

Transport-reaction dynamics of particulate organic matter and oxygen in riverbed sediments

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BACKGROUND & PURPOSE

Introduction

The interface between rivers and alluvial sediments adjacent to them is a critical zone for ecological and biogeochemical processes (Boano et al., 2014). Large-scale changes in river stage can lead to extended flooding of the nearshore hyporheic zone, with major attendant impacts on hyporheic exchange flows (HEFs) (Zachara et al., 2020). Excursions in HEFs have important implications for the input and transformation of river-derived organic materials and nutrients in river corridors.

This study deals with the riverbed of the Columbia River (CR) in eastern Washington State (Fig.1). We are working in the vicinity of the Hanford 300 Area within the Hanford Reach (HR) of the CR (Fig.2). This and other locations within the HR experience large fluctuations in river stage (see Fig. 12), which take place both naturally on a seasonal basis, and on shorter time scales (hours to day) in conjunction with hydroelectric power dam operations (Zachara et al., 2016; Stegen et al., 2016).

Observational and modelling studies in the HR of the CR have demonstrated that the alluvium layer (i.e. the riverbed) exerts significant control on river corridor HEFs (Zachara et al., 2020), and is associated with elevated levels of biogeochemical activity (Moser et al., 2003; Stegen et al., 2016; Hou et al., 2017; Liu et al., 2017).

Although accumulation of fine-grained particulate materials has long been recognized as a significant process in permeable



Fig.1. Columbia River basis, showing location of the Hanford Reach immediately downstream of the Priest Rapids Dam (inset). Source: USArmy Corp of Engineers.

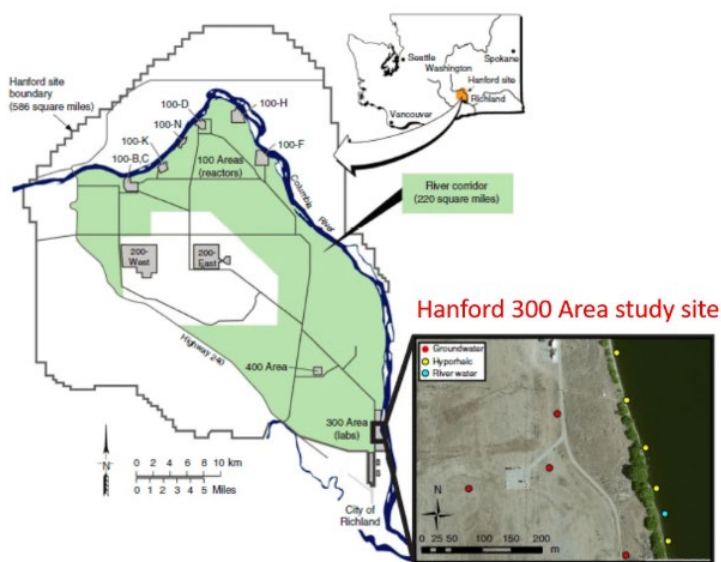


Fig. 2. Hanford Reach of the Columbia River illustrating Hanford 300 Area study site. Source: PNNL SFA.

riverbed sediments (Brunke, 1999), the input and processing of particulate organic matter (POM) in riverbed sediments has been understudied (Trimmer et al., 2012) and remains an important knowledge gap (Graham et al., 2018; Yang et al., 2018). Large fluctuations in river stage create conditions conducive to the influx and transport of fine-grained POM (a biological colloid originating from the river water and/or in situ periphyton production), within near-surface riverbed sediments (Fig. 3).

