

# Particulate organic carbon (POC) in relation to other pore water carbon fractions in drained and rewetted fens in Southern Germany

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**Abstract.** Numerous studies have dealt with carbon (C) contents in Histosols, but there are no studies quantifying the relative importance of the individual C components in pore waters. For this study, measurements were taken of all the carbon components (particulate organic carbon, POC; dissolved organic carbon, DOC; dissolved inorganic carbon, DIC; dissolved methane, CH<sub>4</sub>) in the soil pore water of calcareous fens under three different water management regimes (rewetted, deeply and moderately drained). Pore water was collected weekly or biweekly (April 2004 to April 2006) at depths between 10 and 150 cm.

The main results obtained were: (1) DIC (94–280 mg C l<sup>-1</sup>) was the main C-component. (2) POC and DOC concentrations in the pore water (14–125 mg C l<sup>-1</sup> vs. 41–95 mg C l<sup>-1</sup>) were *pari passu*. (3) Dissolved CH<sub>4</sub> was the smallest C component (0.005–0.9 mg C l<sup>-1</sup>). Interestingly, about 30% of the POM particles were colonized by microbes indicating that they are active in the internal C turnover. Certainly, both POC and DOC fractions are essential components of the C budget of peatlands. Furthermore, dissolved CO<sub>2</sub> in all forms of DIC appears to be an important part of peatland C-balance.

## 1 Introduction

The carbon (C) storage in ecosystems and the C balance between the atmosphere and terrestrial ecosystems is vulnerable to changes in environmental conditions (global change). Soils hold the largest C pool of terrestrial ecosystems (IPCC, 2007). To fully understand soil C dynamics and potential feedback with the atmosphere, greater insight into the internal soil C dynamics (turnover and pathways) is needed.

Internal C dynamics takes place in the pore system and the medium is predominately water. Total carbon (TC) in pore water is made up of dissolved organic carbon (DOC), dissolved inorganic carbon (DIC = CO<sub>2</sub> in all dissociation species), dissolved methane (CH<sub>4</sub>), and particulate organic carbon (POC). Organic matter (OM) in pore water is differentiated by size: Particulate organic matter (POM), and dissolved organic matter (DOM). There is no unified definition separating DOM and POM. Usually DOM and POM are quantified by analyzing the carbon content (DOC, POC). For the hydrosphere and pedosphere, DOM is commonly defined as organic matter in water samples smaller than 0.45 μm (Thurman, 1985). However, POM is frequently defined as organic matter larger than 0.7 μm (Hope et al., 1997; Dawson et al., 2004). Consequently, given the two frequent definitions, there is a gap in particles between >0.45 μm and <0.7 μm. Therefore for this study the definition of Zsolnay (2003) was applied separating DOC as particles <0.45 μm and POC as particles >0.45 μm.

A global agreement on the definition of DOM and POM obligatory for all scientific disciplines would guarantee direct comparisons of data from different studies. An option is



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**Table 1.** Descriptive statistics of C components in pore water and characteristics of the Histosols of the Donaured study site. The sampling period was 1 April 2004 to 31 March 2006. Means, standard deviations (SD) and sample numbers (n) of all measured values are shown; statistically significant differences between sites and depth for each carbon component are indicated by different letters ( $p < 1\%$ ), n.d. = not determined.

