

*Original Research*

# Labile Organic Matter and Heavy Metals in Waters of Agricultural Landscape

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## Abstract

This paper describes some characteristics and properties of low molecular compounds - labile fraction, isolated from dissolved organic matter in ground and surface waters on arable land. The differences in composition of labile fraction using IR spectroscopy were studied. Also, the ability of labile fraction to heavy metals complexation was analyzed.

**Keywords:** labile fraction, heavy metals, water transport

## Introduction

In aquatic ecosystems the concentration of dissolved organic compounds (DOC) varies both with season and type of water [23]. Moreover, composition of DOC, essential for biota, chemical and biological processes taking place in surface and ground waters, also undergoes changes [1]. The composition of two important fractions of DOC, hydrophobic (humic substances, polysaccharides, polyamides) and hydrophilic (low-molecular compounds - labile fraction) with different susceptibility to microbial decomposition is, to a large extent, dependent on leaching of chemical organic compounds from arable land as well as on components applied through organic fertilizers, chemical plant protection, organic substances formed in the process of organic soil transformation [13,1,16]. Fractionation of dissolved organic compounds and estimation of labile fraction concentrations is a step toward a better understanding of their function in aquatic environments, in particular their ability to complex metals [7].

The role of humic substances (HS), being a huge part of DOC, (ranging from about 50% up to 90%) in chelation and complexing of some nutritionally important ani-

ons and cations including heavy metals is well known [15]. The importance of labile fraction in these processes is less recognized than humic substances, although this fraction may be of geochemical significance in the environment. Labile fraction has been largely ignored in the study of DOC, which is connected, among other things, to low concentrations of labile fraction and its weak resistance to microbiological decomposition [13]. Study of labile fraction degradation has indicated that about 50% of soluble labile material was degraded by microorganisms within 48 hours [14].

The aim of this paper was to analyze labile fraction isolated from organic compounds dissolved in ground and surface waters and estimation of its concentrations in these waters depending on the season. Moreover, investigations tend to identify this fraction, which will allow us to explain the complexing ability of labile fraction towards heavy metals.

## Terrain, Materials and Methods

This study was carried out in waters located among arable lands in the Wielkopolska Lowland in Poland, 40 km south of Poznan, where intensive agriculture dominates. In this area arable lands constitute about 70%,

meadows and pastures 12%, small forest and shelterbelts 14%. Hapludalf soils originating from boulder clay predominate in this region. Organic matter content in the ploughing layer ranges from 1.1 to 1.8% [12].

Two types of water samples were taken for these studies in June and November 1998: surface water from a mid-field pond (500-600 m<sup>2</sup>) and ground water from a well near the pond. Mean yearly level of examined ground water was 140 cm.

The water samples were filtered through a glass fibre filter (Whatman GF/C). A part of water was evaporated in a boiling water bath and dried to constant weight at 105°C for determining dry mass (DM) yields. Isolation of DOC from waters and separation on hydrophilic (labile organic compounds not retained by XAD-2 resin after acidification of water to pH=2) and hydrophobic fraction (adsorbed into resin) was carried out according to the method described by Szpakowska et al. [19]. Total organic carbon and labile organic carbon were determined on TOC-5050 A (Shimadzu). Infrared analysis of labile organic compounds isolated from waters (mg of labile fraction/200 mg KBr) were carried out using an IR spectrophotometer ATI Mattson Infinity Series Stir (USA).

Total concentrations of zinc, cadmium, lead and copper in dry mass and in labile fraction were analyzed using differential pulse anodic stripping voltammetry (DPASV). The working electrode was mercury, supplementary was platinum, while the reference electrode constituted an Ag/AgCl system in potassium chloride [20].

## Results and Discussion

It is well known that leaching of both inorganic and organic chemical elements from agroecosystems to surface and ground waters causes problems in protecting the aquatic environment. In examined waters whose pH ranged from 7.3 to 7.7, concentrations of dissolved elements in surface water amounted to from 751 mg·dm<sup>-3</sup> to 881 mg·dm<sup>-3</sup> and in ground water from 981 mg·dm<sup>-3</sup> to 1070 mg·dm<sup>-3</sup>. Concentrations of total carbon in studied months were 55.1 mg·dm<sup>-3</sup> (in June) and 54.0 mg·dm<sup>-3</sup> (in November) in ground water, in water of reservoir 43.9 mg·dm<sup>-3</sup> and 102.1 mg·dm<sup>-3</sup>, respectively.

Long-term studies carried out in the examined area indicated an increase of dissolved compounds in waters [22]. Increased leaching of organic compounds could be due to both a rise in soil acidity caused mostly by acid rains [22] and a rapid rise in soil reaction caused by e.g. liming [6, 10]. Concentrations of DOC were highest in the surface water and ranged from 23.3 mg·dm<sup>-3</sup> in November to 38.2 mg·dm<sup>-3</sup> in June. In the ground water concentrations of these compounds were three to four times lower (Tab. 1). The labile fraction, although often ignored, according to Shuman [19] account for about 20-50% of DOC. In our waters concentrations of this fraction constituted 30% to 48% of DOC and were higher in surface water in comparison with ground water in both analyzed seasons.