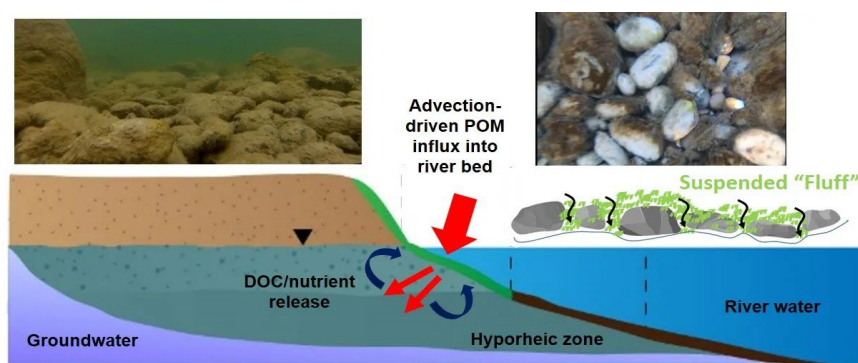


Fig. 3. Conceptual model for hydrologically (river stage) driven advective input of POM (suspended "fluff") into the riverbed at the Hanford 300 Area, leading to its accumulation in a near-surface sediment that underlies the armoring layer of large cobbles (see photos). River cross section diagram and upper left photo sources: PNNL SFA.

Purpose of Study

Much is known about dissolved organic matter (DOM) transport and metabolism in hyporheic zone sediments, but there is a paucity of quantitative information on POM dynamics and its influence on hyporheic zone biogeochemistry (e.g. dissolved oxygen dynamics). POM input has the potential to strongly impact the biogeochemistry of both the river itself as well as the hyporheic zone (Trimmer et al., *Sci. Tot. Environ.*, 2012), with important implications for CO₂ and/or CH₄ production as well as retention and/or release of nutrients (e.g., N, P, S) associated with POM decomposition.

Recent studies have suggested that deposition of fresh POM can lead to elevated rates of aerobic microbial metabolism, increased activity of anaerobic heterotrophic organisms, and release of labile dissolved organic carbon (DOC) in riverbed sediments from the Hanford 300 Area (Stern et al., 2017).

The central purpose of this study was to develop a hydrobiogeochemical model capable of simulating the transport and metabolism of POM and its impact on dissolved oxygen (DO) distribution within the riverbed as influenced by periodic changes in river stage and fluid flow rate and direction. The model was employed as a tool to interpret the results of *in situ* measurements of POM intrusion into the riverbed made using "POM traps" emplaced within the upper 20 cm of the riverbed, as well as *in situ* dissolved oxygen concentrations determined with a novel optical sensor buried directly in the riverbed at 20cm depth.

EXPERIMENTAL METHODS & RESULTS

POM Trap Experiments

We developed a novel technique for estimating the input of fresh POM to near-surface Hanford 300 Area riverbed sediments (see Fig. 4 and embedded YouTube video), based on a prior approach used to quantify input of fine-grained materials to salmon bed environments within the HR of the CR (Hanrahan et al., 2007).

Ashed bulk riverbed sediment (ca. 2 kg) is placed in baskets within collars embedded in the riverbed. The baskets are slotted to allow fluid and fine particle ($< 100 \mu\text{M}$) throughput. Traps were deployed for ca. 4-6 weeks in February/March and June/July 2020. Recovered materials were sieved to collect the $< 0.25 \text{ mm}$ fraction for POC/PON analysis. Separate POM addition experiments verified that this approach recovers virtually all added POM.



Fig. 4. Photo of POM trap deployed in the Hanford 300 Area riverbed, February 2020. See the following URL for a video of trap deployment and collection: (<https://www.youtube.com/watch?v=jeWB6zTm2o8&fs=1&modestbranding=1&rel=0&showinfo=0>)

The results of the two deployment showed that the dry weight POC content in the $< 0.25 \text{ mm}$ fraction increased from a background of ca. 0.06% to up to 0.3%, corresponding to mmol/dm³ quantities of bulk POC accumulation (Fig. 5).

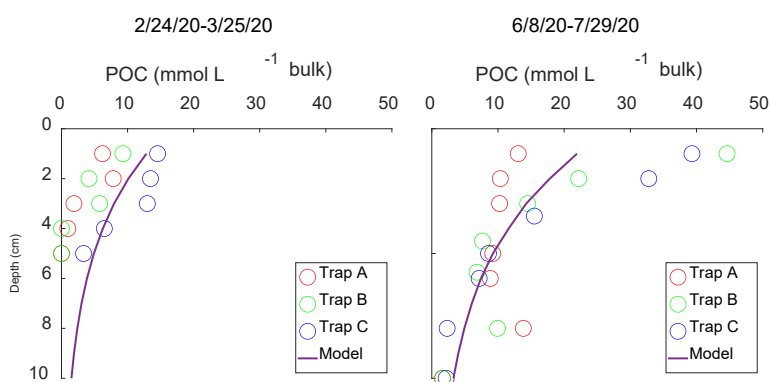


Fig. 5. Results of POM trap deployments in Feb-Mar and Jun-Jul 2020. Open symbols show measured POC accumulation; solid lines show results of transport-reaction model simulations for the time period of POM trap deployment.

