, its large quantities observed in groundwater appear not to be without impact on its quality.

4. The principles of long-term storage of manure on the ground must be re-examined in the light of environmental protection requirements.

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