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## Discharge determines production of, decomposition of and quality changes in dissolved organic carbon in pre-dams of drinking water reservoirs



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#### HIGHLIGHTS

#### GRAPHICAL ABSTRACT

- A proportion of 0–30% of the total gained OC was produced within the pre-dams.
- Ratio of OC production to total OC gain was negatively related to discharge.
- Proportion of algae-derived DOC ( $\beta/\alpha$  index) decreased with higher discharges.
- Heterotrophic bacteria utilized older DOC under base flow conditions.



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#### ABSTRACT

Pre-dams are small reservoirs constructed upstream of the main drinking water reservoirs and are used for nutrient removal and sediment trapping. Little is known about the role of pre-dams regarding the production and decomposition of dissolved organic carbon (DOC) in relation to discharge and how this affects the quality of DOC in the water. We combined quantitative and qualitative investigations under different hydrological conditions at three pre-dams exhibiting a gradient from oligotrophic/high-DOC to eutrophic/low-DOC. All pre-dams were mainly autotrophic in their upper water layers. The ratio of OC production to total gained OC (i.e. OC import + OC production) decreased with increasing discharge. On average, 0-30% of the total gained OC was produced within the pre-dams. The amount of microbially decomposed DOC increased with the average water residence time (WRT) and with the trophic status of the pre-dams. Radiocarbon analyses of respired CO<sub>2</sub> revealed that heterotrophic bacteria preferentially utilized old DOC components (195–395 years before present) under base flow conditions, whereas younger components (modern, i.e. OC produced after 1950) were utilized at high discharge. DOC quality changed significantly over the year within the pre-dams: High proportions of algae-derived DOC were observed during base flow in summer, and the freshness index ( $\beta/\alpha$  ratio) decreased significantly with higher discharges. DOC production and quality changes in response to hydrological conditions

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should be considered for future water quality management in reservoirs, as climate scenarios for temperate regions predict decreased runoffs leading to longer WRT and increased eutrophication and production of algaederived OC.

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#### 1. Introduction

The majority of organic carbon (OC) in inland waters is in dissolved form (Wetzel, 2001) and originates from external (i.e. allochthonous; Aitkenhead-Peterson et al., 2003) and internal (i.e. autochthonous; Bertilsson and Jones, 2003) sources. Over the last few decades, concentrations of dissolved organic carbon (DOC) have been increasing in freshwaters in the northern hemisphere (Evans et al., 2005; Monteith et al., 2007), leading to a browning of inland waters. This increase has been attributed to several causes such as decreased acid deposition (Monteith et al., 2007), increased terrestrial primary production (Freeman et al., 2004; Hagedorn et al., 2008), changes in catchment hydrology (Evans et al., 2005; Schindler et al., 1997), land use changes (Mattsson et al., 2005), and increasing iron concentrations (Kritzberg and Ekström, 2012; Weyhenmeyer et al., 2014) due to the release of formerly adsorbed soil organic compounds by increased reduction of Feoxyhydroxides (Knorr, 2013; Lambert et al., 2013). Elevated DOC concentrations affect the lake ecosystem structure (reviewed by Solomon et al., 2015) at both the abiotic level (e.g. changes in light attenuation and heat balance; Lean, 1998; Zwart et al., 2016) and the biotic level (e.g. planktonic species composition; Jansson et al., 2000), as well as lake metabolism and its biomass production (Ask et al., 2009; Hanson et al., 2003; Karlsson et al., 2015). DOC cycles in freshwaters as it is simultaneously mineralized by heterotrophic bacteria (Eiler et al., 2003; Franke et al., 2013; Tranvik, 1998), produced and released by photosynthetic organisms (Børsheim et al., 2005; Fogg et al., 1965; Larsson and Hagström, 1979) or transformed by chemical pathways such as photoreactions (Bertilsson and Tranvik, 2000; Granéli et al., 1996; Tranvik, 1996). DOC quality in freshwaters is affected by hydrological conditions as well. For instance, old carbon (100 to 1000 of years) is introduced from soils into freshwaters during base flow conditions (Schiff et al., 1997; Trumbore, 2009), while OC derived from recent terrestrial vegetation is often transported during rain events or snow melts (Raymond et al., 2007; Schiff et al., 1997).