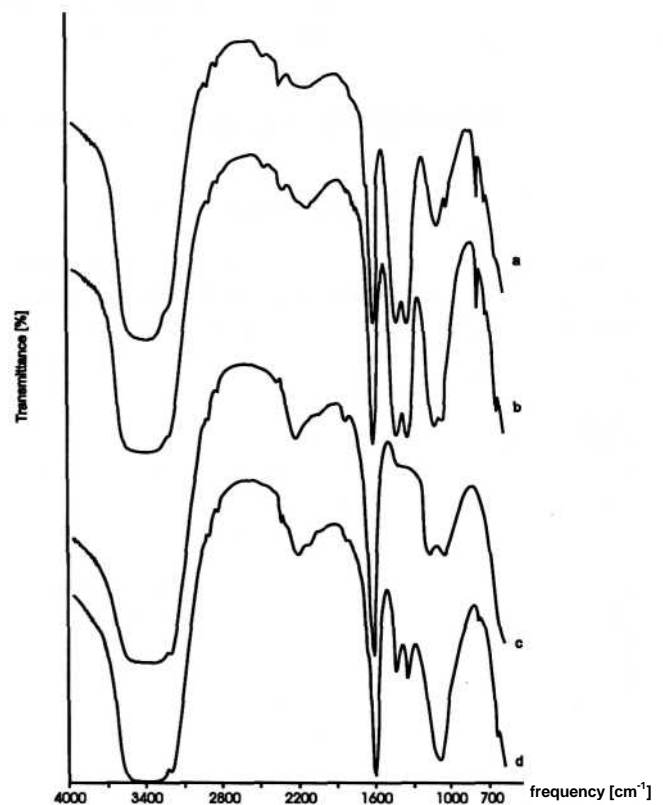
It is recognized that different extents of metal complexation depend on heavy metal amounts as well as on physico-chemical properties and composition of labile fraction. This hydrophilic material is usually a mixture of simple organic acids such as fatty acids and hydroxy

Table 1. Composition and concentration of dissolved organic substances in examined waters [mg·dm<sup>-3</sup>].

Examined parameter	Surface water		Ground water	
	June	November	June	November
Total carbon	43.9	102.1	55.1	54.0
Dissolved organic compounds	38.2	23.3	10.5	7.9
Labile organic compounds	18.7	10.1	4.1	2.4

acids. For structured studies of this fraction infra red (IR) analytical method has been used generally. On the basis of IR spectroscopy labile fraction isolated from surface and ground waters in two seasons were compared (Fig. 1). In each spectrum (Fig. 1 a-d) great similarities can be seen in absorption bands for samples of labile organic matter obtained from ground as well as surface water in two analyzed seasons. However, more similarities can be seen in spectra obtained from ground water sampled in June and November. The only difference is observed in spectrum for samples taken from surface water in June (Fig. 1 c). Lack of absorption bands at

Fig. 1. Infrared spectra of labile organic matter isolated from



ground water: a (in June), b (in November) and from surface water: c (in June), d (in November).

1300-1600  $\text{cm}^{-1}$  in this sample suggests that among organic compounds which created labile fraction obtained from surface water taking in this period there are not substances with -OH groups such as alcohols, acids and phenolic acids as well as stretching vibration of -CH<sub>3</sub> in esters and ketones with absorption bands in the 1380-1360  $\text{cm}^{-1}$  region [9, 18]. The presence of these structures in surface water taken in November (Fig. 1 d) can be connected with inflow to the examined pond compounds created as a result of soil organic matter transformation and mineralization of fresh plants residual. In IR spectra of samples obtained from ground waters (Fig. 1 a, b) the absorption band in this range is strongly developed.

Occurrence of heavy metals in waters localized among agricultural lands depend on abiotic and biotic parameters which characterized drainage catchment. Inflow of trace metals is related to type and permeability of soils, amounts of rainfall, land configuration and proportion of arable land to grassland and forests [24, 25]. The amount of inflowing metals is also connected with farming in the catchment, crop structure, amount and type of fertilizers introduced to the soils and chemical plant protection agents [5].

The analysis of total heavy metals concentration indicated higher concentrations of cadmium, lead and copper in ground water as compared to concentrations of these metals in surface ones (Tab. 2). Comparing metal concentrations in the studied waters with those obtained by other authors for waters also running through farming areas great similarities can be found [3]. In the waters localized on soils considerably contaminated with dust emitted by metallurgical industrial plant, Pb and Cd concentrations are much higher both in ground and surface waters [2].

Table 2. Total concentration of heavy metals in examined waters [ $\mu\text{g}\cdot\text{dm}^{-3}$ ].

