



# Flood-Controlled Excess-Air Formation Favors Aerobic Respiration and Limits Denitrification Activity in Riparian Groundwater

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The saturated riparian zones of rivers act as spatially and temporally variable biogeochemical reactors. This complicates the assessment of biogeochemical transport and transformation processes. During a flood event, excess-air formation, i.e., the inclusion and dissolution of air bubbles into groundwater, can introduce high amounts of dissolved O<sub>2</sub> and thereby affect biogeochemical processes in groundwater. With the help of a field-installed membrane-inlet mass-spectrometer we resolved the effects of flood induced excess-air formation on organic carbon (OC) and nitrogen transformations in groundwater of different riparian zones of a restored section of the River Thur, Switzerland. The results show that the flood event triggered high aerobic respiration activity in the groundwater below a zone densely populated with willow plants. The flood introduced high concentrations of O<sub>2</sub> (230 μmol L<sup>-1</sup>) to the groundwater through the formation of excess air and transported up to ~400 μmol L<sup>-1</sup> OC from the soil/root layer into groundwater during the movement of the water table. A rapid respiration process, quantified via the measurements of O<sub>2</sub>, CO<sub>2</sub>, and noble-gas concentrations, led to fast depletion of the introduced O<sub>2</sub> and OC and to high CO<sub>2</sub> concentration (590 μmol L<sup>-1</sup>) in the groundwater shortly after the flood. The synchronous analysis of different nitrogen species allowed studying the importance of denitrification activity. The results indicate that in the willow zone excess-air formation inhibited denitrification through high O<sub>2</sub> concentration input. Instead, the observed decrease in nitrate concentration (~50 μmol N L<sup>-1</sup>) may be related to fostered nitrate uptake by plants. In the other riparian zones closer to the river, no significant excess-air formation and corresponding respiration activity was observed. Overall, analyzing the dissolved gases in the groundwater significantly contributed to deciphering biogeochemical processes in the riparian aquifer characterized by pronounced changes in the flow regime and by spatial heterogeneity of the vegetation. Measuring excess-air formation helped identifying and explaining the low denitrification activity in a zone with high OC turnover and to quantify OC sources.

**Keywords:** excess air, organic carbon, flood, denitrification, riparian groundwater, spatial and temporal variability

## INTRODUCTION

Rivers play an important role in global nutrient cycles, as they connect terrestrial and marine ecosystems. The saturated zones of stream-riparian interfaces act as important biogeochemical reactors (Baker and Vervier, 2004; Romani et al., 2006). The large spatial and temporal variability in these systems and the technical challenges of performing measurements *in situ* and in real time in the subsurface complicate a sound investigation of biogeochemical transport and transformation processes.

Organic carbon (OC) is of particular interest for river ecosystems as its availability usually limits groundwater heterotrophic activity (Sobczak and Findlay, 2002; Findlay and Sinsabaugh, 2003) and is a major control of oxygen ( $O_2$ ) concentrations. Besides OC infiltrating with the river water, the major OC pools in riparian soils, i.e., roots, carbon-rich lenses, and buried A-horizons, may introduce OC to groundwater (Blazejewski et al., 2009). Mineralization of this OC leads to redox conditions favorable for anaerobic microbial processes, such as denitrification. Subsurface flow paths are known as efficient nitrogen (N) removal zones, particularly through the removal of nitrate ( $NO_3^-$ ) by denitrification (Hinkle et al., 2001; Baker and Vervier, 2004), or plant uptake (Clement et al., 2003). Denitrification in  $NO_3^-$ -rich groundwater is primarily controlled by the redox conditions (suboxic) and the availability of electron donors, e.g., OC (Hill et al., 2000; Baker and Vervier, 2004; Mayer et al., 2010).

Organic carbon turnover and denitrification in a riparian groundwater system can be temporally and spatially highly dynamic. In the framework of an interdisciplinary study in a restored riparian section of the River Thur, Switzerland, pronounced hot spots and moments (McClain et al., 2003) for these biogeochemical processes were identified (Peter et al., 2012a,b). Especially flood events locally intensified OC turnover in the groundwater and impacted N transformation pattern in the riparian soils (Huber et al., 2012; Shrestha et al., 2014). Furthermore, during flood events, significant amounts of air can be delivered to groundwater by the entrapment and dissolution of air bubbles in response to water table fluctuations or groundwater recharge (Mächler et al., 2013). This so called excess-air formation commonly occurs in groundwater and can contribute substantially to the overall input of  $O_2$  and  $N_2$  into groundwater (Heaton, 1981; Williams and Oostrom, 2000; Kipfer et al., 2002; Klump et al., 2007). Thus, a balanced analysis of C and N transformations need to account for the influence of excess-air formation (Mächler et al., 2013). Atmospheric noble gases (He, Ne, Ar, Kr, and Xe) are biogeochemically inert and are therefore excellent tracers to study air/water partitioning and excess-air formation in aquatic systems (e.g., Kipfer et al., 2002). In particular, noble gas measurements enable to reconstruct the amount of introduced excess-air (Pauwels et al., 2000; Mächler et al., 2013), and hence to distinguish between physical and biogeochemical processes influencing gas concentrations in water.