Depth [cm]	BD	H	CaCO <sub>3</sub>	C <sub>org</sub>	N <sub>f</sub>	Timewith water saturation [%]	TOC(DOC+POC) mean±SD(n)	POC mean±SD(n)	DOC mean±SD(n)	DIC mean±SD (n)
	[g cm <sup>-3</sup> ]		[g kg <sup>-1</sup> ]							
Deeply drained fen (Foli-Calcare Histosol); 48°29'7.48" N, 10°11'29.03" E; land use: extensive grassland since about 25 years Vegetation: <i>Achillea millefolium</i> L., <i>Agrostis stolonifera</i> L., <i>Alopecurus pratensis</i> L., <i>Lolium perenne</i> L. and <i>Poa pratensis</i> , <i>Trifolium repens</i>										
5–15	0.31	H10	69	407	28	0	n.d.	n.d.	n.d.	n.d.
15–25	0.29	H9–10	84	397	26	0	n.d.	n.d.	n.d.	n.d.
35–45*	0.22	–	820	189	2.5	5	90±23 (9) <sup>b,d,h</sup>	14±14 (9) <sup>A,B</sup>	86±34 (17) <sup>A,B</sup>	126±76 (21) <sup>h,k</sup>
55–65	0.18	H6	70	451	25	16	101±39 (26) <sup>c,d,e</sup>	30±39 (26) <sup>A,B</sup>	81±27 (49) <sup>A,C</sup>	152±77 (91) <sup>g,h</sup>
75–85	0.39	–	22	86	5.0	33	132±40 (44) <sup>g,h</sup>	45±36 (44) <sup>A</sup>	95±25 (68) <sup>A</sup>	176±71 (74) <sup>e,f</sup>
145–155***	–	–	–	–	–	87	130±74 (61) <sup>d,f,h</sup>	125±166 (61) <sup>A</sup>	72±30 (97) <sup>A</sup>	280±111 (212) <sup>a</sup>
Moderately drained fen, (Calcare-Fibric Histosol); 48°28'59.63" N, 10°12'19.50" E; land use: extensive sheep pasture, nature protection area since 1992, Vegetation: <i>Festuca ovina</i> , <i>Thymus pulegioides</i> , <i>Arabis hirsuta</i> , <i>Bromus erectus</i> , <i>Campanula rotundifolia</i> , <i>Deschampsia caespitosa</i>										
5–15	0.24	H9	62	406	36	29	115±59 (15) <sup>d,c,h</sup>	55±63 (15) <sup>A,B</sup>	73±30 (41) <sup>A,B</sup>	94±46 (78) <sup>k</sup>
15–25	0.21	H6	49	425	27	52	141±94 (52) <sup>d,h</sup>	74±94 (52) <sup>A</sup>	79±29 (81) <sup>B,C</sup>	152±78 (121) <sup>f,h</sup>
35–45	0.13	H5	41	465	24	86	138±122 (56) <sup>h</sup>	67±121 (56) <sup>A</sup>	88±33 (104) <sup>B,C</sup>	173±85 (177) <sup>f,g</sup>
55–65	0.17	H5	29	469	23	97	104±41 (79) <sup>d,f</sup>	38±36 (79) <sup>A,B</sup>	76±29 (129) <sup>B</sup>	189±69 (212) <sup>e</sup>
Re-wetted fen, (Calcare-Sapric Histosol); 48°28'59.15" N, 10°11'51.92" E; land use: nature protection area since 1972 Vegetation: <i>Calliargon cordifolium</i> (Hedw.) Kindb.; <i>Carex acuta</i> L., <i>Carex rostrata</i> Stokes, <i>Equisetum palustre</i> , <i>Typha latifolia</i> (<10%)										
5–15	0.17	H9	57	398	31	91	107±89 (53) <sup>c,b,f</sup>	72±87 (53) <sup>A</sup>	41±21 (80) <sup>D</sup>	193±72 (116) <sup>d,e</sup>
15–25	0.20	H9	56	414	33	94	90±53 (65) <sup>b,e,g</sup>	46±53 (65) <sup>A,B</sup>	50±24 (121) <sup>D</sup>	222±88 (201) <sup>c,d</sup>
35–45	0.21	H7	47	407	32	97	81±53 (55) <sup>a,b</sup>	46±26 (55) <sup>A,B</sup>	52±34 (117) <sup>D</sup>	249±79 (188) <sup>a,b</sup>
55–65	0.16	H7	51	498	27	100	73±51 (57) <sup>a</sup>	37±52 (57) <sup>B</sup>	55±41 (126) <sup>D</sup>	231±66 (208) <sup>b,c</sup>

H humification index (according to von Post), \*calcareous horizon (Kalkmulde), \*\*silty horizon (Schluffmulde), \*\*\*gravel aquifer

to separate DOC and POC according to whether the particles are truly colloidal and suspended – though it is probably not possible to define an exact size for that. Currently, DOC is often considered as truly colloidal and POC as strictly suspended, which is not the case. Studies also defined different upper limit for the size of POC, e.g. Chow et al. (2005) proposed 1.2  $\mu\text{m}$  and Michalzik and Stadler (2005) used 2 mm as an upper limit. An upper limit is needed to separate POM from crushed peat material since POM does not have to be suspended in water. Separating the terms of POM in water (measured in suspended form) from “dry” POM (measured in dried form) or differentiating the water collection (pore water in situ or extraction of soil in the laboratory) would be helpful as well. Most studies dealing with POC in soils extract the POC fraction from the bulk soil on the basis of particle size separation, by extraction, density flotation or sieving (Oades and Waters, 1991; Nordén et al., 1992; Chow et al., 2005). To study the temporal dynamics of suspended POM it is indispensable to perform in situ measurements.

Up to date most studies on carbon concentrations in pore waters of Histosols have concentrated on DOC and DIC (Billett et al., 2004; Worrall et al., 2005; Fiedler et al., 2006) and POC seems to be a forgotten component. However, studies of POC in aquatic systems highlight peatlands as a major POC source to the adjacent aquatic systems (Bouchard, 2007; Dawson et al., 2004; Laudon et al., 2004). It is known that significant amounts of POC moving from peatlands are derived from the erosion of exposed peat (Pawson et al., 2008). However, less disturbed wet ecosystems can lose a significant fraction of the net carbon uptake via leaching (Neal and Hill, 1994; Waddington and Roulet, 1997; Pastor

et al., 2003; Worrall et al., 2003). It is not known how much C is leached as POC via this pathway.

Therefore, the importance of POM is potentially being underestimated but there is no study that allows an estimation of the relative importance of the individual C components in the soil pore water of Histosols. It can be assumed that POC is an important component of the pore waters of Histosols, as it must originate from there, i.e. moving from the peat to the pore water and then to the stream water. Consequently, the objective of this study was to evaluate the temporal and spatial patterns of the individual C components (POC, DOC, DIC and dissolved CH<sub>4</sub>) in the pore water profiles of a fen throughout the year along a gradient of water management to achieve some insights into the relative importance of POM compared to the other C fractions.

## 2 Material and methods

### 2.1 Environmental settings

The study site is located in the Donaured fen area near Ulm, Germany. The Donaured area extends over 472 km<sup>2</sup> and includes the largest coherent peatland area (30 km<sup>2</sup>) in southern Germany. The peatland is fed by productive karst springs (1100–8800 l s<sup>-1</sup>) originating from the neighboring Swabian Alb (Geyer and Gwinner, 1986). The mean annual air temperature of the study area is 7.7°C, and the mean annual precipitation is 744 mm.

