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ORIGINAL RESEARCH ARTICLE

Natural and forced soil aeration during agricultural managed aquifer recharge

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Abstract

One of the suggested approaches to mitigate the chronic groundwater depletion in California is agricultural managed aquifer recharge (Ag-MAR), in which farmland is flooded using excess surface water in order to recharge the underlying aquifer. Successful implementation of Ag-MAR projects requires careful estimation of the soil aeration status, as prolonged saturated conditions in the rhizosphere can damage crops due to O₂ deficiency. We studied the soil aeration status under almond [Prunus dulcis (Mill.) D.A. Webb] trees and cover crops during Ag-MAR at three sites differing in drainage properties. Water application included several cycles (2–7) and flooding durations (27-63 h) that varied according to the soil infiltration capacity at each site. We used O₂ and redox potential as soil aeration quantifiers to test the impact of forced aeration by air-injection compared with natural soil aeration. Results suggest an average increase of up to $2\% O_2$ at one site, whereas mixed impact was observed at the two other sites. Additionally, no impact on crop yield was observed for one growing season. Results further suggest that natural aeration can support crop O2 demand during Ag-MAR if flooding duration is controlled according to O₂ depletion rates. In large Ag-MAR projects, forced aeration might be useful to improve local zones of O₂ deficiency, which are expected to occur due to topographic irregularities and spatial variability of drainage properties.

1 | INTRODUCTION

In recent decades, ubiquitous use of groundwater in California and other parts of the world have led to chronic groundwater overdraft and water quality issues. Worldwide recognition of groundwater depletion and its adverse effects on human and environmental well-being has increasingly led to actions, policy, and legislative change to manage water resources jointly and sustainably (Gleeson et al., 2020). For example, the Sustainable Groundwater Management Act formed in 2014 in California requires groundwater users to achieve long-term groundwater sustainability by managing groundwater extraction and intentionally replenishing water in groundwater aquifers (Faunt et al., 2016; Harter, 2015; SGMA, 2014). One possible technique for groundwater replenishment is agricultural managed aquifer recharge (Ag-MAR; on-farm recharge, agricultural groundwater banking are all synonym terms, under the general category of flood-MAR) in which

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Abbreviations: Ag-MAR, agricultural managed aquifer recharge; CT, Campbell Tract; DO, dissolved oxygen; Eh, redox potential; KARE, Kearney Agricultural Research and Extension Center; NSL, Nickels Soil Laboratory; SAGBI, soil agricultural groundwater banking index; SDI, subsurface drip irrigation; VWC, volumetric water content; ZOI, zone of influence.

farmland is flooded using excess surface water in order to recharge the underlying aquifer (Kocis & Dahlke, 2017). As most agricultural fields have lower infiltration capacities compared with dedicated recharge basins, Ag-MAR is designed to capture high-volume excess surface water by flooding large areas of farmland at relatively low recharge rates of less than one meter per Ag-MAR event (Kocis & Dahlke, 2017; Kourakos et al., 2019).

Ideally, flooding for Ag-MAR is preferably done on fallow fields or during crop dormancy periods, when agricultural fields have the potential to serve as percolation basins for groundwater recharge. O'Geen et al. (2015) recommended potential areas in California for Ag-MAR using an index (Soil Agricultural Groundwater Banking Index [SAGBI]) that combines five soil characteristics: deep percolation, root zone residence time, chemical properties, topography, and surface conditions. An ideal Ag-MAR site will comprise an effective deep percolation (beyond the root zone), adequate crop tolerance for flooding, low soil salinity, leveled soil surface, and lack of compaction and erosion. O'Geen et al. (2015) identified an area of 22,500 km² of agricultural land (31% of the studied area), mostly in the Central Valley, as having excellent to moderately good potential for Ag-MAR.

Root zone residence time is defined as the duration of saturated (or near saturated) conditions in the soil root zone after water is applied (O'Geen et al., 2015). It is a key factor in Ag-MAR, as prolonged saturated conditions in the rhizosphere can damage perennial crops due to O₂ deficiency hypoxia—a well-known situation in agricultural soils under intensive irrigation. Root functioning, nutrient and water uptake, vegetative growth, and crop yield are all affected by low O₂ concentration (Glinski & Stepniewski, 1985). Moreover, in flooded fields, complete depletion of O2-anoxiamay occur, which affects crops severely and can lead to plant mortality (Kozlowski, 1997). Therefore, quantifying the soil aeration status is of great importance for implementation of Ag-MAR on fields with perennial crops (e.g., almonds [Prunus dulcis (Mill.) D.A. Webb], grapes [Vitis vinifera L.], alfalfa [Medicago sativa L.]) with potentially no yield lost.