POM Transport Experiments

The framework for modeling POM transport in riverbed sediments was adapted from the results of column transport experiments (Bulur, 2020; Bulur et al., 2021a,b) conducted with Hanford formation sediments and freshly-grown periphyton biomass from the Hanford 300 Area (Fig. 6). The experiments showed that the transport of POM could be described by a model (adapted from Harter et al., 2000) that includes reversible sorption and irreversible filtration.

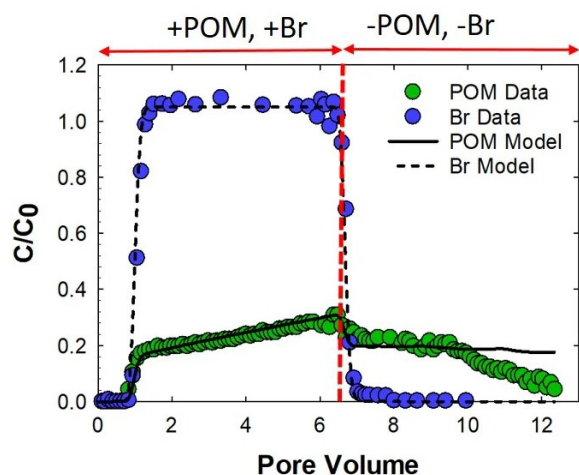


Figure 6. POM transport experiment with freshly-grown periphyton biomass (POM, ca. 1 mmol C/L) in columns (15 cm length x 2.5 cm diameter) packed with Hanford formation sediment (0.25-2 mm diameter). The solid line shows the results of a transport-reaction simulation that included reversible sorption/desorption and irreversible filtration of POM by the sediment matrix.

locations.

A k-means clustering analysis was conducted on the first derivatives of DO, specific

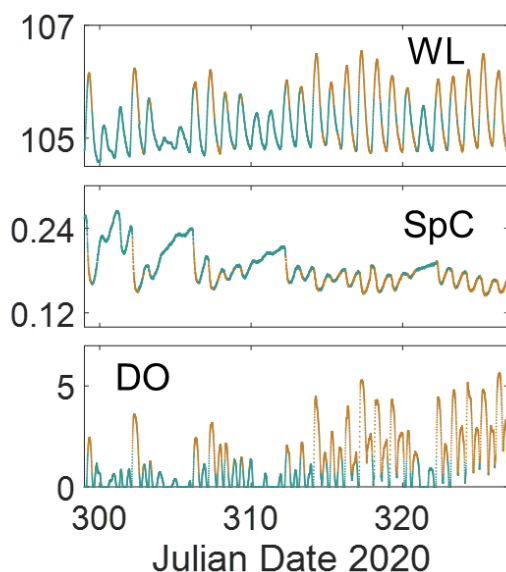


Figure 8. k-means clustering analysis of temporal change water level (WL, m), specific conductivity (SpC, $\mu\text{ohm/cm}$), and dissolved oxygen (DO, mg/L) at ca. 20 cm depth in Hanford 300 Area sediments in Nov-Dec 2020. The green and gold colored lines indicate identified clusters.

In situ DO Probe Measurements

In collaboration with PNNL SFA personnel, Ghosh and colleagues at Opti O₂, LLC deployed novel in situ optical (molybdenum chloride cluster phosphorescence based) DO probes (Ghosh et al., 2011; 2019a,b, and Gooseff et al., 2019) at 20 ca. cm depth at three locations at the Hanford 300 Area between August and December 2020. The results (Fig. 7A) revealed sustained periods of very low DO at two of the locations, as well as large periodic fluctuations in DO concentration at all three