In order to investigate the role of excess-air formation on OC and N transformations in riparian groundwater we compared different functional process zones (Thorpe et al., 2006)

characterized by different riparian vegetation of a restored river corridor of River Thur, Switzerland, during a flood event. In previous studies at this field site, it was shown that the riparian zones and water level changes are important constraints on the distribution and availability of OC and  $NO_3^-$  resulting in spatially and temporally highly variable biogeochemical activities (Huber et al., 2012; Peter et al., 2012a,b; Shrestha et al., 2014). We hypothesized that the formation of excess air in response to the hydraulic condition of the river additionally constrains these biogeochemical processes. Especially respiration processes (both aerobic and anaerobic) are expected to be highly affected by  $O_2$  that becomes available during flood events. We quantified concentrations of DOC and N compounds in the main channel and in the groundwater of the individual riparian zones and compared it to the estimated intrusion of  $O_2$  and  $N_2$  due to excess-air formation in response to changing discharge regime of the River Thur. The  $O_2$  and  $N_2$  injection through excess-air formation were evaluated in a separate study by Mächler et al. (2013). That study used dissolved noble gas concentrations (He, Ar, and Kr) as tracers to quantify the amount of  $N_2$  and  $O_2$  injection due to excess-air formation. In this present study we combine the analysis of excess-air formation by Mächler et al. (2013) with the measurements of DOC and N compounds to assess groundwater biogeochemical processes. We demonstrate how determining dissolved gas concentrations in the groundwater add to decipher spatial and temporal variability of biogeochemical processes within a dynamic riparian groundwater system.

## MATERIALS AND METHODS

### Study Site

The River Thur originates in the limestone formation of the Mount Säntis region (2500 m asl), drains a catchment area of 1700 km<sup>2</sup> on the NE Swiss Plateau, and enters the River Rhine at 345 m asl. The River Thur exhibits the dynamic flow regime of an Alpine river because reservoirs and natural lakes are absent in the catchment. Maximum, mean, and minimum flow rates are 1130, 50, and 2 m<sup>3</sup> s<sup>-1</sup>, respectively, for the recording period of 1904–2000 (Binderheim-Bankay et al., 2000). The River Thur receives high reactive-N loads from diffuse agricultural sources and during dry summer condition substantial input from effluents of waste water treatment plants (Abbaspour et al., 2007). The river was channelized in the 1890s to prevent flooding of the river valley. In the 1970s, a plan to concurrently improve the flood protection and ameliorate the ecological state of the river corridor was elaborated and set into operation. Since the early 1990s, several 1–3 km long river sections were widened to allow alternating gravel bars to develop and to increase hydrological connectivity between the main channel and its riparian zone. Riparian succession processes were stimulated and as a consequence habitat diversity increased (Pasquale et al., 2010).

The study site, instrumented for an interdisciplinary research project on river restoration (Schneider et al., 2011), is located at Niederneunforn (Canton Thurgau, Switzerland) and covers a

2 km long restored river corridor (**Figure 1**). We investigated the biogeochemistry of groundwater along a transect away from the river covering three distinct riparian zones: 1) a bare gravel bank (gravel), 2) exposed gravel, colonized by the tall pioneer grass *Phalaris arundinacea* (grass), and 3) a second flooding terrace dominated by *Salix viminalis* (willow bush). The piezometers penetrated the unconfined aquifer down to 8 m depth (3–7 m screened), allowing water to be collected from the saturated zone (**Figure S1**). The aquifer consists of a deep sandy gravel layer (5–6 m), sealed by an impermeable clay layer at the bottom and covered by a poorly permeable sand and loam layer at the top (Schneider et al., 2011). The piezometer transect does not reflect the subsurface flow direction (**Figure 1**). As a consequence, the individual piezometers and riparian zones are not directly connected by the groundwater flow but the river water feeds directly into the individual zones (Peter et al., 2012b). In general, the restored river stretch is characterized by a good hydraulic and hydrological connectivity between river water and riparian groundwater, being recharged by river infiltration (Vogt et al., 2010). The groundwater below the gravel bar and the grass zone is comprised of infiltrated river water with very short residence time ( $\sim 23$  h travel time). The groundwater in the willow bush zone originates also from river water, but has a considerably longer residence time of  $\sim 4.5$  days (Vogt et al., 2010). Distances from the main channel along the groundwater flow path are  $\sim 20$ ,  $\sim 75$ , and  $\sim 135$  m for the gravel, grass and willow bush zones, respectively.