Soil aeration is essential to support aerobic soil respiration which includes O_2 consumption by plant roots and microbial population. The O_2 level in unsaturated soils depends highly on the gas phase since the O_2 concentration in atmospheric air is ~250 mg L⁻¹ while water in equilibrium with the atmosphere contains dissolved O_2 (DO) of only ~8 mg L⁻¹ (at 25 °C and 1 atm). The two transport mechanisms for meeting soil oxygen demand are diffusion of O_2 in both the liquid and gas phases and convection of O_2 in flowing water or air. However, low diffusion rates in water and the low solubility of O_2 in water make the liquid phase contribution for O_2 replenishment negligible. Therefore, gas transport is considered the main mechanism for supplying soil O_2 , and gas diffusion, driven by the O_2 concentration gradient between

Core Ideas

- Soil aeration is suppressed by saturation during Ag-MAR, which may lead to yield loss.
- Ag-MAR soil aeration is better characterized by measuring both soil O₂ and redox potential.
- Adequate aeration of the root zone can be sustained by limiting flood duration.
- Forced aeration by air injection with subsurface drip can enhance soil aeration during Ag-MAR.

the atmosphere and the soil, is considered the dominant transport process (Friedman & Naftaliev, 2012). The composition and magnitude of the gas phase in soils (mainly O_2 and CO_2) determines the soil aeration status, which controls O_2 availability to soil respiration. Soil aeration status can be evaluated by the following quantifiers: volumetric air content (air-filled porosity), O_2 concentration in the gas or liquid phase (assuming equilibrium between the two phases through Henry's law), O_2 diffusion rate and soil redox potential (Eh) (Ben-Noah & Friedman, 2018).

Under flooded conditions, as expected during Ag-MAR, O_2 supply by gas transport is suppressed by soil saturation, as water occupies most of the air-filled soil pores. If ponding occurs, the ponded water layer at the soil surface will act as a barrier that effectively blocks soil gas exchange with the atmosphere, because the diffusivity of O_2 in water is 10,000 times lower than in air (Scott & Renaud, 2007). Under these conditions, hypoxia is expected to develop rapidly as the result of root respiration, microbial activity, displacement of air by water and impeded soil gas exchange (Fi

gure 1). The depletion rate of O_2 from the soil solution and entrapped air pockets will depend on temperature and respiration activity, so depletion will be slow at low temperatures and low organic-matter content (Colmer & Greenway, 2005). Upon waterlogging, the rate of decline in soil O_2 from ~21% to 0% can vary, ranging from one (Trought & Drew, 1980) to several days (Blackwell, 1983).

To minimize crop damage during Ag-MAR due to poor soil aeration, an adequate supply of O_2 to the root zone must be provided. This can be achieved by natural- or forced-aeration of the root zone. Natural aeration refers to the replenishment of O_2 to the root zone from the atmosphere during the drainage period (noted as the post-flooding stage in Figure 1). It depends on the drainage class of the soil because O_2 supply to the root zone is possible only after some critical air content ($\theta_a = \phi - \theta_w$; where θ is the volumetric content of air or water in soil, and ϕ is porosity) is reached (Cook et al., 2013). Note that the critical air (or water) content represents the connectivity between the root zone and the atmosphere by air-filled pores. In the context of Ag-MAR, natural reaeration



FIGURE 1 Schematic of soil aeration during agricultural managed aquifer recharge (Ag-MAR) and the corresponding soil aeration status (O_2 ; volumetric water content $[\theta_w]$) in the root zone (soil profile modified from Christiansen & Hamblin, 2004)

of the soil after flooding can be controlled by considering the soil parameters, the water application duration, and the crop tolerance to saturation.

Forced aeration refers to intentional oxygenation of the root zone by several methods such as air injection, air bubbles,

H₂O₂ (all the formers are usually applied through subsurface drip), and solid peroxides. These methods are currently not used in commercial agriculture, although some of them have shown positive results in previous studies (see Table 3 in Ben-Noah & Friedman, 2018). Among these methods, air injection through subsurface drip systems might have higher potential in terms of O₂ delivery and implementation costs, because it uses the in situ subsurface drip system (Ben-Noah & Friedman, 2018). Previous forced aeration studies with air injection have focused on its impact on improving crop yield, nutritional value, and water use efficiency (Abuarab et al., 2013, 2019; Ben-Noah & Friedman, 2016; Busscher, 1982; Lee et al., 2014; Melsted et al., 1949; Niu et al., 2013; Shahien et al., 2014; Xiao et al., 2015), but it has not been studied in Ag-MAR applications as a method to protect yield lost due to prolonged flooding.