The historical peat layer, which was approximately 7 m thick, has gradually diminished due to anthropogenic interventions over the last 200 years, i.e. lowering of the groundwater level and direct peat removal. Between 1951 and 1990, the average loss of peat was  $7.2 \text{ mm a}^{-1}$  (Flinsbach et al., 1997) which is equivalent to  $5.67 \text{ t C ha}^{-1} \text{ a}^{-1}$ . In 1966, certain areas within the peatland were established as protected areas. Since 1984, an area of approximately  $0.5 \text{ km}^2$  has been flooded by regulating water inflow and outflow ( $11\text{--}24 \text{ l s}^{-1}$ ). For this study, three anthropogenically affected peatlands (previously used as peat cuts) were investigated (Table 1):

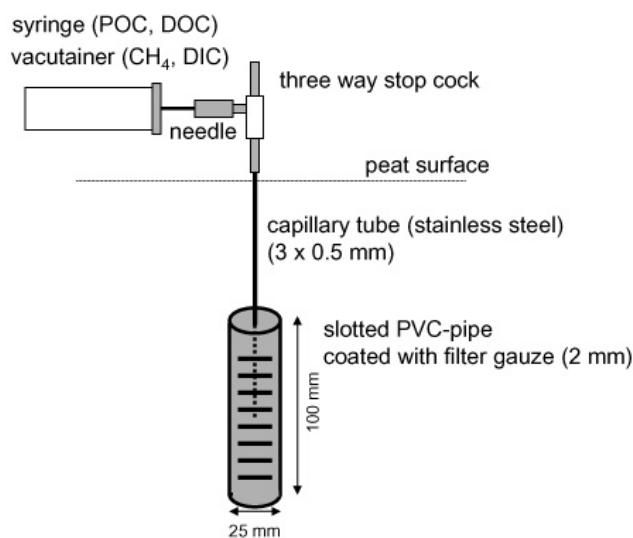
1. a deeply drained fen site ( $48^\circ 29' 7.48'' \text{ N}$ ,  $10^\circ 11' 29.03'' \text{ E}$ ) with a mean groundwater level (GWL) of  $-99 \pm 37 \text{ cm}$ ,
2. a moderately drained fen site ( $48^\circ 28' 59.63'' \text{ N}$ ,  $10^\circ 12' 19.50'' \text{ E}$ ) with a mean GWL of  $-22 \pm 16 \text{ cm}$ , and
3. a long-term re-wetted fen site ( $48^\circ 28' 59.15'' \text{ N}$ ,  $10^\circ 11' 51.92'' \text{ E}$ ), re-wetted for  $\sim 20$  years, with a mean GWL of  $-5 \pm 12 \text{ cm}$  (Höll, 2007).

The areas can be differentiated by their respective plant communities resulting from the long-term differences in water supply of the peatland. While mainly *Typha spec.*, *Carex spec.* and *Equisetum spec.* were found on the re-wetted fen, the plant community of the deeply and moderately drained areas were characterised by meadow species (*Lolium perenne* L, *Poa pratensis* and *Festuca ovina*, *Bromus erectus*).

## 2.2 Sampling

Sampling of freely drained pore water was carried out at either weekly (DOC, DIC,  $\text{CH}_4$ ) or biweekly (POC) intervals between April 2004 and April 2006. Samples were collected at different depths (from 10 to 150 cm, Table 1) at the respective sites using slotted PVC wells (3 replicates per depth). Whenever the given soil depth was below groundwater level, pore water could be collected. The PVC well (Stockmann, Warendorf, Germany) (Fig. 1) was sealed at both ends and coated with filter gauze ( $>2 \text{ mm}$ ) in order to prevent coarse particles ( $>2 \text{ mm}$ ) from entering. A stainless steel capillary ( $3 \times 0.5 \text{ mm}$ , Hero, Berlin, Germany) was inserted via the top of the centre of the tube. The end of the capillary was closed using a three-way stop-cock (Fleischhacker, Schwerte, Germany).

The pore-water samplers were inserted to pre-defined depths using a stab drill. The hollow space above the well was filled with a mixture of peat and coarse sand. Samples for the determination of DIC and dissolved  $\text{CH}_4$ , were collected using a three-way stop-cock and evacuated  $\text{N}_2$ -rinsed vacutainer (22.5 ml; Altmann-Analysentechnik,



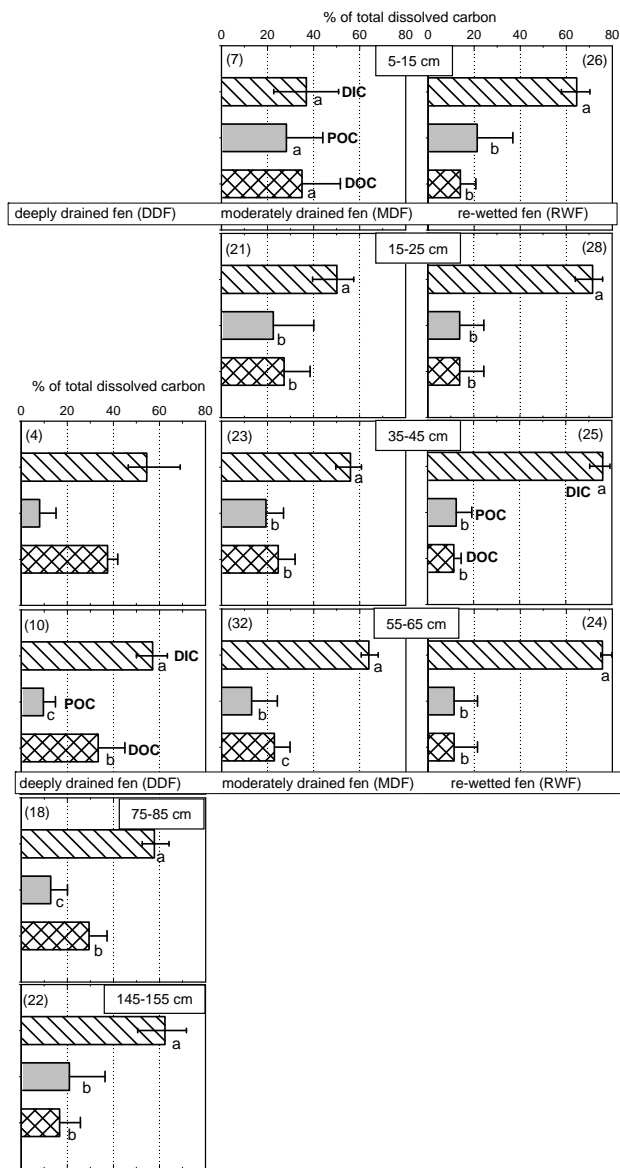
**Fig. 1.** Scheme of in situ pore water sampling device. Water samples were drawn by vacutainer (DIC,  $\text{CH}_4$ ) or syringe (POC, DOC) connected to the stop cock.