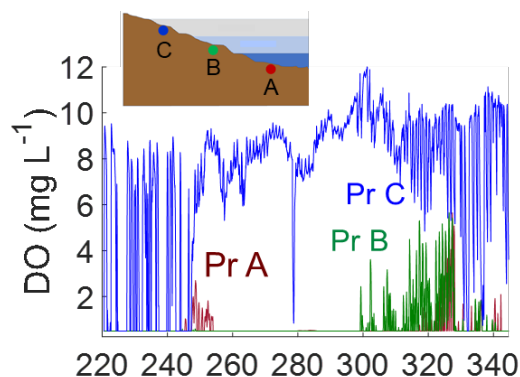


Figure 7. In situ DO probe (Pr) measurements at three locations (inset) at the Hanford 300 Area in Aug-Dec 2020 (data courtesy of Ruby Ghosh, OptiO₂, LLC). DO values < 0.5 were set equal to a baseline value of 0.5 mg L⁻¹, as it was difficult to distinguish noise from signal below this concentration.

conductivity, and water level (measured by a separate pressure sensor co-deployed at the same depth as the DO probe) with respect to time for data from probe A. The results (Fig. 8) revealed that temporal variations in DO during Nov-Dec were directly linked with variations in fluid conductivity (groundwater = high, river water = low). The variation in conductivity in turn reflected changes in fluid flux rate and direction driven by changes in water level. These results

suggest a strong hydrological coupling between fluid advection rate/direction and DO, which was explored by transport-reaction modeling (see Fig. 15).

REACTIVE TRANSPORT MODELING

POM Transport-Reaction Model

A one-dimensional advection-dispersion-reaction model was developed to simulate the transport and metabolism of POM (and DOM) within the upper 100 cm of the Hanford 300 Area riverbed. The central objective of the modeling was to predict the potential impact of fresh POM influx on dissolved oxygen (DO) distributions. Key to this analysis was inclusion of periodic changes in the direction (either into or out of the sediment) and rate of fluid flow within the riverbed (see Hydrological Modeling section below).

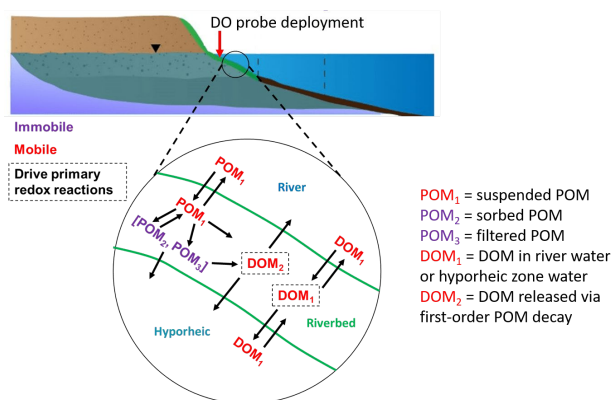


Fig. 9. Diagram illustrating the coupled POM-DOM degradation model.

The model considers suspended (mobile) POM, sorbed/filtered (immobile) POM, dissolved organic matter (DOM) present in the river water, and DOM that originates from POM decay (Fig. 9). The representation of POM sorption and filtration is based on the results of the POM transport experiments (Fig. 6), with parameter values adjusted to reproduced observed POM trap results (Fig. 5). Both POM and DOM degradation are treated as first-order reactions (Fig. 10), with rate constants determined from laboratory incubation experiments with Hanford 300 Area sediments amended with freshly-grown periphyton POM (Stern et al., 2021). The rate constants determined at room temperature (22C) were adjusted for in situ temperature assuming a Q10 value of 2.

Degradation of DOM drives a sequence of primary redox reactions (see Fig. 11) according to the "Modified Monod" approach (Fig. 10; Boudreau and Westrich, 1984; Van Cappellen and Wang, 1996; Hunter et al., 1998). The model includes a comprehensive set of "secondary redox reactions" by which reduced compounds generated via anaerobic metabolic pathways are re-oxidized (dashed lines in Fig. 11) through second-order reactions (Fig. 10) with higher redox potential electron acceptors. Inclusion of such reactions is crucial for proper simulation of highly dynamic redox environments such as 300 Area riverbed sediments.