Monitoring soil physical-biogeochemical processes during MAR has been extensively studied (Danfoura & Gurdak, 2016; Ganot et al., 2018; Gorski et al., 2019; Greskowiak et al., 2005; McNab et al., 2009; Rodríguez-Escales et al., 2020; Schmidt et al., 2011; Vandenbohede et al., 2013); however, since Ag-MAR is a relatively new technique in the MAR toolbox, to date only a few studies have monitored these processes in actual agricultural fields during Ag-MAR (Bachand et al., 2014, 2016, 2019; Dahlke et al., 2018; Dokoozlian et al., 1987). Most Ag-MAR studies have focused on developing soil suitability guidelines (O'Geen et al., 2015), regionalscale aquifer storage estimations (Scanlon et al., 2016), water availability analysis (Kocis & Dahlke, 2017), hydro-economic

	Site					
	KARE	NSL Sacramento Valley, Arbuckle Almonds		СТ		
	San Joaquin Valley, Parlier			Sacramento Valley, Davis		
	Almonds			Cover crop		
Property	Hanford fine sandy loam ^a	Arbuckle sandy loam ^b	Hillgate loam ^b	Yolo silt loam ^b		
Bulk density, g cm ⁻³	1.55	1.69	1.76	1.52		
Sand, %	88.0	61.1	37.4	7		
Silt, %	4.2	21.6	33.1	67.5		
Clay, %	7.8	17.3	29.5	25.5		
Organic matter, %	0.56	0.39	0.80	1.54		
рН	6.66	6.83	6.97	7.25		
$K_{\rm s}^{\rm c}$, cm h ⁻¹	2.17	1.64	0.81	1.36		
Depth ^d , cm	0–120	0–173	0-182	0–165		
SAGBI class (unmodified) ^e	Excellent	Moderately good	Poor	Good		
Precipitation ^f , mm	285	40	6	475		
December avg. min/max ^f , °C	2/13	2/13		3/13		
July avg. min/max ^f , °C	17/35	15/34		14/33		
Experiment season, yr	Winter (2019)	Summer	(2019)	Spring (2020)		

TABLE 1Properties of the field sites

^aWang et al. (2003) ^bSSURGO database ^cCalculated as the harmonic mean ^dThe above soil parameters were averaged along this depth ^cO'Geen et al. (2015) ^fCIMIS database

 TABLE 2
 Water application during agricultural managed aquifer recharge (Ag-MAR) experiments

Site	KARE	NSL	СТ
Flooded treatments area, m ²	1,000	625	960
Total application time, h	37	27	63
Avg. discharge, m ³ h ⁻¹	20.6	1.5	44.2
Total applied water volume, m ³	764	40.5	2785
Total applied water per area, m	0.76	0.065 ^a	2.9 ^b
Avg. infiltration rate, m h^{-1}	0.021	0.0024	0.046
Flooding/drainage cycles	2	2	7

^aLower bound due to poor drainage and plot slope.

^bUpper bound, as adjacent plots were flooded intermittently; see text for details.

analysis (Gailey et al., 2019), and benefits evaluation using numerical modeling (Kourakos et al., 2019; Niswonger et al., 2017). Among the few Ag-MAR field studies that exist, the soil aeration status, which may impair the implementation of future Ag-MAR projects, has been largely neglected. Dahlke et al. (2018) estimated soil aeration status using Eh measurements during 3 d of Ag-MAR in an alfalfa field on a well-drained gravelly sandy loam. The Eh values were closely correlated to water content and Eh was quickly returned to preflooding aerobic conditions when water application ceased. The report of Bachand et al. (2019) is the only work that examined the impact of flooding on soil O₂ during Ag-MAR, which was studied in three almond, walnut [Juglans regia L.], and pistachio [Pistacia vera L.] orchards all located on well-drained soils (according to the NRCS drainage class). Bachand et al. (2019) calculated O_2 depletion and recovery rates based on soil O2 and water content measurements in the root zone and suggested a few best management guidelines for growers: (a) avoid standing water for more than 3-4 d, (b) reduce time with water saturation above 74%, and (c) plan Ag-MAR flood duration based on past, soil-specific flood irrigation guidelines. The applied water amounts in these demonstrations were relatively conservative (an average of 0.01-0.07 m d^{-1} ; Table 2 in Bachand et al., 2019), and therefore in the current study, we sought to explore soil aeration during Ag-MAR with higher hydraulic loads.

The goal of this study is to quantify the soil aeration status during Ag-MAR experiments and to test air injection as a technique for improving soil aeration during continuous flooding, thus reducing the risk of root and crop damage due to anoxia. For this purpose, three field experiments were conducted: one at a cover-crop field, and two at almond orchards, all located in the Central Valley, California, USA. The experiments were used to compare natural aeration and forced aeration by air injection through the subsurface drip system during Ag-MAR. The three field experiments differ in soil drainage properties ranging from excellent to poor SAGBI rating (O'Geen et al., 2015). In the following, we first explain the method we chose to quantify soil aeration and the methodology of the experiments. Next, we present the results of the Ag-MAR field experiments. Finally, we discuss the impact of forced aeration during flooding and implications for Ag-MAR projects.