## Sampling and Sample Preparation

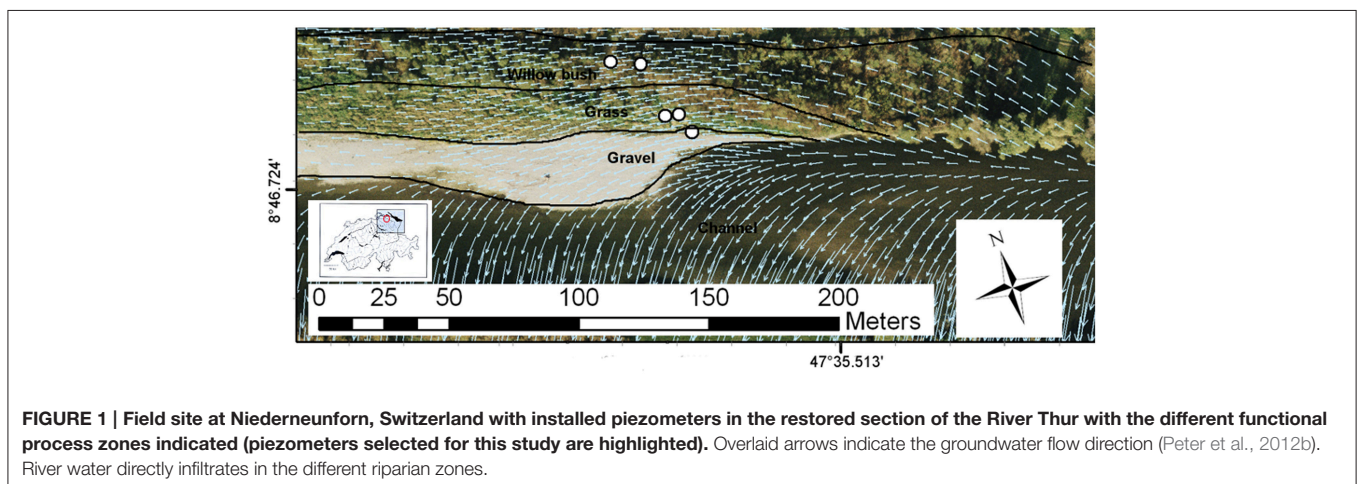
To analyse OC and N dynamics in response to the hydraulic flow/discharge regime of the river Thur a sampling campaign was conducted from 11 May to 24 May 2011 during a small flood event, covering pre-flood, flood, and post-flood conditions (**Figure 2**). Piezometers were sampled in the gravel zone, grass zone upstream and downstream, and willow bush zone upstream and downstream once a day (except for willow bush upstream twice a day) on 11, 13, 15, 16, 17, and 20 May and additionally on 24 May in the willow bush zone (**Figure 1**). Water samples for chemical analyses were collected directly from the river or

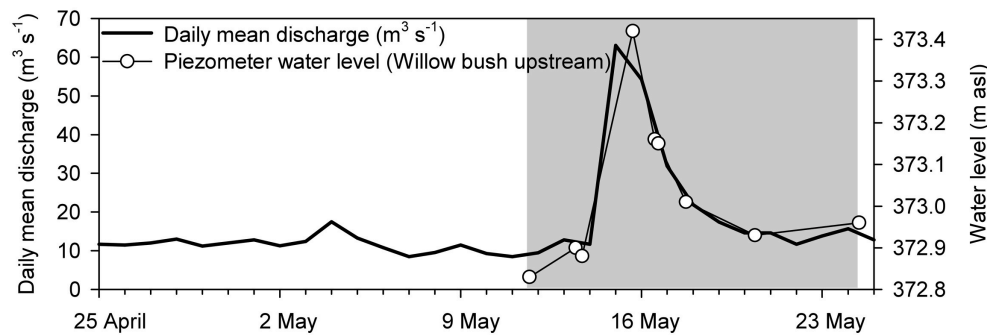
from piezometers using a submersible pump and after having monitored the water to reach stable and constant values for temperature, electrical conductivity, and  $O_2$  concentrations. Water for nitrous oxide ( $N_2O$ ) analysis was filled bubble-free in serum flasks, amended with  $CuCl_2$ , and sealed gas-tight. Cooled water samples were stored in acid-cleaned and combusted glass vials until filtration (GF/F Whatman). Filtered aliquots for DOC concentrations were acidified to pH 3 using  $2 \text{ mol L}^{-1}$  HCl.

