



# Metalimnetic oxygen minima alter the vertical profiles of carbon dioxide and methane in a managed freshwater reservoir

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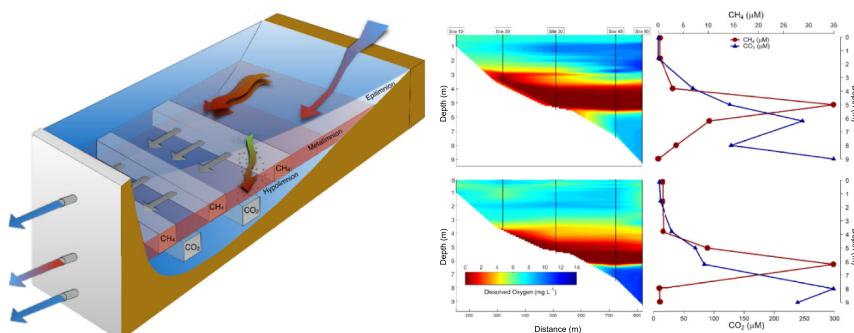
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## HIGHLIGHTS

- Metalimnetic oxygen minimum zones (MOMs) commonly develop in freshwater reservoirs.
- Dissolved greenhouse gases and emissions were monitored in a reservoir with MOMs.
- MOMs altered the seasonal profiles of CH<sub>4</sub> and CO<sub>2</sub> in the water column.
- Methane (CH<sub>4</sub>) accumulated in the MOMs that developed both monitoring periods.
- Evaluation of MOMs on GHGs is critical as reservoir construction increases.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Metalimnetic oxygen minimum zones (MOMs) commonly develop during the summer stratified period in freshwater reservoirs because of both natural processes and water quality management. While several previous studies have examined the causes of MOMs, much less is known about their effects, especially on reservoir biogeochemistry. MOMs create distinct redox gradients in the water column which may alter the magnitude and vertical distribution of dissolved methane (CH<sub>4</sub>) and carbon dioxide (CO<sub>2</sub>). The vertical distribution and diffusive efflux of CH<sub>4</sub> and CO<sub>2</sub> was monitored for two consecutive open-water seasons in a eutrophic reservoir that develops MOMs as a result of the operation of water quality engineering systems. During both summers, elevated concentrations of CH<sub>4</sub> accumulated within the anoxic MOM, reaching a maximum of 120 μM, and elevated concentrations of CO<sub>2</sub> accumulated in the oxic hypolimnion, reaching a maximum of 780 μM. Interestingly, the largest observed diffusive CH<sub>4</sub> effluxes occurred before fall turnover in both years, while peak diffusive CO<sub>2</sub> effluxes occurred both before and during turnover. Our data indicate that MOMs can substantially change the vertical distribution of CH<sub>4</sub> and CO<sub>2</sub> in the water column in reservoirs, resulting in the accumulation of CH<sub>4</sub> in the metalimnion (vs. at the sediments) and CO<sub>2</sub> in the hypolimnion.

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## 1. Introduction

Human-made reservoirs are major contributors of diffusive carbon dioxide (CO<sub>2</sub>) and methane (CH<sub>4</sub>) effluxes to the atmosphere (Deemer et al., 2016). Despite their small global surface area relative

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to naturally-formed lakes (Downing et al., 2006), reservoirs may contribute up to 36.8 Tg CO<sub>2</sub> yr<sup>-1</sup> and 13.3 Tg CH<sub>4</sub> yr<sup>-1</sup> to the atmosphere, representing approximately 1.3% of gross anthropogenic CO<sub>2</sub> equivalent emissions (Deemer et al., 2016). Reservoir construction is increasing globally to satisfy the demands for renewable energy, agriculture, and drinking water (Zarfl et al., 2015); thus, determining the factors that control the magnitude of diffusive CO<sub>2</sub> and CH<sub>4</sub> efflux from reservoirs is critical for constraining the global carbon (C) budget (Cole et al., 2007; Tranvik et al., 2009).

Reservoir CO<sub>2</sub> and CH<sub>4</sub> dynamics are controlled in part by dissolved oxygen (DO) concentrations in the water column and at the sediments. Many reservoirs exhibit anoxic hypolimnia (DO concentrations <0.5 mg L<sup>-1</sup>) that accumulate high concentrations of CH<sub>4</sub> during the summer stratified period. As a result, peak diffusive CH<sub>4</sub> efflux in these reservoirs generally occurs on the day of fall turnover when the CH<sub>4</sub> in the anoxic hypolimnion reaches the upper mixed layer (e.g., Musenze et al., 2014; Rasilo et al., 2015). As CH<sub>4</sub> diffuses upward through the water column to the surface during turnover, most of it will be oxidized to CO<sub>2</sub> upon contact with oxic waters, resulting in peak CO<sub>2</sub> diffusive efflux rates during turnover as well (Bastviken et al., 2004).

In contrast to reservoirs that develop anoxic hypolimnia, some reservoirs instead develop metalimnetic oxygen minima (MOMs), or zones of depleted DO in the middle of the water column (Thornton et al., 1990), which may affect CH<sub>4</sub> and CO<sub>2</sub> vertical profiles. In a review of the literature, we identified 40 reservoirs in which MOMs were reported (Appendix 1, Table I), or a MOM was observed in a figure but not reported explicitly in the text (Appendix 2, Table I). Many of these reservoirs developed MOMs during the stratified period and were managed with engineered systems used to improve water quality. An analysis of the morphometric characteristics of these reservoirs suggests that MOMs can form in a wide range of varying-sized reservoirs (Table 1).