2 | MATERIALS AND METHODS

2.1 | Soil aeration quantifiers

We used soil O₂ concentration (in %) and Eh (in mV) measurements to quantify soil aeration status during Ag-MAR. Using these aeration quantifiers in combination allows assessing the soil aeration status during both aerobic and anaerobic conditions (Blackwell, 1983). We set a soil O₂ threshold of 5% as a lower bound, since O2 concentrations below that are considered inadequate for root function (Costello et al., 1991). In all O_2 measurements, we assume an equilibrium (through Henry's law) in the bulk soil between the gas and liquid phases (Friedman & Naftaliev, 2012). Redox potential is a useful soil aeration quantifier in waterlogged soils where O₂ levels are low. Generally, Eh above and below 300 mV indicates aerobic and anaerobic conditions, respectively. The Eh values of 300 to -50 mV indicate moderately reducing conditions, which are dominated by facultative reducing microbes. In this range, O_2 is the preferred electron acceptor in cellular respiration, followed by NO_3^{-} , Mn^{4+} , and Fe^{3+} . The Eh below -50 mVindicates highly reducing conditions where SO_4^{2-} and CO_2 are the electron acceptors (Reddy et al., 2000). Note that Eh is a qualitative aeration quantifier, as it measures the mixed potentials of the soil and therefore cannot be used for identifying a specific redox couple. As such, it is only useful for indicating trends over time of more reducing or oxidizing conditions (Fiedler et al., 2007; Peiffer, 2000).

2.2 | Field experiments

2.2.1 | Study sites

Field experiments were conducted at three sites, all located in the Central Valley, California: (a) an almond orchard at the Kearney Agricultural Research and Extension Center (KARE) located near Parlier; (b) an almond orchard at Nickels Soil Laboratory (NSL) located near Arbuckle; and (c) a cover-crop field (a mixture of bell bean [*Vicia faba* L.], hairy vetch [*Vicia villosa* Roth], and field pea [*Pisum sativum* L.]) at Campbell Tract (CT) located on the west side of the University of California Davis campus. The three sites differ mainly by their soil type and SAGBI rating, whereas the climate is semiarid at KARE and Mediterranean at NSL and CT (Table 1).

		Flooding	Drainage	
Site	Treatment	Depletion	Recovery ^a	Recovery
KARE	air	-0.413 (0.551) ^b	1.23 (1.61)	0.295 (0.526)
	no-air	-0.294 (0.265)	0.372 (0.446)	0.215 (0.332)
СТ	air	-0.187 (0.204)	0.258 (0.582)	0.131 (0.110)
	no-air	-0.253 (0.303)	0.310 (0.462)	0.358 (0.495)

TABLE 3 Soil O_2 depletion and recovery rates (% O_2 h⁻¹) at Kearney Agricultural Research and Extension Center (KARE) and Campbell Tract (CT) shown as average (standard deviation)

^aRecovery rates during flooding were affected by air injection (air treatments only) and/or by short durations of drainage when water applied in cycles. ^bDepletion rates were enhanced by air injection at KARE (see text for more details).

2.2.2 | Experimental design

At each site three treatments were tested: (a) flooding with air injection by subsurface drip irrigation (SDI); (b) flooding without air injection; and (c) control (no flooding and no air injection). The treatments were divided by berms (about 30 cm high, 50 cm wide) to prevent flooding of adjacent plots. Each treatment comprised a row of 11-12 almond trees at KARE and NSL, or four beds of cover crop along 80 m, at CT. Plot area, including all three treatments, was 1,500, 940, and 1,440 m² at KARE, NSL, and CT, respectively. In each treatment, one to four profiles were installed with soil sensors at 15-, 30-, and 50-cm depth. Soil sensors measured volumetric water content (VWC), temperature, gas-phase soil O₂, and Eh (for sensor details see Supplemental Table S1). To complete the Eh measurements, a commercial Ag/AgCl reference electrode was placed in a salt bridge (Veneman & Pickering, 1983) that was installed at a depth of 30 cm at each profile.

Redox potential readings in the field were corrected to standard Eh by adding ~210 mV (based on the average temperature of the soil profile). Soil O₂ readings in the soil were temperature and pressure corrected as recommended by the manufacturer. Note that these galvanic-cell O₂ sensors are diffusion based, and when its membrane is clogged (as may occur under prolonged flooding conditions; Kallestad et al., 2008), it will measure zero O₂ concentration, although a porewater sample from the same location might show higher DO concentration. Still, these sensors are widely used in soil studies (Assouline & Narkis, 2013; Ben-Noah & Friedman, 2016; Friedman & Naftaliev, 2012; Ityel et al., 2014; Kallestad et al., 2008; Turcu et al., 2005) and our experience under flooded conditions shows that this issue is more prominent, as expected, in clayey soils.

All sensors readings were taken every 1 min, and 10-min mean values were recorded with data loggers (Supplemental Table S1). In addition to the continuous monitoring, following the method of Friedman and Naftaliev (2012), air samples were extracted with a 100-ml syringe from perforated 100-ml plastic bottles that were buried inside the soil (only at NSL and CT) at depths of 15, 30, and 50 cm. Air samples were measured onsite with an O₂ flow-through sensor (SO-110, Apogee

Instruments). In several cases where the plastic bottles were filled with pore water, samples were extracted using a syringe and measured onsite for DO with an optic sensor (DP-PSt3, Fibox 4, PreSens). At CT, dedicated pore-water samplers were installed at depths of 15 and 30 cm and used for routine manual measurements of DO. The detailed setup of the three sites is shown in Figure 2.