Hydrological Modeling

The 1-D transport-reaction equations were solved via finite differences for a 100 cm spatial domain with 1 cm node spacing using the numerical method of lines (Boudreau, 1997). Fluid flow was driven by hourly river water and groundwater level measurements at the 300 Area in 2020 (Fig. 12). The water level data was used to compute fluid flow rate and direction using measurements of the hydraulic conductivity of the upper ca. 1 m of 300 Area sediments Fritz and Arntzen (2007).

Boundary conditions for solutes in the river water and groundwater/hyporheic zone fluid were established based on previous publications (Stegen et al., 2016) and the PNNL SFA database.

POM input to the riverbed was simulated by assuming a fixed upper boundary suspended POC concentration of 1 mmol C/dm³ fluid. This boundary condition corresponds to the suspended "fluff" layer illustrated in Fig. 3. The suspended "fluff" concentration is consistent with measurements made on suspended materials collected in the vicinity of the riverbed in February 2020 (see photo in upper right corner of Fig. 4). Here again this is an over-simplification, as the abundance and organic content of material at or near the riverbed surface is likely to vary significantly over an annual cycle. However, runs of the transport-reaction model over time periods (30 or 40 d) corresponding to the two POM trap deployments produced results generally consistent with the POM trap results (Fig. 5).

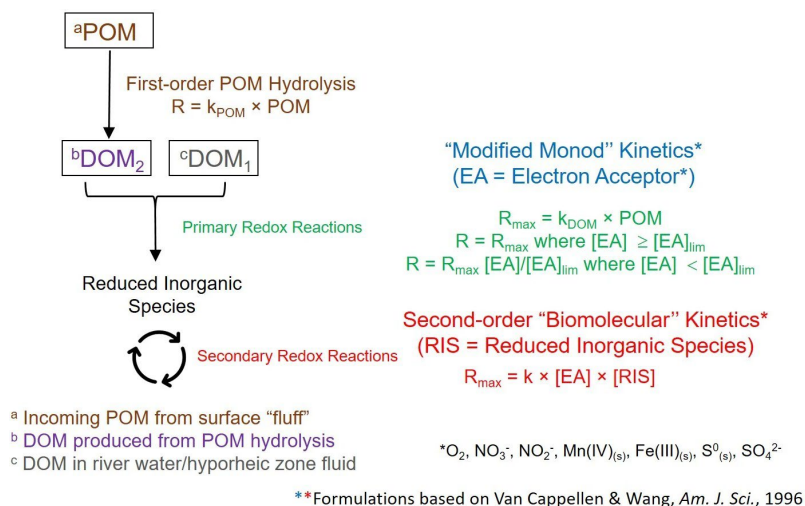


Figure 10. Reaction framework used to model POM degradation and associated redox cycling in Hanford 300 Area sediments.

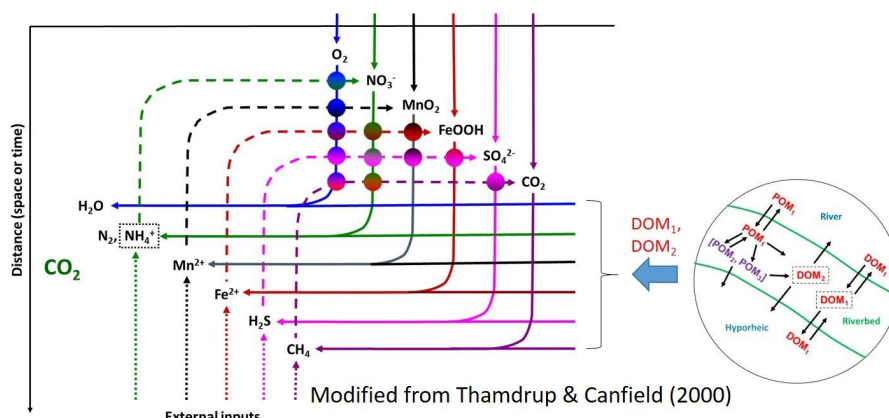


Figure 11. "Train station" diagram of the coupling of primary (solid lines) and secondary (dashed lines) redox reactions in sediments. Modified from Fig. 6.1 in Thamdrup and Canfield (2000).