## Dissolved Gas Measurements And Excess-air Formation

In the following the results and methodology of the excess air input determinations used for this study and which are published in Mächler et al. (2013) are summarized. The dissolved gas concentrations (He, Ar, Kr,  $O_2$ ,  $N_2$ , and  $CO_2$ ) were measured with a recently developed gas equilibrium membrane-inlet mass spectrometer (GE-MIMS) (Mächler et al., 2012). Daily concentrations were measured by pumping water from the river or the respective piezometers to the GE-MIMS. The acquired noble-gas concentrations allowed to physically describe the partitioning of air and water and thus enabled to quantify the aeration of groundwater due to excess-air formation and to determine the injected concentrations of  $O_2$  and  $N_2$ . The input of  $O_2$  and  $N_2$  due to excess-air formation in response to the flood can be calculated from the accumulating noble-gas concentrations which in contrast to  $O_2$  and  $N_2$  are only subject to physical gas exchange and not reactive and thus ideal to track excess-air formation. For details on the analysis of dissolved gas concentrations and the excess-air model see Mächler et al. (2012) and Mächler et al. (2013), respectively.

The consumption of  $O_2$  during excess-air formation will result in a difference from measured concentrations and concentrations estimated by the excess-air model which can be used to quantify aerobic respiration activity in the groundwater. When assessing denitrification activity,  $N_2$  concentrations need to be corrected for the intrusion of  $N_2$  from excess-air formation. Through this pathway significant amounts of atmospheric  $N_2$  can be delivered to the groundwater. Only the difference ( $\Delta N_2$ ) of the measured  $N_2$  concentrations and the estimated  $N_2$  introduction





**FIGURE 2 |** Daily mean discharge of the River Thur and water level changes in the willow bush zone during the course of the sampling campaign in 2011 (<http://www.hydrodaten.admin.ch/de/2044.html?>). Water level changes in the other zones were highly similar to the ones presented here and ranged from 0.59 to 0.68 m. The gray area indicates the monitoring period from 11 to 24 May 2011. The peak of the flood event occurred on 15 May 2011.

through excess air and from river advection indicates microbial production through denitrification. The calculations, however, showed that  $N_2$  formation resulting from denitrification ( $\Delta N_2$ ) was within the analytical error (3% of total  $N_2$  concentration,  $30\text{--}40\ \mu\text{mol N L}^{-1}$ ) and that the measured  $N_2$  concentrations can be fully explained ( $100 \pm 1.7\%$ ) by excess-air formation and the prevailing air saturated water concentrations (Mächler et al., 2012, 2013).

## Chemical Analyses

DOC concentrations were measured by using high-temperature catalytic oxidation on a Shimadzu TOC analyzer (TOC-V CPH) (Benner and Strom, 1993). The accuracy of the analysis was 1.5% and the detection limit  $80\ \mu\text{mol C L}^{-1}$ . Nitrate, nitrite ( $\text{NO}_2^-$ ) and ammonium ( $\text{NH}_4^+$ ) were determined colorimetrically on a Technicon autosampler (Dev, 2004). The analytical errors were 2.5% for  $\text{NO}_2^-$ , and 6% for  $\text{NO}_3^-$ . Dissolved  $N_2O$  was quantified by headspace analysis on a Trace GC Ultra (Thermo Scientific) fitted with electron capture detector and Supel-Q PLOT column (Sigma-Aldrich).  $N_2O$  concentrations in the samples were calculated according to Weiss and Price (1980) accounting for the non-ideal gas behavior of  $N_2O$ . The analytical error was 0.2–4.6%.