Holzkirchen, Germany). This technique is specific for the sampling of freely-drained pore water under water-saturated conditions. The carbonates were converted to  $\text{CO}_2$  by the injection of  $0.5 \text{ ml H}_2\text{SO}_4$  (10%) into the vacutainer being half filled with sample solution.

Pore water was removed with a syringe (Omnifix, 50 ml, VWR, Bruchsal, Germany) in order to determine TOC and DOC. On return to the laboratory, samples for obtaining TOC and DOC were shaken and half of these samples were filtered ( $0.45 \mu\text{m}$  pore size, PET45/25, Macherey-Nagel, Düren, Germany) to determine DOC. Samples were stored at  $4^\circ\text{C}$  and analyzed the next day. POC was calculated as the difference between TOC and DOC. Total carbon (TC) in the pore water was calculated as sum of POC, DOC, DIC, and  $\text{CH}_4$ . Samples for the determination of microbial colonization of POM particles were taken twice in autumn 2006 at the moderately drained fen (MDF) at depths of 20, 40 and 60 cm.

Additionally, samples were collected for analysis of size distribution of POM (July, August and November 2006) at the moderately drained fen and re-wetted fen at depths of between 10 and 60 cm.

Samples for analysis of  $\delta^{13}\text{C}$  ( $\text{CO}_2$  of soil atmosphere, DIC of pore water) were collected once in April 2005. The soil atmosphere samples for determining  $\delta^{13}\text{C}\text{-CO}_2$  of unsaturated soil pores (gaseous phase) originated from depths of 5, 10, 20, 40, 60, and 80 cm at the respective sites using evacuated vacutainers (for more details see Höll, 2007). The pore water for determining  $\delta^{13}\text{C}\text{-DIC}$  was collected from depths of 10, 20, 40, 60, and 80 cm. For samples from the karst aquifer we were allowed to use the wells of the local water supply company (Zweckverband Landeswasserversorgung). Samples of open aquatic systems were taken at a nearby river,



**Fig. 2.** Relative contribution of each C-component [%] with regard to the overall annual dissolved C content (numbers in brackets are numbers of measurements). Statistically significant differences between C-components are indicated by different letters.

spring and drain outlet (five replicates each at 2 cm below water surface). DIC of all water samples was converted to  $\text{CO}_2$  by acidification with 85%  $\text{H}_3\text{PO}_4$  and stored under  $\text{N}_2$ .

### 2.3 Analyses

$\text{CH}_4$  and DIC as  $\text{CO}_2$  were analyzed in the headspace of the vacutainers by gas chromatography ( $\text{CH}_4$ : Flame Ionization Detector (FID),  $\text{CO}_2$ : Electron Capture Detector (ECD) and FID with methanizer; PE Autosystem XL Gas Chromatograph, Perkin Elmer, Wellesky, MA, USA). External stan-

dards for  $\text{CH}_4$  and  $\text{CO}_2$  were used to calibrate the system at 1, 101, 1024  $\mu\text{l l}^{-1}$   $\text{CH}_4$ ; 293, 14890, 2983  $\mu\text{l l}^{-1}$   $\text{CO}_2$ . Following acidification, no dissociated forms of  $\text{CO}_2$  exist in the water but pure  $\text{CO}_2$ . Consequently, the gas concentration in the water can be calculated, like for  $\text{CH}_4$ , from the determined headspace concentration applying the Bunsen solubility coefficient (Clever and Young, 1986). Original gas content in the water can be calculated from determined concentrations and from known volumes of headspace and water. Applying this method the risk of degassing of supersaturated solutions under ambient conditions is minimized. For more details see Fiedler et al. (2006).

Organic carbon of pore water (with and without filtration) was analyzed using a DIMA-TOC 100 (Dimatec, Essen, Germany). All samples were continuously homogenized by a magnetic stirrer during the measurement. Two external standards for TOC were used to calibrate the system.

The size distribution (0.45  $\mu\text{m}$  to 2000  $\mu\text{m}$ ) of POM particles was measured using a laser diffractometer (Coulter LS200, Fa. Beckmann, Krefeld, Germany). The sum frequency distribution was made on the assumption that all particles were spherical (Coulter Software, version 3.01).