Both almond sites (KARE and NSL) were regularly irrigated with surface micro-sprinklers, and therefore a dedicated SDI was installed for the air injection treatment as follows: holes were augured to 30-cm depth using a 5-cm- (KARE) or 2.5-cm-diam. (NSL) hand auger and then a 4-mm polyethylene (PE) tube was inserted inside, and the holes were backfilled with a soil-bentonite slurry. This was done carefully using an outer rigid pipe as a guide, to prevent soil clogging of the tubes. The tubes were connected to drippers that were connected to an on-surface lateral line (17-mm PE tube), which delivered the injected air. In order to mimic an SDI system of a commercial orchard, we used a configuration of two lateral lines, each at a distance of 90 cm from the tree trunks, with drippers (2 L h^{-1} for water discharge, WPC, Netafim) at a depth of 30 cm, spaced 120 cm apart (Schwankl et al., 1999). Note that the horizontal distance between the buried emitters centerline and the soil sensors was in the range of 40-60 cm. The cover crop site (CT) was rainfed, and air injection was based on an SDI system (0.8 L h⁻¹ at 100 kPa for water discharge, depth = 30 cm, spacing = 30 cm; Neptune, Toro) that was already installed in the soil for several years. The horizontal distance between the buried emitters centerline and the soil sensors was in the range of 0-15 cm (for a technical summary of the irrigation, flooding, and air injection methods, see Supplemental Table S2).

Each experiment started by flooding the plots (excluding the control row) with groundwater (KARE) or surface water (NSL and CT) using flood-irrigation-gated pipes (KARE and CT) or sprinklers (NSL). Applied water volumes were measured by water meter (KARE) and doppler flow meter (CT). At NSL, the continuous discharge was not measured but applied water volume was estimated manually several times during the experiment using a graduated measuring bucket. Water was applied continuously for a few hours and up to



FIGURE 2 Top view of the field experimental setup at each site. Almond orchards at (a) Kearney Agricultural Research and Extension Center (KARE) and (b) Nickels Soil Laboratory (NSL) (each filled circle represents a tree). Letters represent different almond varieties: $N = Nonpareil, C = Carmel, P = Padre, B = Butte, W = Winters, and A = Aldrich. (c) Cover crop at Campbell Tract (CT). Tables on the right show details on the installed soil sensors: <math>\theta =$ water content, T = temperature, R = soil redox potential, and $O_2 = oxygen$. (d) Location map of the experimental sites in California

1 d, depending on the infiltration rate of each site. When O_2 concentrations started to decline, air was injected through the SDI with a pressure-regulated air compressor (AM1-PH65-08 M, Mi-T-M), which kept the absolute pressure at the range of 160–200 kPa (i.e., within the SDI's regulated range). Air injection was ceased a few hours and up to 2 d after water application ceased. At the end of the experiment at NSL, we conducted a preliminary test of aeration using CaO₂ powder, which reacts with water to produce O₂ and H₂O₂ (which

decomposes further to O_2). A 600 g of CaO₂ powder was scattered on the soil surface, covering an area of 9 m² around one tree only (Tree 3 in the air treatment row), and a small amount of water was sprayed over it.

Gross almond yield was collected per tree for all varieties at KARE and for the Nonpareil variety at NSL at the end of August after the recharge season. At CT, plant height, dry root length, and dry root weight of bell beans were measured before and after the flooding experiment. Plant sampling included careful excavation of the roots using a shovel, measurement of stem height in the field, washing roots in the laboratory, and measuring dry root weight and vertical root length. From each treatment 12 bell beans plants were sampled (i.e., four plants from each profile) before and after the flooding experiment, and a total of 68 plants were analyzed (Profile 3 after flooding in the control treatment was omitted because it was affected by flooding). Root weight was normalized to root vertical length and plant height, to reduce the sampling error due to natural variability in root and plant morphology, and averages values were calculated for each treatment.

2.2.3 | Statistical analysis

Data were analyzed using ANOVA performed with the software R (version 3.6.1; R Core Team, 2019). A one-way ANOVA was applied to the manually collected data (soil O_2 and plant indices) and differences between means were determined with Tukey's test (p < .05). Continuous data collected with sensors (soil water content, O_2 , redox, and temperature) were not analyzed with ANOVA due to heteroscedasticity and lack of independence of the high-resolution continuous measurements. For these measurements, we report the summary statistics and compare the distribution of differences of the soil aeration quantifiers (ΔO_2 and ΔEh) between the treatments with and without air injection.