## RESULTS

### Hydrological Conditions

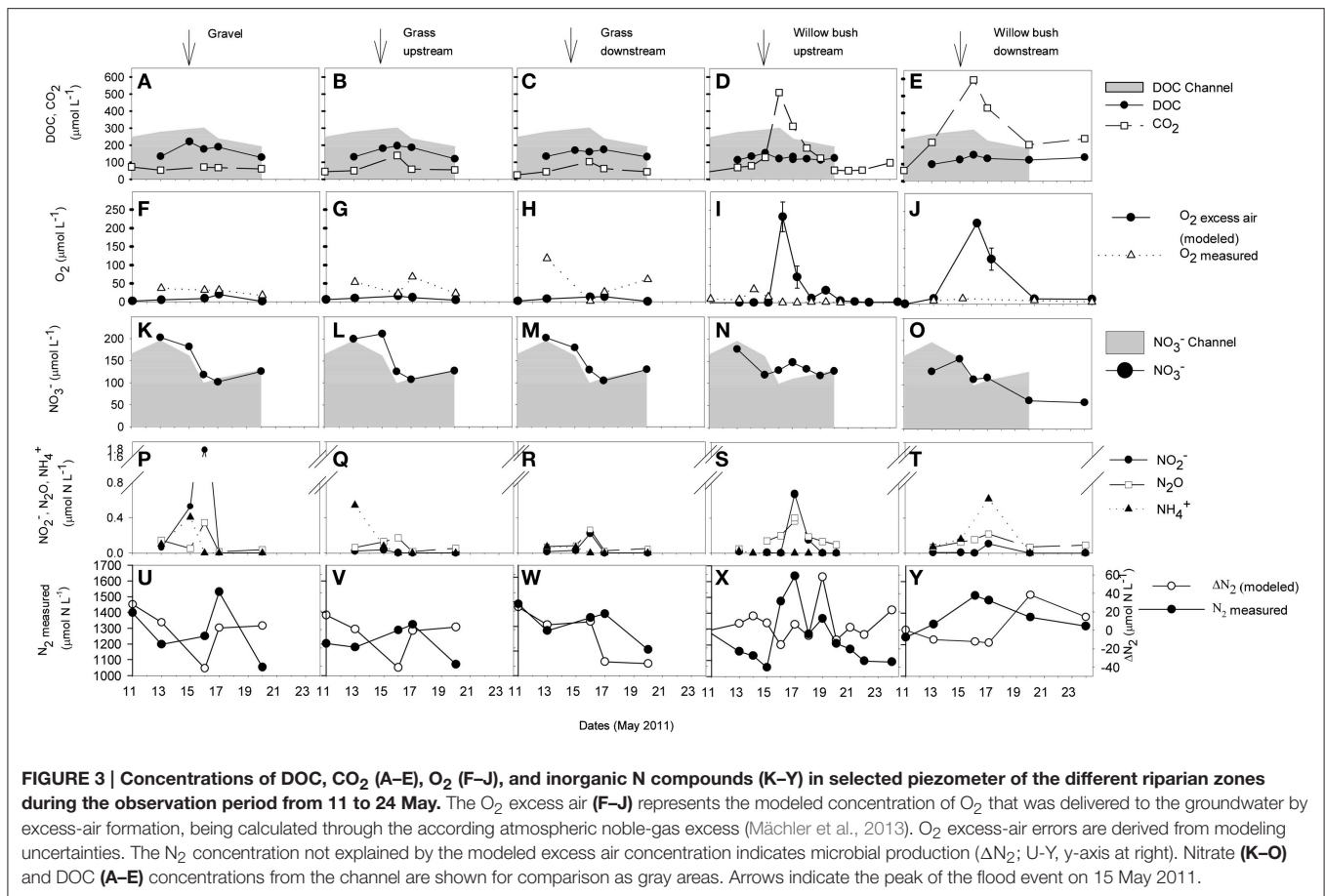
The field campaign started in May 2011 after a dry period of several weeks and covered a small flood event (Figure 2). At the start of sampling, the discharge of River Thur was below  $10\ \text{m}^3\ \text{s}^{-1}$ . On 15 May 2011, in response to a small flood event discharge increased to ( $100\ \text{m}^3\ \text{s}^{-1}$ ) and forced the water table in the riparian aquifer to rise (Figure 2). The fast response of groundwater table increase even far away from the river reflected the high hydraulic conductivity at this field site (Vogt et al., 2010). During peak flood, the gravel zone was flooded whereas the groundwater table in the grass and the willow zones remained below the soil surface. Within 3 days after the peak flow discharge rapidly decreased to  $20\ \text{m}^3\ \text{s}^{-1}$ .

### DOC, $O_2$ , and $CO_2$ Dynamics for Different Riparian Zones

DOC concentrations generally decreased with distance from the River Thur. During the period of the elevated water table on 15 to 16 May 2011 a small increase of DOC concentrations occurred in the channel and weak maxima were also observed in the aquifer (Figure 3).  $CO_2$  concentrations in the channel were in the range of  $13\text{--}40\ \mu\text{mol L}^{-1}$  and were slightly elevated in the gravel and grass zones (Figure 3). In the willow bush zone, during river base flow,  $CO_2$  concentrations were about  $30\text{--}200\ \mu\text{mol L}^{-1}$  and increased substantially during the flood event ( $510\text{--}590\ \mu\text{mol L}^{-1}$ ).  $O_2$  in the river water was usually close to saturation ( $350\text{--}500\ \mu\text{mol L}^{-1}$ ). In the gravel zone, measured  $O_2$  concentrations were higher compared to the other zones and were more variable in the grass zone (Figure 3). In the willow bush zone,  $O_2$  concentrations were generally low ( $<50\ \mu\text{mol L}^{-1}$ ). The calculated  $O_2$  input concentrations from excess-air formation differed markedly from the measured  $O_2$  concentrations during the flood event (Figure 3). Especially in the willow bush zone high amounts of  $O_2$  ( $220\text{--}230\ \mu\text{mol L}^{-1}$ ) were temporary delivered to the groundwater by excess-air formation.