The water samples for straining POC particles were filtered using a 2  $\mu\text{m}$  nylon membrane (Millipore, Germany). Standard fixation and dehydration procedures (Amann et al., 1990) were slightly modified, according to Assmus et al. (1995). Filters were transferred to a fixation buffer (4% paraformaldehyde in PBS) and fixed for 2 h at 28°C. The samples were washed and dehydrated in 50, 80, and 96% ethanol (5 min each). Filters were stained with the DNA-specific dye DAPI (Sigma, Germany). DAPI was stored in a 0.35-mg  $\text{ml}^{-1}$  aqueous stock solution at 4°C. For staining, the stock solution was diluted 500-fold in distilled water and 20 ml of the working solution was applied to each filter. After incubation for 10 min at room temperature, the filters were rinsed with distilled water and air-dried. Afterwards, the filters were transferred to slides and mounted in antifading solution (Johnson et al., 1981). Epifluorescence microscopy was performed with an Axioplan microscope (Zeiss, Germany) supplying an excitation wavelength at 365 nm. In total more than 500 particles were analyzed.

For isotope measurements, samples were injected in gas-tight flasks (volume 1 ml). The  $\delta^{13}\text{C}$ -ratios were determined on a continuous flow isotope ratio mass spectrometer (IRMS), (DELTAplus XP, Thermo Finnigan, Bremen, Germany) which was equipped with a GasBench II for automatically analysing dissolved inorganic carbon (DIC) and gases at the Max Planck Institute for Biogeochemistry (Jena, Germany).

## 2.4 Statistical analyses

Non-parametric analyses were used as the data were not normally distributed (Sharpo-Wilks' W Test) and could not be transformed. The Mann-Whitney (U) Test was used to detect significant ( $\alpha = 1\%$ ) differences between individual sites and depths. Analyses were made using Statistica 6.0 (StatSoft Inc., Tulsa, USA).

## 3 Results

### 3.1 Distribution of carbon components

#### 3.1.1 Spatial pattern

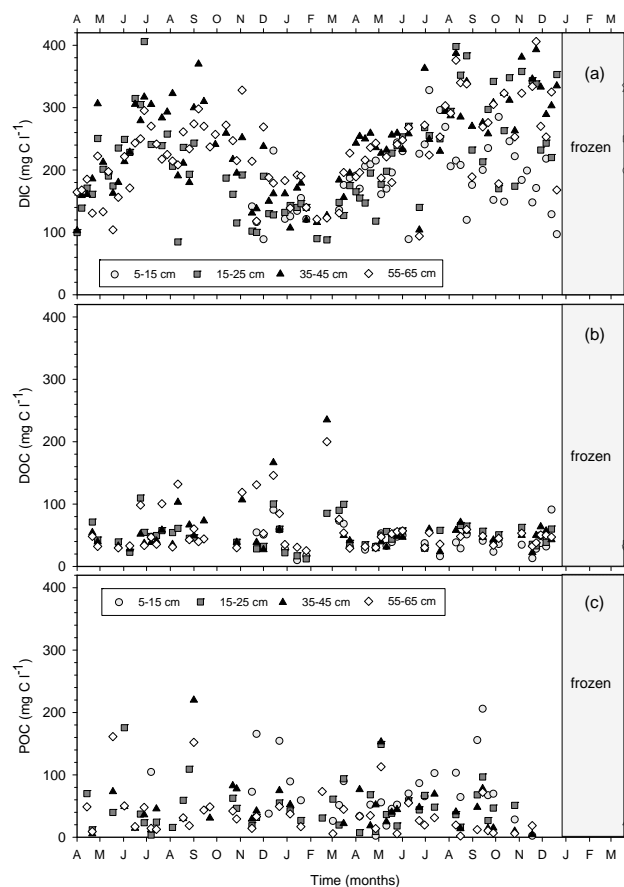
The site-specific position of the groundwater level did not affect the concentrations of total carbon (TC) (around  $300 \text{ mg C l}^{-1}$ ) in pore waters.

The mean POC concentrations ranged from  $14$  to  $125 \text{ mg l}^{-1}$  (Table 1). No statistically significant trends in sites and depths were found. The highest concentrations of POC were systematically found at the depth of the site-specific mean groundwater table (deeply drained  $-150 \text{ cm}$ ,  $125 \text{ mg C l}^{-1}$ ; moderately drained, between  $-20$  and  $-40 \text{ cm}$ ,  $67\text{--}74 \text{ mg C l}^{-1}$ ; re-wetted fen  $-10 \text{ cm}$ ,  $72 \text{ mg C l}^{-1}$ ). The POC fraction of TC varied between 15 and 30% (Fig. 2). Particularly for the re-wetted and moderately drained peatland, the POC proportion was nearly identical to the DOC. The mean DOC to POC ratios of the present study ranged between 0.4 and 2.8.

Dissolved organic carbon concentrations decreased insignificantly with increasing wetness of the site. Mean DOC concentrations were lowest in the re-wetted fen (around  $50 \text{ mg C l}^{-1}$ ), while the mean DOC concentrations in drained areas ranged between  $72$  and  $95 \text{ mg C l}^{-1}$  and were irregularly distributed in depth. For all sites, the most important C component of pore water (up to  $280 \text{ mg C l}^{-1}$ ) was DIC. The DIC proportion increased insignificantly with increasing wetness of the site i.e., deeply drained (50–60%) < moderately drained (up to 70%) < re-wetted fen (75% of TC). DIC concentrations significantly increased with soil depth (Table 1) – in some cases DIC concentrations were twice as high as in the upper horizon ( $189$  vs.  $94 \text{ mg C l}^{-1}$  in moderately drained fen). Dissolved  $\text{CH}_4$  had the lowest concentrations of all C components ( $\sim 0.1\%$  of TC in pore waters). The mean  $\text{CH}_4$  concentrations ranged from  $0.005$  to  $0.006 \text{ mg C l}^{-1}$  (deeply drained fen),  $0.005$  to  $0.196 \text{ mg C l}^{-1}$  (moderately drained fen), and  $0.363$  to  $0.175 \text{ mg C l}^{-1}$  (re-wetted fen), respectively.