Reservoirs alter the DOC load and DOC quality. They can be both sinks and sources of DOC during different times of the year (Kraus et al., 2011). Likewise, reservoirs can be both sources and sinks of CO<sub>2</sub> depending on hydrological conditions, showing reduced CO<sub>2</sub> evasion under low-flow conditions during dry summer periods (Knoll et al., 2013). Parks and Baker (1997) observed that reservoirs in arid regions can be a significant source of autochthonously derived DOC. Nearly one-third of the exported DOC was produced within their studied reservoirs, although these accounted to <1% of the watershed area. In contrast, Romero-Martínez et al. (2013) observed net heterotrophy in the mixed layers of two monomictic Mediterranean reservoirs. Such diverse results underline that lakes and reservoirs are hotspots of carbon cycling (Cole et al., 2007; Tranvik et al., 2009) and indicate the importance of hydrological conditions and lake turnover time for DOC dynamics in inland waters (Dalzell et al., 2007; Köhler et al., 2013; Lambert et al., 2013; Raymond and Saiers, 2010). High DOC concentrations cause problems in drinking water production (Ledesma et al., 2012; Matilainen and Sillanpää, 2010) by increasing the amount of precipitants to remove DOC, shortening filter operation times and forming potentially carcinogenic disinfection by-products (DBP) during the purification treatments (Chow et al., 2003; Jeong et al., 2012; Lavonen et al., 2013; Matilainen et al., 2010).

In Germany, drinking water reservoirs are predominantly constructed in low mountain ranges and are usually built with pre-dams. Predams are small reservoirs constructed upstream of the main reservoirs and have typically low water residence times (WRT) of a few days or weeks. Pre-dams are constructed with a surface overflow similar to natural lakes and are used for sediment trapping and nutrient removal (Benndorf and Pütz, 1987a; Benndorf and Pütz, 1987b; Paul, 2003; Pütz and Benndorf, 1998). Thus, they represent an important tool for reservoir water quality management (Pütz and Benndorf, 1998; Zhang et al., 2011). A high carbon turnover might be expected within predams, as the water is impounded after a short travel time of a few days from the headwaters. However, to our knowledge, a study investigating the role of pre-dams regarding the production and decomposition of OC is missing to date. Hydrological conditions greatly influence the WRT in these systems, and discharge is therefore expected to have a strong impact on OC decomposition and production within and the export from the pre-dams (into the main reservoirs). The upper 3 m of the water column (commonly corresponding to the euphotic zone) is the zone of phytoplankton growth, nutrient cycling and water transport during stratification. Therefore, we focused on the processes taking place within the upper 3 m of the water column of three pre-dams which differed in DOC concentrations and trophic status.

We addressed the following hypotheses: (1) higher trophy (higher P concentrations) and/or low discharge lead to considerably higher amounts of autochthonously produced OC, (2) higher P concentrations and longer WRT within the pre-dams increase the amount of DOC decomposed by heterotrophic microbes, and (3) the proportion of algae-derived DOC to total DOC is negatively related to discharge. Further, we hypothesized that (4) the age of microbially utilized DOC is dependent on discharge conditions, with older carbon preferentially decomposed at low discharge. To investigate these hypotheses, we conducted a combination of quantitative and qualitative investigations such as in-situ oxygen production and consumption measurements, lab incubation experiments, radiocarbon analyses and fluorescence measurements to characterize the production, decomposition and quality of the DOC within the pre-dams.

#### 2. Methods

#### 2.1. Study sites and sampling

All three study pre-dams belong to drinking water reservoirs located in Germany and exhibit a gradient in DOC and phosphorus concentrations (Table 1). The oligotrophic and DOC-rich Rote Mulde pre-dam

#### Table 1

Properties of the three studied pre-dams. Chemical values represent ranges during sampling campaigns in 2013 and 2014.

Pre-dam	Rote Mulde	Rappbode	Hassel
Catchment area [km <sup>2</sup> ]	5.35	39.1	40.5
- Forest [%]	98	72	37
- Grasslands and fields [%]	1	24	58
- Urban areas [%]	1	3	5
Surface area [km <sup>2</sup> ]	0.098	0.218	0.288
Volume [mio m <sup>3</sup> ]	0.06	1.25	1.45
Mean depth [m]	1.8	5.3	5.0
Maximum depth [m]	4	17	14
Water residence time [days]	6	16	27
рН	5.2-6.6	7.1-7.8	6.8-8.9
Total P [µg $L^{-1}$ ]	9.5-33	14-40	22-51
DOC $[mg L^{-1}]$	5.1-21.1	2.4-5.4	4.2-6.9

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