### Nitrogen Dynamics For Different Riparian Zones

In the channel,  $\text{NO}_3^-$  concentrations decreased shortly after the flood (Figure 3), and concurrently,  $\text{NH}_4^+$  and  $\text{NO}_2^-$  concentrations increased (from  $1$  to  $9\ \mu\text{mol L}^{-1}$  and from  $2$  to  $3\ \mu\text{mol L}^{-1}$ , respectively, not shown). The  $N_2O$  concentration in the channel stayed low ( $<0.04\ \mu\text{mol L}^{-1}$ ) during the entire sampling period. In the gravel and grass zones close to the channel,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ , and  $\text{NH}_4^+$  concentrations were similar to the concentrations in the river and shared a similar dynamics. Increasing  $N_2O$  concentration were observed shortly after the flood. In the willow bush zone, the two sampled piezometers differed in  $\text{NO}_3^-$  concentrations. During pre-flood conditions, the concentration in the more downstream piezometer was lower than in the upstream piezometer and the channel and decreased after the flood event to a low level until the end of the sampling



campaign. However, in both locations, elevated concentrations of  $NH_4^+$ ,  $N_2O$ , and  $NO_2^-$  were observed 2 days after the peak flood. Most of the observed  $N_2$  increase in the groundwater of all zones during the flood was related to physical excess-air formation (Figure 3).  $\Delta N_2$  surplus concentration, e.g.,  $N_2$  that is not introduced in the groundwater by physical air/water partitioning and is the result of biological production was hardly detectable with the given experimental precision (<3% of the total  $N_2$  concentration).

## DISCUSSION

### Aerobic Respiration in the Riparian Groundwater During and After a Flood Event

The riparian groundwater at the restored section of the River Thur exhibits a strong spatial and temporal variability in the transport and transformation of DOC (Peter et al., 2012a). The willow bush zone is known to be a pronounced hot spot for microbial activity fuelled by labile DOC from the overlying root and soil layer. Especially during flood events, high amounts of DOC are introduced into the groundwater. In this study, we therefore aimed at investigating in more detail the effect of a flood event and potential excess-air formation on DOC mineralization

in different riparian zones and coupling our work to groundwater aeration in response to hydraulic changes (see Mächler et al., 2013).

As documented in Mächler et al. (2013), the amount of excess air formed by the studied flood varied significantly among the riparian zones. Only in the willow bush zone significant excess-air formation was observed. The O<sub>2</sub> input due to excess air in this zone was found to be of the same order of magnitude as O<sub>2</sub> input from the advection of river water into groundwater. In sharp contrast to the willow bush zone the excess-air formation in response to the flood was found to be very low in the gravel and grass zones. The clear zonation of the results suggest that the input of O<sub>2</sub> into groundwater as a result of excess-air formation is controlled not only by the hydraulic conditions prevailing in the river and the groundwater, but also by geomorphological factors, like the thickness of the confining bed, which was different in the willow zone than in the other riparian zones. The gravel aquifer is too coarse to trap a significant amount of air during the water level rise whereas the confining clay layer hinders the escape of air from the subsoil to the surface, and hence is likely to be a key factor controlling the trapping and dissolution of air in groundwater. Root growth of the willows might influence soil structures, e.g., pore space, which may be an additional factor influencing excess-air formation in this riparian zone.

Following DOC, O<sub>2</sub> (both measured and modeled as excess air input), and CO<sub>2</sub> concentrations in different riparian zones during and after the small flood event resolved in detail the distribution of relevant compounds that drive biogeochemical processes (**Figure 3**). In the aquifer adjacent to the channel, respiration of riparian organic matter immediately reduced O<sub>2</sub> concentrations about 70–90% and stoichiometrically equally elevated CO<sub>2</sub> levels compared to the open channel. River water can supply plenty of labile OC to riparian groundwater and stimulate microbial activity (Fischer et al., 2005; Romani et al., 2006). In the willow bush zone, during the flood event CO<sub>2</sub> concentrations were substantially above the concentrations found in the gravel and grass zones, indicating a hot spot of microbial respiration. Also during the flood event, substantial amounts of O<sub>2</sub> (~250 μmol L<sup>-1</sup>) were introduced into the willow bush groundwater by excess-air formation (**Figure 3**). This surplus O<sub>2</sub> from hydraulically induced local air/water partitioning appears to be suddenly consumed by stimulated respiration activity, as elevated O<sub>2</sub> concentration was not directly measurable in the groundwater. This locally injected and consumed O<sub>2</sub> can explain a large fraction (~90%) of the CO<sub>2</sub> being generated in response to the flood [**Figure 3**, see also Mächler et al. (2013)].