#### 3.1.2 Temporal pattern

Neither the total C concentrations nor the individual POC, DOC, and DIC concentrations revealed a statistically significant dependence on soil temperature, precipitation or



**Fig. 3.** Temporal pattern of (a) dissolved inorganic carbon (DIC), (b) dissolved organic carbon (DOC), and (c) particulate organic carbon (POC) of the re-wetted fen of Donauried (Germany) from April 2004 to March 2006.

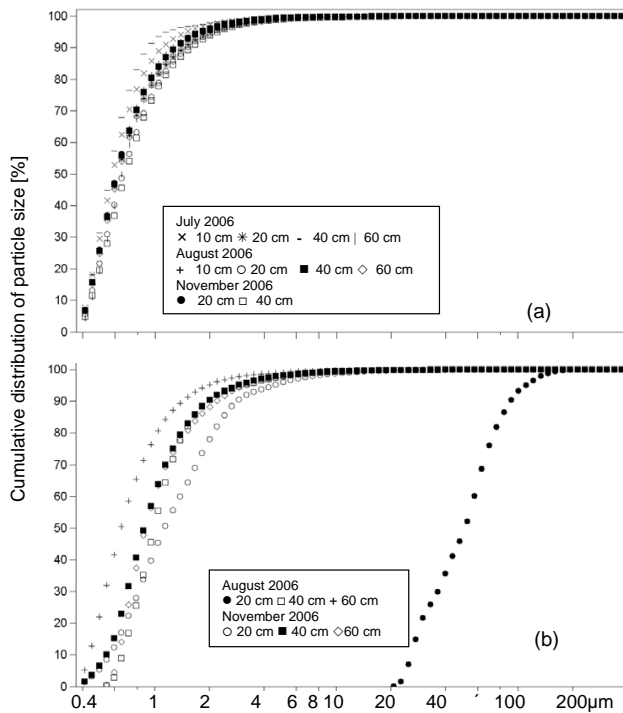
groundwater level. Exemplarily, the dynamics of all C-components over time at the re-wetted fen is illustrated in Fig. 3. A seasonal trend for DIC concentrations is indicated – high values during summer and low during winter – but not statistically significant.

Dependence was particularly expected for the upper soil layers, however, groundwater tables tended to be low when air temperatures were high. Consequently, the number of samples and the temporal coverage of the topsoil levels for higher temperatures were significantly lower than for lower temperatures. Additionally, the temperature amplitude in greater depths with constant water saturation was reduced.

In both years, the rainfall was lower than the long-term mean of  $744 \text{ mm}$  ( $580 \text{ mm}$  from April 2004 to March 2005, and  $685 \text{ mm}$  from April 2005 to March 2006). The lower precipitation in the first study period led to significantly lower groundwater levels compared to the second year (GWL: re-wetted fen  $-9$ , period 2004/2005 vs.  $0 \text{ cm}$ , period 2005/2006); moderately drained fen  $-29$  vs.  $-19 \text{ cm}$ , deeply drained fen  $-125$  vs.  $-75 \text{ cm}$ ). High TC concen-

**Table 2.** Isotopic ratios of dissolved inorganic carbon and CO<sub>2</sub> of gaseous phase (average above all depth, n = sample numbers).

	$\delta^{13}\text{C}$ -ratios [‰]			
	Deeply drained fen	Moderately drained fen	Re-wetted fen	Hydrosphere
Pore water	$-17.9 \pm 0.7 (n=10)$	$-18.4 \pm 0.6 (n=10)$	$-16.7 \pm 0.6 (n=10)$	
Groundwater				$-11.8 \pm 0.2 (n=3)$
Karst groundwater				$-12.4 \pm 0.1 (n=3)$
Karst spring				$-14.3 \pm 0.1 (n=3)$
Drainage ditch				$-16.7 \pm 0.6 (n=10)$
River (Nau) close to fens				$-13.0 \pm 0.8 (n=5)$
Gaseous phase in pores	$-26.2 \pm 1.2 (n=13)$	$-26.6 \pm 0.4 (n=14)$	$-23.9 \pm 1.3 (n=14)$	

**Fig. 4.** Sum curves [cumulative%] of particle size in the POM fraction ( $>0.45 \mu\text{m}$ ) at different managed peatlands of the Donauried (Germany), (a) re-wetted fen, (b) moderately drained fen at distinct sampling depths and times.

trations were measured in both years ( $300 \text{ mg C l}^{-1}$ ). In the re-wetted fen, mean POC concentrations were mostly around  $50 \text{ mg C l}^{-1}$ , with the exception at 10 cm depth, where mean concentrations ranged between  $75 \text{ mg C l}^{-1}$  (wetter period) and  $105 \text{ mg C l}^{-1}$  (drier period). Lower mean POC concentrations in the wetter period than in the drier period were also found in all depths of the moderately drained fen ( $37$  to  $73 \text{ mg C l}^{-1}$ , period 2005/2006 vs.  $56$  to  $114 \text{ mg C l}^{-1}$ , period 2004/2005). However, in the deeply drained fen, higher POC concentrations were found in the drier than in the wetter period (except at 150 cm depth).