MODELING RESULTS, INTERPRETATION, & CONCLUSIONS

Overview

The basic goal of the transport-reaction modeling was to evaluate whether or not POM input and degradation could play a role in producing anoxic conditions in the upper few dm of the riverbed (Fig. 7). The observation of sediment anoxia was unexpected given the high rates of fluid flow into and out of the riverbed (Fig. 12), and the fact that both the river water and the groundwater and deeper hyporheic zone fluid are rich in DO (Song et al., 2018; Kaufman et al., 2021).

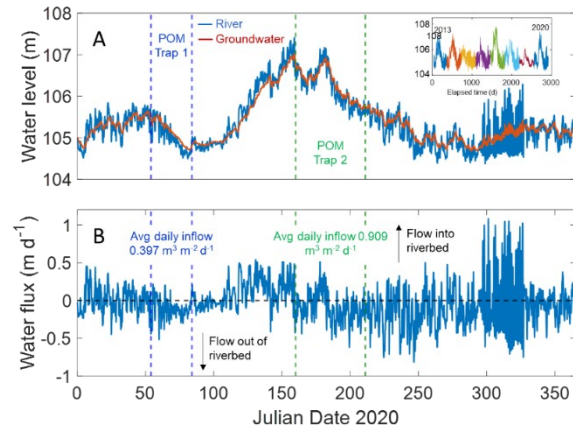


Figure 12. Measured (hourly) RW and GW levels (data provided the PNNL SFA team) (A) and estimated fluid flow rate/direction (B) at the Hanford 300 Area in 2020. The difference in RW and the GW level was used to compute hourly fluid flow rate, employing temperature-dependent sediment permeability values constrained by in situ measurements of hydraulic conductivity in 300 Area alluvium sediments at the Hanford 300 Area study site (Fritz and Arntzen, 2007). Inset in panel A shows variation in RW levels from Jan 2013 through Dec 2020.

Existing models of organic matter metabolism in Hanford 300 Area sediments assume either that metabolism is driven by (1) degradation of soluble DOM (e.g. Song et al., 2018), or (2) degradation of river water DOM together with a pool of POM that is renewed by input/burial of terrestrial organic matter (Yang et al., 2018). The latter assumption is problematic given that no major deposition or redistribution of alluvium sediments has taken place since emplacement of the upstream hydroelectric power dams in the 1950s (Fecht et al., 2004). Thus, any relic pool of POM in the sediment must be highly depleted in POM. This creates a disconnect in that the Yang et al. (2018) analysis suggests that this relic POM turns over on a time scale of less than one year. These observations set the stage for our investigation of the possible influence of mobile fresh POM input on sediment DO consumption.

Can DOM metabolism alone create anoxia?

A key first test for the model was to ask if, based on estimated fluid flux rates (Fig. 12) and known river/groundwater end-member DOC concentrations (ca. 0.1 and 0.01 mM, respectively; Stegen et al., 2016), DOM metabolism alone could produce anoxic conditions over an annual cycle. The results (Fig. 13) suggest that this is **NOT** the case. Sustained river water input was associated with periods of only partial DO depletion. On shorter time-scales (not evident in Fig. 13), transient slow-down in flow rate and eventual reversal of flow direction did lead to changes in DO concentration that are qualitatively analogous to DO measurements on fluids pumped from piezometers at the 300 Area site in 2018 (Kaufman et al., 2021).

However, DO levels never fell to values lower than ca. 8 mg/L.

Influence of advective POM input

Simulations that included advective POM input and degradation produced periods of transient anoxia within the upper several dm of the riverbed (Fig. 14).

Sorbed/filtered POM accumulated in the upper ca. 10 cm of sediment during periods of sustained river water intrusion during the spring and early summer (Fig. 14A). Degradation of this material led to release of labile DOM that was transported throughout the sediment column (Fig. 14B). Metabolism of this material led to DO depletion that lagged the main peak in POM accumulation by ca. 1 month.

On a shorter time scale (hours to days), changes in fluid flow rate and direction were associated with spikes in DO analogous to those observed during the Aug-Sep in situ DO probe deployments (Fig. 14C inset). The model predicted co-variations in water level, specific conductivity, and DO qualitatively similar to those recorded during the in situ probe deployments.

Declining rates of river water intrusion were associated with decreasing DO and increasing specific conductivity, reflecting the balance of forces between OM metabolism and DO resupply.