Examined metal	Surface water		Ground water	
	June	November	June	November
Zinc	371	171	506	134
Cadmium	0.444	0.316	0.906	0.444
Lead	18.7	22.6	29.2	40.1
Copper	9.6	5.4	12.1	7.5

Comparing the total concentrations of metals in waters according to the season, higher concentrations of zinc, cadmium and copper were observed in summer than in autumn (Tab. 2). It was particularly clear in the case of zinc, whose summer concentrations in surface water were 117% higher, whereas in ground water they were 260% higher as compared to autumn. Similar results were noticed by Koc and Rochwerger [8]. These authors analyzed concentrations of zinc in waters of agricultural areas and found much higher concentrations of this metal in waters during early summer in comparison with late autumn. The above relationship was not observed in

the case of lead, whose concentrations in waters were higher in autumn.

The characterization of metal forms in natural aquatic environments requires assessing biological impact because bioavailability and toxicity is directly related to the concentration of metal ion species [4]. While the inorganic speciation is fairly well characterized, not much is known about the chemical nature and co-ordinating strength of naturally occurring organic ligands [11]. Depending on physico-chemical composition of labile fraction, waters may show different extents of metal complexation. The analysis of zinc, cadmium, lead and copper in isolated labile fractions indicated their higher concentrations in samples obtained from ground water in comparison with content of these metals in surface water in two analyzed periods (Tab. 3).

Table 3. The amount of heavy metals in labile fractions [ $\mu\text{g}\cdot\text{dm}^{-3}$ ].

Examined metal	Surface water		Ground water	
	June	November	June	November
Zinc	33.6	12.7	63.1	22.1
Cadmium	0.090	0.082	0.560	0.172
Lead	2.6	3.8	19.3	8.2
Copper	2.4	0.5	5.9	2.2

Comparing the concentrations of examined metals in labile fractions both in surface and ground waters with respect to analyzed periods lower concentrations of these metals were observed in autumn. Only in the case of lead were slightly higher concentrations of this metal found in November in surface water. However, a comparison of metal contents (in percent) in labile fractions with total concentrations of these metals indicated that such relationships occur also for lead (Fig. 2). Less heavy metal bound with labile fraction in surface water can presumably be connected with its composition. Labile fraction in surface water is less differentiated as compare to ground water which was confirmed by the lack of absorption band at 1300-1400  $\text{cm}^{-1}$ .

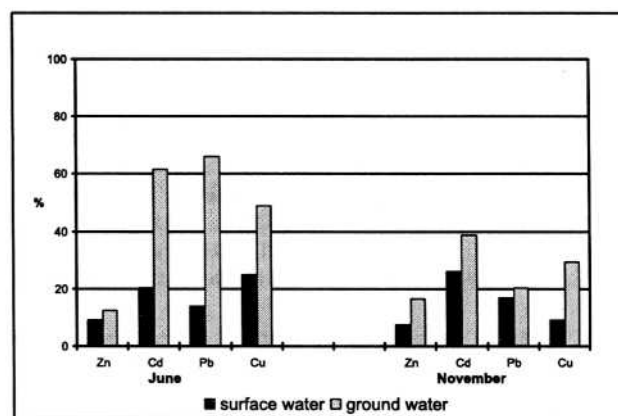


Fig. 2. Percentage of heavy metals in labile fractions isolated from surface and ground waters in different seasons.

## Conclusions

Concentrations of dissolved organic matter in examined surface waters were higher in comparison with ground water and ranged from 7.9 mg·dm<sup>-3</sup> to 38.2 mg·dm<sup>-3</sup>. Labile fraction consisted of 46.9% of total dissolved organic matter in case of surface water and 34.7% in the case of ground water. It can be stressed that in November percentage of labile fraction was lower in both examined water in comparison with summer.

Infrared studies of labile fractions isolated from surface and ground waters showed existing similar absorption bands in each spectrum generally. Only the lack of absorption band at 1360-1460 cm<sup>-1</sup> in spectrum of examined labile fraction obtained for surface water sampling in June required additional analysis, for example degree of DOC susceptibility to UV radiation. Shuman [19] showed, on the basis of IR and <sup>13</sup>C NMR, that hydrophilic material have carboxyl bands comparable to the hydrophobic acids. If the trends of carboxyl acidity with molecular size are valid, then the hydrophilic acid fraction, because of its small size, is expected to have a higher acidity than the XAD-extracted fraction. Also, Thurman [26] pleads that although the chemical nature of hydrophilic material is unknown, they are thought to be similar to humic material, with more carboxyl and hydroxyl character and lower molecular weight. These hydrophilic acids may have as many binding sites (1 µeq/mg of C) as humic substances [26]. Appearance of additional binding sites in hydrophilic material can explain the relatively high amounts of metals present in examined waters in form bound to labile fraction of DOC.

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