3 | RESULTS

3.1 | Water application

Water was applied continuously at all sites according to the site-specific infiltration rate, in order to maintain a ponding depth of few centimeters. To avoid flooding of adjacent plots, the water supply was decreased or stopped occasionally during the experiment. Although maintaining even flooding within the flooded treatments was a difficult task at all sites (due to soil-surface irregularities), it was practically impossible at the NSL site due to a combined effect of poor soil drainage and plot slope (towards the northeast corner of the air treatment; Figure 2b). Nevertheless, an estimated total water amount per area of 0.76, 0.065, and 2.9 m, was applied at KARE, NSL, and CT, respectively (Table 2). Note that these estimations are averages that are based on the total plot area (as opposed to the actual flooding area). Although at KARE flooded area and total plot area were almost identical, at NSL and CT, it represents lower and upper bounds for the total applied water, due to smaller and larger effective flooding area, respectively.

3.2 | Soil aeration status

Flooding of the plots led to the expected trend of increasing soil water content (θ_w) and decreasing O₂ and redox (Eh) levels, whereas at the control treatments, high soil aeration status was observed at relatively low θ_w . An example of the soil aeration status is shown in Figure 3, where for each site one profile from each treatment at 30-cm depth is presented (the full dataset is shown in Supplemental Figure S1). For the airinjection treatments, the impact of air injection on soil aeration status can be detected as an increase in O₂ and Eh levels during air-injection periods; it is limited at KARE and NSL, but consistent at CT (Figure 3).

The distribution of the continuous measurements of all sensors at all depths is summarized in Figure 4, where results are grouped according to treatment and period. The period before air injection was defined as the time before the first air injection started, the period during air injection includes active air injection and the times between air injection cycles, and the period after air injection starts when the last injection ends. Accordingly, in all flooded treatments (excluding the air-injection treatment at CT), aeration status decreased below the soil-aeration lower bounds (5% O_2 and Eh of 300 mV for this study) for few hours at CT, a few days at KARE, and up to several days at NSL (Supplemental Table S3). At NSL, hypoxic to anoxic, and anaerobic conditions were mainly observed in the air-injection treatment, likely as a compounding effect of plot slope and specific poor-drainage conditions where the soil sensors were located (Supplemental Figure S2). After the air-injection period (during drainage), all sites except NSL showed a similar recovery in soil aeration status in all flooded treatments (see trendlines in Figure 4), which is another indication of the local drainage issue at NSL.

The average impact of air injection varies among sites. The impact was small at CT (for each depth an average increase of up to $\sim 2\%$ in O₂ and up to ~ 75 mV in Eh) compared with the flooded treatment without air injection, whereas no impact and even negative impact was observed at KARE and NSL (Figure 5). However, the wide variability in O₂ data in the air-injection treatments at KARE and NSL implies that air injection may improve the aeration status for a limited time (as demonstrated in Figures 3 and 5).

The fast increase in soil O_2 at the end of the experiment at NSL is the result of the CaO₂ preliminary test (applied only at one tree), which demonstrates the potential of this technique for improving soil O_2 during Ag-MAR (Figure 3, dashed line in the air treatment).

The soil sensors measurements presented in Figures 3-5 provide continuous high-resolution temporal data, but with limited spatial resolution. A complementary spatial description of the soil aeration status was obtained by the manual



FIGURE 3 Soil temperature, aeration quantifiers (O_2 , soil redox potential) and volumetric water content of all treatments at 30-cm depth in Kearney Agricultural Research and Extension Center (KARE), Nickels Soil Laboratory (NSL), and Campbell Tract (CT). Only selected trees and profiles are shown: KARE Trees 9, 10 and 2 for air, no-air, and control; NSL Trees 3, 4, and 4 for air, no-air, and control; CT Profile 2 for all treatments (see specific location of trees and profiles in Figure 2). The dashed line in the air-injection treatment of NSL represents O_2 increase due to calcium peroxide (see details in Section 4.5)

measurements of soil O₂ (Figure 6; measurements were taken only at NSL and CT). At NSL, these measurements show results that differed from the continuous measurements (Figure 4), indicating that air injection improves average O₂ levels by ~1% compared with the flooded treatment without air injection, at 15 cm (p = .13, probably due to small sampling size, n = 5) and at 30-cm depth (p < .05), whereas no impact was observed at 50-cm depth. At CT, the manual soil O₂ measurements are consistent with the continuous measurements, showing improvement of up to ~2% O₂ at all depths.

3.3 | Plant indices

For the experiments at the almond orchards, gross yield was measured during the harvest season after the Ag-MAR experiments. At KARE, the Nonpareil was the only variety that showed a higher average yield in the air-injection treatment than the no-air injection treatment (p < .01), whereas all other varieties showed no statistical difference between treatments (Figure 7a). At NSL, the average yield of the air-injection treatment was lower than the no-air injection treatment (p < .05), but this yield



FIGURE 4 Distribution of all the continuous measurements at Kearney Agricultural Research and Extension Center (KARE), Nickels Soil Laboratory (NSL), and Campbell Tract (CT). Each boxplot represents all the measurements of a specific treatment at all depths, at different times (before, during, and after air injection). Outliers were omitted for clarity

reduction is correlated with annual precipitation, which implies a drainage issue in the specific row of the air treatment (Figure 7b).