In a previous study in 2008 at the same field site, increased microbial enzymatic activity and secondary production were documented in the willow bush zone during flood events (Peter et al., 2012a). Based on those data, respiration rates were determined to be 0.18 μmol C L<sup>-1</sup> h<sup>-1</sup> in the willow bushes zone during flood events (Del Giorgio and Cole, 1998). We used the approach by Peter et al. (2012b) and the therein given groundwater discharge values from the same field site to calculate the respiration rate along the whole flow path in the willow bush zone, e.g., from the recharge area to the point of sampling. This yields a respiration rate of 8.1 μmol C h<sup>-1</sup> for the willow bush zone. Hence, the elevated CO<sub>2</sub> concentrations would be produced within 2.7 days at this calculated constant mineralization rate. As the water residence time is considerably longer (~4.5 days; Vogt et al., 2010) for this riparian zone, the increase in CO<sub>2</sub> concentration appears to be the result of microbial respiration. The given rates only take in account free living bacteria, and the actual *in situ* rates might be even higher due to biofilm activity. It is likely that the elevation of the water table increases the connectivity of the aquifer with the overlaying willow root zone, a highly stimulating environment for bacteria (de Neergaard et al., 2002), and thereby promotes high microbial respiration activity in the groundwater.

Consumption of riverine DOC alone cannot explain the accumulation of CO<sub>2</sub> measured within the willow bush zone, as the CO<sub>2</sub> concentration there (590 μmol L<sup>-1</sup>) exceeded by far the DOC concentrations that could be provided by the river water (190–300 μmol L<sup>-1</sup>). The loss of DOC from the channel to the willow bush zone (DOC concentration difference channel to willow bush zone) accounted for only 65–175 μmol L<sup>-1</sup>. We calculated missing (not detectable) DOC concentration inputs for the groundwater pool to explain the measured CO<sub>2</sub> production: ~25 μmol L<sup>-1</sup> pre-flood, ~400 μmol L<sup>-1</sup> during the flood, and a declining range from ~300 to ~100 μmol L<sup>-1</sup> post

flood. As both, DOC and O<sub>2</sub> increase, was experimentally not detectable with the temporal resolution of the measurements we conclude that the flood activated a highly bioavailable OC source which is plausibly related to the soil or the roots of the willow plants and the mobilization through the rising water table (Peter et al., 2012a).

## Effect of Excess Air on Nitrogen Transformation in Different Riparian Zones

Nitrogen transport and transformation within the riparian zone at the River Thur is known to be spatially and temporally highly variable in the transport and transformation of N (Peter et al., 2012b; Shrestha et al., 2014). The soils of the riparian zones act either as sink or source for inorganic N and flood events stimulate hot moments for N transformations. Nitrate removal through denitrification occurred both in the soils and in the riparian groundwater and appear to be locally constrained to the willow bush zone. Despite that the willow bush zone receives high amounts of labile DOC during flood events, which induces high microbial activity, denitrification was never observed during flood events. Only post flood (>1 week) and during average flow conditions, nitrate removal through denitrification is evident (Peter et al., 2012b).

This study covers on a finer resolution the functioning of the different riparian zones for N transformation processes during a flood event. We took advantage of the MIMS to be able to measure N<sub>2</sub> concentrations, and distinguish between N<sub>2</sub> excess due to excess-air formation in response to air/water partitioning and N<sub>2</sub> being produced by denitrification. The gravel and grass zones close to the channel were dominated by N-dynamics in the river, e.g., by mainly reflecting river water concentrations (**Figure 3**). Denitrification might reduce some NO<sub>3</sub><sup>-</sup> in these zones, as after the flood event slightly increased N<sub>2</sub>O concentrations, an intermediate product of denitrification were measured. The lowest NO<sub>3</sub><sup>-</sup> concentrations within the entire riparian area were detected in the hot spot for OC respiration, the willow bush zone after the flood event. Denitrification might contribute to this reduction in NO<sub>3</sub><sup>-</sup> concentration because N<sub>2</sub>O and NO<sub>2</sub><sup>-</sup> accumulated there temporally shortly after the flood event (**Figure 3**). However, the N<sub>2</sub> produced by denitrification (ΔN<sub>2</sub>), was in the range of the measurement error (3% ~30–40 μmol N L<sup>-1</sup> Mächler et al., 2013) (**Figure 3**). Hence, it is not evident if denitrification contributed substantially to the decrease in NO<sub>3</sub><sup>-</sup> concentration (~50 μmol N L<sup>-1</sup>) occurring after the flood event in the willow bush zone. This is surprising since the willow bush zone receives substantial amounts of OC during flood events that fuels high microbial activity. We can exclude that dilution by a different groundwater source may have caused the low NO<sub>3</sub><sup>-</sup> concentrations in the willow bush zone, as this zone is hydrologically directly fed by the channel (**Figure 1**; Vogt et al., 2010). Other NO<sub>3</sub><sup>-</sup> consuming processes, such as microbial assimilation, dissimilative NO<sub>3</sub><sup>-</sup> reduction to ammonia, or plant uptake might be involved (Clement et al., 2003; Dhondt et al., 2003; Hefting et al., 2004). From previous isotopic investigations we have already presented evidence for plant uptake as a competitive NO<sub>3</sub><sup>-</sup>

removal mechanism to denitrification for the same field site (Peter et al., 2012b).