The inter-annual variation for DOC concentrations was similar to POC. In the wetter period, higher DOC concentrations were found in the deeply drained fen (except at 150 cm depth), while lower concentrations were observed in the moderately drained ( $66$  to  $87 \text{ mg C l}^{-1}$ , period 2005/2006 vs.  $81$  to  $92 \text{ mg C l}^{-1}$ , period 2004/2005) and rewetted fen ( $37$  to  $49 \text{ mg C l}^{-1}$  vs.  $52$  to  $64 \text{ mg C l}^{-1}$ ). In the wetter year, the proportion of DIC of TC in the pore water was higher (51–79%) at all sites and depths than in the drier year (26 to 73%).

The  $\delta^{13}\text{C}$  values of DIC ranged between  $-16.7 \pm 0.6$  and  $-18.4 \pm 0.6$ ‰, and were lower than those in the aquatic system (karst spring  $-14.3 \pm 0.1$ ‰, surface water  $-11.7$  to  $-13.0 \pm 0.8$ ‰), but higher than those of the CO<sub>2</sub> of the gaseous phase in pores ( $-23.9 \pm 1.3$  to  $-26.6 \pm 0.4$ ‰) (Table 2).

### 3.2 Characterization of particulate organic matter

The particle size distribution of POM at the re-wetted fen was rather uniform regardless of sampling depth or time (Fig. 4a). In the re-wetted fen, 75–95% of all particles were smaller than  $1 \mu\text{m}$ . The moderately drained fen had larger particles (see Fig. 4b, 60–100%  $>1 \mu\text{m}$ ) than the re-wetted fen. In particular the rewetting of the area after a longer dry period (see Fig. 4b, 20 cm, August) led to the presence of very large particles of  $>20 \mu\text{m}$  (100%) in the pore waters.

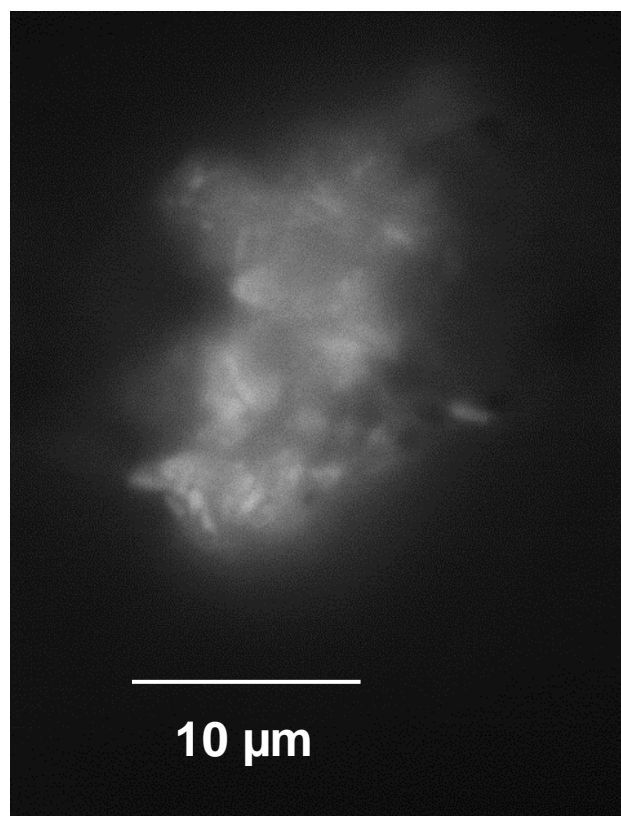
Staining the POM particles with DAPI, followed by analysis with an epifluorescence microscope, revealed that about 30% of the particles  $>1 \mu\text{m}$  were colonized by microbes. Interestingly, most cells were rod shaped and formed microcolonies up to 10 cells. Filamentous microbes were not observed, indicating that fungi play a minor role in colonizing POM particles. An example of a colonized POM particle is given in Fig. 5.

## 4 Discussion

### 4.1 Particulate organic matter and dissolved organic matter – twin components

The mean DOC concentrations of the investigated peat sites exhibit concentrations that are in the same range of published data for drained (81 to 129 mg l<sup>-1</sup>; Moore and Clarkson, 2007) and rewetted peatlands (70–100 mg l<sup>-1</sup>; Glatzel et al., 2003). Because of a lack of data from other peat pore waters, we can not compare our data with POC data from other peatlands. Consequently more studies on POC in peat pore waters are urgently needed. This study suggested a similar importance of POC as DOC on a quantitative basis. Furthermore we suggest a global agreement on defining DOM < 0.45 μm and POM > 0.45 μm (Zsolnay, 2003), which would guarantee the highest number of direct comparison of the data between DOC studies for the future. Our study demonstrated that the flooding of soil horizons releases large particles. Therefore, we support the upper size limit of 2 mm for POM as defined by Michalzik and Stadler (2005) since an important mobile C fraction would otherwise be discounted in the pore water dynamics of peat.