At CT, plant indices measured before and after the experiment showed an average decrease for the no-air injection treatment, whereas an increase was observed for the air-injection and the control treatments (Figure 7c). Changes were not statistically different based on a significance level of $\alpha = .05$ (Tukey's test), but the difference between the no-air injection and the control treatments after flooding is significant at the significance level of $\alpha = .1$ (dry root weight/length: p = .0535; dry root weight/plant height: p = .0663).

4 | DISCUSSION

4.1 | Water application

The water application results demonstrate the degree of suitability of the selected sites for Ag-MAR projects in terms of infiltration rates. Both the KARE and CT sites are suitable for Ag-MAR, as their infiltration rate is greater than 1 m in a few days (Kourakos et al., 2019), whereas the low infiltration rate measured at NSL makes the site unsuitable for Ag-MAR. Indeed, the NSL site was selected in this study to demonstrate the difference among Ag-MAR sites with different soil texture, SAGBI class, and hydraulic



FIGURE 5 Distribution of ΔO_2 and ΔEh (where Eh is redox potential) during active air injection. Each count represents a 10-min average. Δ is the difference between measurements in the air and no-air flood treatments. Hence, positive and negative Δ values represent the positive and negative (or lack of) impact of air injection, respectively

properties. The soil at NSL has a SAGBI rating of moderately good to poor (Table 1), which illustrates the role that SAGBI has as a first approximation planning tool for locating potential Ag-MAR sites. However, the final selection of an Ag-MAR site should also consider the growers' experience (who are usually familiar with the infiltration and drainage patterns of their fields). Apart from soil suitability for Ag-MAR, technical constraints (e.g., water availability and distribution system) and agronomic constraints (e.g., crop suitability, pesticide, and fertilizer application) should all be considered when designing an Ag-MAR project (Flores-Lopez et al., 2019).

Naturally, well-drained soils, which are more suitable for Ag-MAR, are also well aerated. This characteristic is manifested in the flood-drainage intervals (as used in this study at CT) that allow reaeration of the soil during drainage, even without the use of forced aeration. Conversely, poorly drained soils (such as found at NSL) are unsuitable for Ag-MAR, even if forced aeration can maintain adequate soil aeration status, due to the low infiltration rates and insufficient deep percolation that these soils achieve, which does not promote recharge of large amounts of water to the groundwater.

4.2 | Soil aeration quantifiers

4.2.1 \mid O₂ and Eh

Ideally, O_2 and Eh measurements are complementary soil aeration quantifiers for aerobic and anaerobic conditions, respectively. In this study, the duration of soil saturation was shorter than 48 h at all sites (excluding the sloping ponded patch at NSL, Supplemental Figure S2), and therefore root zone residence time was relatively short, and aerobic conditions prevailed most of the time.

Besides the duration of saturation, soil aeration status is also affected by soil respiration, which differed among the sites. Based on the O_2 measurements of the control treatments (i.e., assuming low O_2 concentration represents high respiration rates and vice versa), the lowest soil respiration rates were observed in the almond experiment during the winter (KARE), followed by higher rates in the cover crop during the spring (CT), whereas the highest rates were observed in the almonds during the summer (NSL). The increase in soil respiration with increasing temperatures is well documented, and generally soil respiration increases by a factor (commonly known as Q_{10}) of two to three for a temperature increase of 10 °C (Ben-Noah & Friedman, 2018).



FIGURE 6 Distribution of the manual measurements of soil O_2 for depths of 15, 30, and 50 cm. Nonshared letters indicate statistical difference (p < .05). NSL, Nickels Soil Laboratory; CT, Campbell Tract

The relationship between O2 and Eh measurements is complex, as sometimes high O_2 levels may coexist with low Eh levels, and vice versa (Figure 8a). Some of this complexity can be explained by the lag of Eh behind O2 in response to flooding. Data showing this Eh-O₂ lag can be found in a handful of studies (Blackwell, 1983; Cannell et al., 1985; Mukhtar et al., 1996), but Blackwell (1983) was the only one who explicitly related this lag to the soil volume over which the measurement is integrated. Blackwell (1983) concluded that O_2 measurements are more affected by large pores compared with redox measurements that are measured by a small-size electrode. Some of our data support this explanation as indicated by the Eh minima, which lags up to 20 h behind the O_2 minima, which might correspond to the lag in draining small pores vs. larger pores during soil drainage. Another explanation for the lag in Eh readings is related to slow reaction kinetics and mixed potentials, where the latter is inherent in most measurements done with redox electrodes (Fiedler et al., 2007). Hence, to obtain an unbiased result of the soil aeration status during Ag-MAR, a paired measurement of O2 and Eh is needed even in relatively well-drained soils with short flooding events (such as KARE in this study).