MOMs can form in reservoirs due to both natural processes and human management. Several natural processes were identified as drivers of MOMs in the literature review, including the lateral entrainment of low-oxygen or nutrient and organic-rich water from inflows that stimulates microbial respiration in the metalimnion (Effler et al., 1998; Joehnk and Umlauf, 2001; Shapiro, 1960; Bolke, 1979); and settling of organic matter from the surface that slows at the thermocline and is consumed, subsequently depleting DO (Kreling et al., 2017; Thornton et al., 1990). In addition to natural processes, water that is discharged from a reservoir's dam at a depth that corresponds with the thermocline can exacerbate the development of a MOM in reservoirs by increasing the internal flows that entrain upstream nutrients toward the intake (Williams, 2007).

Water quality management systems that are commonly deployed in reservoirs, such as hypolimnetic oxygenation (HOx) and epilimnetic mixing (EM) systems, also promote the development of MOMs (Gerling et al., 2014; Chen et al., 2017, 2018). HOx systems can result in MOMs when laterally-entrained low-oxygen water depletes DO conditions in the metalimnion (Chen et al., 2017, 2018), and the hypolimnion is successfully oxygenated due to HOx operation (reviewed by Gerling et al., 2014). HOx systems can also generate a MOM if they are unable to oxygenate the entire hypolimnion, leaving low DO water just below the thermocline (e.g., Gerling et al., 2014). Similarly, operation of EM systems can increase the lateral entrainment of nutrient-

rich turbid water from shallow upstream regions to the reservoir's metalimnion in the lacustrine zone (Munger et al., 2016; Chen et al., 2017, 2018).

The development of MOMs may create redox gradients within the water column that affect the vertical distribution of CO<sub>2</sub> and CH<sub>4</sub> in the water column and the magnitude and timing of diffusive efflux. For example, if a MOM becomes anoxic, it may accumulate elevated concentrations of CH<sub>4</sub> in the middle of the water column instead of the hypolimnion. Moreover, MOMs may also alter the timing of peak CH<sub>4</sub> and CO<sub>2</sub> emissions. If CH<sub>4</sub> is present in a MOM, deeper mixing into the water column due to storms or other disturbances could entrain low-oxygen metalimnetic water to the surface, thereby resulting in increased CH<sub>4</sub> and CO<sub>2</sub> diffusive effluxes before turnover.

We conducted a whole-reservoir monitoring study to examine how MOMs in reservoirs affect CH<sub>4</sub> and CO<sub>2</sub> water column concentrations and diffusive CH<sub>4</sub> and CO<sub>2</sub> emissions during two consecutive summers. MOMs were developed by operating a HOx and EM system in a eutrophic drinking water reservoir that has previously exhibited MOMs (Chen et al., 2017; Gerling et al., 2014, 2016; Munger et al., 2016) during the open-water seasons of 2015 and 2016. The EM system was operated independently from the HOx to stimulate lateral entrainment of nutrients from upstream and to further promote the development of the MOM (following Chen et al., 2018). HOx and EM systems are increasingly being used to suppress hypolimnetic anoxia and algae blooms in lakes and reservoirs globally (Chen et al., 2017; Liboriussen et al., 2009; Singleton et al., 2010; Beutel and Horne, 1999); however, to our knowledge there are no studies that specifically investigate the effects of HOx and EM operation on MOMs and their consequences for greenhouse gas (GHG) dynamics.

Throughout the whole-reservoir monitoring study, we measured the effects of the MOMs on the vertical profiles of CO<sub>2</sub> and CH<sub>4</sub> in the water column and diffusive CH<sub>4</sub> and CO<sub>2</sub> effluxes. We predicted that CH<sub>4</sub> would accumulate in the MOM after it had become anoxic, in comparison to CO<sub>2</sub>, which would accumulate in the oxygenated hypolimnion because of HOx operation and increased aerobic respiration rates at the sediments. We also predicted that any CH<sub>4</sub> that accumulated in the MOM would result in increased CH<sub>4</sub> diffusive effluxes if strong winds or mixing events occurred during summer stratified conditions, decoupling the timing of peak diffusive effluxes from fall turnover. In contrast, CO<sub>2</sub> diffusive efflux was predicted to peak during turnover because CO<sub>2</sub> accumulated in the hypolimnion would not be able to reach the upper mixed layer until the entire water column mixed at the end of the summer stratified period (following Vachon and del Giorgio, 2014).

## 2. Materials and methods

### 2.1.1. Site descriptions

The whole-reservoir manipulations to generate and monitor MOMs were conducted in Falling Creek Reservoir (FCR). FCR is a small (surface area = 0.119 km<sup>2</sup>), shallow (Z<sub>max</sub> = 9.3 m, Z<sub>mean</sub> = 4.0 m), eutrophic, drinking water reservoir located in Vinton, Virginia, USA (37.30°N, 79.84°W) (Fig. 1). The reservoir was constructed in 1898 and is owned by the Western Virginia Water Authority (WVWA) and has one primary inflow stream from an upstream reservoir that contributes

**Table 1**

Summary statistics of morphometric characteristics of reservoirs that have reported or observed but not explicitly reported MOMs. S.E. refers to standard error of the mean; S.D. refers to standard deviation of the mean.

	Volume (km <sup>3</sup> )	Maximum depth (m)	Minimum depth (m)	Surface area (km <sup>2</sup> )	Perimeter (km)	Catchment area (km <sup>2</sup> )	Elevation (m)
Mean	3.2	73	34	85	370	32,000	540
Median	0.7	58	25	44	240	4000	340
Minimum	0.01	9.0	3	0.4	4.0	7.0	27
Maximum	37	200	210	650	3800	420,000	2300
S.E. mean	1.3	9.3	7.4	25	120	14,000	98
S.D. mean	7.5	50	38	140	670	85,000	560

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