Both DOM and POM are composed of aggregated colloids, organic filaments, cell fragments, and microbial biomass (e.g., algae and bacteria) (Ranville and Schmiermund, 1998). POM may form from the aggregation of DOM (Kerner et al., 2003). The preferential presence of large particles (>20 μm) after re-wetting and generally higher POC concentrations in the zone of intensive dry / wet cycles suggest that POM of this study mainly originated from the mechanical ablation of the peat. However, high and relatively constant POC concentrations in the permanently water-saturated areas suggest further mechanisms for the formation of POM. Microbes may play an important role in POM dynamics. Polysaccharide-producing microbes can lead to the formation of particles >2 μm. According to Petry (2004), this can lead to a POC increase of 8–72% in waters. Using a DAPI stain it was possible to detect microbes on the particles. Interestingly, only one third of the particles was colonized by microbes, suggesting differences in substrate quality of the POM. However, DAPI staining does not differentiate between active, inactive or dead cells. It is therefore still unclear if the microbes detected on the POM particles were actively metabolizing and functionally important for POM turnover. Therefore, the activity status of microbes colonizing POM particles and consequently the significance of bacteria fungi and Archaea for the stability of POM has to be investigated in further experiments using molecular tools.



**Fig. 5.** DAPI staining POC particle (>0.45 μm) from water sample collected from moderately drained fen collected in 40 cm below surface. The photo shows a microcolony of about 5–10 cells on particle.

### 4.2 Dissolved inorganic carbon – the largest component of total carbon

DIC was the largest C component of the investigated pore waters. The high DIC concentrations resulted from a surplus of CO<sub>2</sub> derived from the karst waters (geogenic carbon) which flow into the area, and the accumulation of biogenic CO<sub>2</sub>. The distribution of δ<sup>13</sup>C values shows the expected distinct variations among the samples. The δ<sup>13</sup>C values determined for CO<sub>2</sub> in the gaseous phase (from –23.0 to –25.1‰) in the Histosols were close to the isotopic signature of decomposed C-3 vegetation in soils (–25‰) (Deines, 1980). Signatures of the different samples of the aquatic systems were comparable to those reported from other aquatic systems, including streams (–13.7‰), springs (–14.2‰), groundwater (–13.7‰), karst groundwater (–10 to –12‰) and soil water (–16.3‰) (Pan et al., 2002; Marfia et al., 2004; Li et al., 2008). The δ<sup>13</sup>C values for DIC of the pore waters (–16.7 to –18.4‰) were lower than values of an aquatic system and higher than CO<sub>2</sub> of the gaseous phase of pore space (up to –26.6±0.4‰). This reveals that the DIC of the pore waters in our site does not exclusively originate from

accumulated CO<sub>2</sub> of *in situ* microbial activity but also from the karst water flowing into the fen. Unfortunately, it is not possible to separate this mixed signal into the two sources, since we neither know the production rates of CO<sub>2</sub> in the soils, nor could we determine the proportion of the karst water that actually reaches the measurement plots. The mean DIC concentrations (94–280 mg C l<sup>-1</sup>) of the pore waters investigated were higher than concentrations found in soil solutions of other studies (30–113 mg C l<sup>-1</sup>, Marfia et al., 2004; Sigfusson et al., 2006). However, it is difficult to compare the result with others using different methods because over-saturated CO<sub>2</sub> is easily lost during sampling and measurement (Fiedler et al., 2006). In this study, the highest DIC concentrations were observed in the re-wetted fen in the permanently water-saturated horizons. We attribute a significant proportion of the DIC to the use of DIC-rich karst water for re-wetting as DIC in the re-wetted fen showed the highest δ<sup>13</sup>C values (−16.7±0.6‰).

#### 4.3 Methane – the smallest and most dynamic component

Dissolved CH<sub>4</sub> exhibited the lowest concentrations of all C components at around 0.1% of TC in pore waters. Nevertheless, the values represent super-saturation of CH<sub>4</sub> of up to 100 000 fold compared to atmospheric equilibrium concentration. Methane levels might not be important for sub-surface C-budgets, but CH<sub>4</sub> concentrations are highly variable in time and space. Fiedler et al. (2005) reported CH<sub>4</sub> concentrations in pore water of hydric soils of up to 1.8 mg C l<sup>-1</sup>. Consequently, CH<sub>4</sub> must be considered for the understanding of C turnover in peat soils. Small CH<sub>4</sub> pools in the soil solution measured synchronously to net CH<sub>4</sub> emissions at the soil surface (data not shown) also point to fast escape from the production zone to the atmosphere or indicate high turnover rates. The level of CH<sub>4</sub> released to the atmosphere was extremely high at the wet site with more than 70 g CH<sub>4</sub>-C m<sup>-2</sup> a<sup>-1</sup>, (Freibauer et al., in prep.) although the small CH<sub>4</sub> pool was no indicator of that. This confirms the hypothesis of fast escape, which is triggered as well by the aerenchymous leaves of the dominating *Typha* and *Carex* species as chimneys for CH<sub>4</sub>.

## 5 Conclusion

For this study, POC and DOC were equally relevant for the pore water carbon composition. Independent of water management, the POC fraction reached means of up to 30% of TC while DOC had means of up to 35% of TC in pore waters. Our results suggest that POC need to be studied together with DOC to better understand their ecological function in peat ecosystem. From a quantitative point of view, the results suggest that POC is an important C fraction in the pore water of organic soils. However, the POC fraction remains an unknown entity. It is only certain that POM particles were

colonized by microbes and therefore it is highly likely that it is part of the active carbon pool involved in current carbon turnover. Hence, the ultimate fate of POM in pore waters of Histosols demands greater consideration when calculating C budgets, particularly the extent to which POM is exported to aquatic systems, or undergoes degradation and returns to the atmospheric C pool.

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