Flood events play a key role for the functional development of the biogeochemical processes in the willow bush zone. The sampling campaign from May 2011 took place after a long dry period (Figure 2). The Pre-flood measurement indicate neither enhanced  $O_2$  respiration nor  $NO_3^-$  removal, which was in sharp contrast to the biogeochemical dynamics during the flood when  $O_2$  was immediately respired (Figure 3) and previous observation during post-flood conditions were  $NO_3^-$  was typically removed by denitrification (Peter et al., 2012b). The enhanced respiration during flood relates to flood induced aeration of the groundwater and OC mobilization from soil/root zone whereby  $O_2$  and DOC were instantly converted into  $CO_2$ , causing DOC and  $O_2$  being almost completely depleted. The presence of injected  $O_2$  favors aerobic respiration and inhibits denitrification activity (Rivett et al., 2008), explaining the observed lack of denitrification during flood event in this study (Figure 3) and in previous studies at the fields site (Peter et al., 2012b). After such an “oxidative” disturbance of a system,  $N_2O$  tends to accumulate (Naqvi et al., 2000; Verhoeven et al., 2006). The peaks in  $N_2O$  and  $NO_2^-$  concentrations 1 day after the flood event may relate to this phenomenon (Figure 3). However,  $N_2O$  concentrations were low and may not be contributing significantly to greenhouse gas emissions. In the present investigation, DOC input seemed to be just enough to fuel  $O_2$  respiration but not the subsequent denitrification (i.e., only the downstream piezometer in the willow bush zone exhibited reduced  $NO_3^-$  concentration). The investigated flood event was a minor and more intense flood events introduce higher OC loads, which could support more intense and longer anoxic periods and hence denitrification activity, as it was observed at this field site in previous studies 1 week after a flood event (Peter et al., 2012b).

## Implications and Conclusions

This case study showed that excess-air formation, triggered by flood induced water table rise, fostered aerobic OC respiration due to local aeration of the riparian groundwater combined with high OC injection from the overlaying soil/root zone. On the other hand, the lack of denitrification activity during flood event indicated that high  $O_2$  input might have suppressed anaerobic respiration processes like denitrification despite the high availability of OC. Through the connectivity of the soil/root zones with the groundwater aquifer, the local variabilities in vegetation cover and aquifer structure can be important drivers for biogeochemical processes in the groundwater.

The *in situ*-gas determination by the field-installed MIMS successfully allowed to decipher the spatial and temporal variability of the biogeochemical processes related to different functional process zones. Only by calculating the contribution of

excess air  $O_2$  and simultaneously measuring  $CO_2$  concentrations, the locally constrained effect of a flood event on microbial OC transformation could be demonstrated. Particularly, the existence of additional OC sources besides the river could be verified and the contribution to the groundwater OC pool estimated. The combination of biogeochemical monitoring with MIMS helped identifying and explaining the low  $N_2$  production by denitrification in a zone with high OC transformation. It is important to note that  $N_2$  production from denitrification in riparian aquifers can only be determined if the effect of atmospheric  $N_2$  introduction by excess-air formation is considered. Neglecting excess-air formation would have resulted in a significant overestimation of denitrification activity. However, with the given analytical precision it is also difficult to detect low biological  $N_2$  production. Studies of flood events of different magnitude and longer time series would improve the understanding of the biogeochemical role of excess air input into riparian systems.

## AUTHOR CONTRIBUTIONS

ED, BW, and RK contributed to the conceptual study design, data interpretation, critical revision and intellectual input. They approved the final version to be published and are accountable for all aspects of the work. LM and SP were involved in conception of the work, data acquisition and analysis, drafting and revision of the written part. They approved the final version to be published and are fully accountable for the work.

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## SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: <http://journal.frontiersin.org/article/10.3389/fenvs.2015.00075>

**Figure S1 | Schematic view of a cross section through the different zones of the riparian aquifer at the restored field site at Niederneunforn (A).** Simplified overview of the sampling set up using the membrane-inlet mass spectrometer (B) (modified from Mächler et al., 2012).

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**Conflict of Interest Statement:** The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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