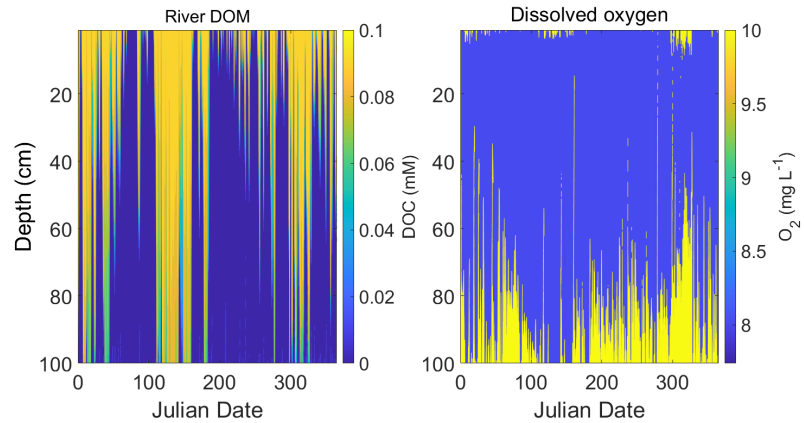


Figure 13. Simulated DOC concentrations (based on estimated fluid flux rates and known river/groundwater end-member DOC concentrations (left panel) and DO (right panel) **without** input of POM at the sediment surface, over the 2020 water cycle.

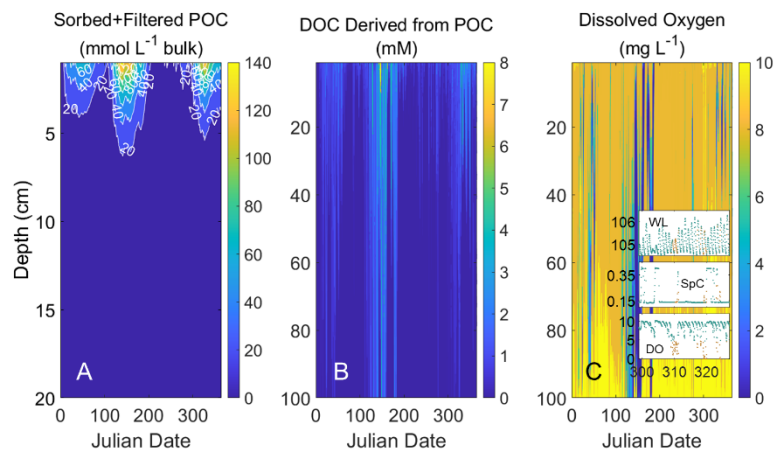


Fig. 14. Riverbed RT model simulation results for bulk POC (A), DOC derived from POC degradation (B), and DO (C) over the 2020 annual cycle. Fluid flow and solute/colloidal POM transport were modeled using measured hourly hydrologic gradients between RW and GW (see Fig. 12). Note periods of DO depletion following periods of enhanced advection-driven POM input. Inset in panel C shows k-means clustering analysis of simulated WL, SpC, and DO (see Fig. 6B)

CONCLUSIONS

The results of our simulations indicate that DOM metabolism alone cannot account for the observation of periodic anoxic conditions within the upper few dm of Hanford 300 Ara riverbed sediments. In addition, the appeal to input/burial of terrestrial organic matter as a driver of sediment metabolism is inconsistent with the fact that no major deposition or redistribution of alluvium sediment has taken place for several decades in the HR of the CR. Thus, our concept of advective input of mobile suspended (colloidal) POM in the upper few dm of the riverbed, together with its degradation to mobile DOM that drives metabolism throughout the sediment column, provides a plausible explanation for the in situ DO sensor results. Collectively our results suggest a complex interplay between fluid flow rate/direction and DO distribution that has important implications for riverbed biogeochemical dynamics at a variety of spatial and temporal scales. The depletion of DO triggered the onset of anaerobic metabolic pathways and changes in N redox cycling specifically during time periods when rates of OM processing were maximal (data not shown). Whether or not these changes occur in situ and are widespread in the HR and other analogous large river systems remains to be determined, e.g. through more sophisticated hydrobiogeochemical modeling together with in situ observation and experimentation.

Acknowledgments

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