Based on our O_2 and Eh measurements and the results of previous studies (Rubol et al., 2012; Song et al., 2019; Wang et al., 2018), denitrification will probably occur dur-



FIGURE 7 Plant indices. (a) Almond gross yield at Kearney Agricultural Research and Extension Center (KARE, four varieties) and Nickels Soil Laboratory (NSL, only nonpareil); nonshared letters indicate statistical difference (p < .01). (b) Normalized yield vs. annual rain at NSL. (c) Dry root weight to root length ratio (left) and dry root weight to plant height ratio (right) at Campbell Tract (CT)

ing Ag-MAR even in well-drained soils. This may promote N_2O emissions as well as prevent NO_3^- leaching to groundwater. The Eh results from KARE demonstrate that during an Ag-MAR event the soil may reach anaerobic conditions even in well-drained soils. At KARE, moderately reducing conditions (300 > Eh > -50 mV) were observed for up to 2 d (Supplemental Table S3), which can promote sequential reduction reactions according to the thermodynamic theory. However, in oxic terrestrial soils, some of these reactions may occur simultaneously; for example, reduction of NO_3^- followed by concurrent reduction of Mn^{4+} , SO_4^{2-} , and Fe³⁺ (Peters & Conrad, 1996). Although these chemical species are stable



FIGURE 8 Correlation in the flooded treatments. (a) Redox potential (Eh) and O_2 ; semitransparent symbols show the periods before and after air injection; opaque symbols show air-injection periods. (b) Water content and O_2 (only the air-injection periods are shown). KARE, Kearney Agricultural Research and Extension Center; NSL, Nickels Soil Laboratory; CT, Campbell Tract

under aerobic conditions, upon flooding they might undergo reduction and might get released from the solid phase into the soil solution, thereby changing the biogeochemical state of the soil and increasing the risk of groundwater contamination (De-Campos et al., 2012).

4.2.2 \mid O₂ and water/air content

Soil O_2 is negatively correlated with soil water content, as high water content reduces the soil O₂ diffusivity and air permeability (Ben-Noah & Friedman, 2016). At the same time O_2 demand by microbial respiration increases, as it highly depends on water content (Or et al., 2007). A similar negative correlation was observed in this study, but in the air injection treatment, higher O₂ levels at relatively higher water contents were observed, which indicates the positive impact of air injection. At the same time, a negative impact of air injection (i.e., relatively low O2 levels compared with the noair-injection treatment) was observed for some trees at KARE (Figure 8b). This negative impact can be explained by the injected air that pushes the pore water towards the O₂ sensors. In this case, the readings of the galvanic O₂ sensors might be different from the actual DO concentration of the pushed pore water (see more discussion on DO in the Section 4.2.3).

Under flooded conditions that are expected in Ag-MAR, O_2 levels will decrease sharply after the water content reaches some critical value. Bachand et al. (2019) suggested a critical value of 74% degree of saturation (θ_w/ϕ) in their report on Ag-MAR and soil O₂, although a critical value based on aircontent is a better quantifier, as it represents an absolute value that can be compared across soils with different porosities (Cook et al., 2013). We calculated the effective volumetric air content at each site based on the VWC data ($\theta_{a,eff} = \theta_{w,max}$ - θ_w) of each sensor. The term effective volumetric air content is used here because we assume it represents only the conducting gas-phase fraction ($\theta_{a.eff} < \theta_a$; Ben-Noah & Friedman, 2018). Omitting the data of air injection and drainage stage, we set the critical air content upper bound as $\theta_{a \text{ eff}} \approx 0.09$ based on the inflection points of O2 levels, identified using a smoothed moving average procedure (Figure 9). It is noted that identifying the critical air content based on this method can be somewhat subjective and that the critical value is subjected to the accuracy of the water content sensors ($\pm 0.02 \text{ m}^3 \text{ m}^{-3}$ in this study). As noted by Bachand et al. (2019), reaching the critical air content is inevitable during Ag-MAR flooding, and therefore attaining hypoxic/anoxic conditions will depend on the soil O₂ depletion/recovery rates and on the flooding duration.

We calculated the average soil O_2 depletion/recovery rates for sites KARE and CT, as each represents a potential site for



FIGURE 9 Impact of effective volumetric air-content on soil O_2 levels during flooding at all sites. Data of active air injection, and the drainage stage were omitted. The shaded area and dashed lines represent the range of critical air content for the three sites. KARE, Kearney Agricultural Research and Extension Center; NSL, Nickels Soil Laboratory; CT, Campbell Tract

Ag-MAR operation (Table 3). The average depletion rate is lower than 0.3% $O_2 h^{-1}$, hence an O_2 reduction from atmospheric conditions to 5% O_2 (this study lower bound) will take about 2 d for the soils tested here. Average recovery rates, excluding the active injection periods, are on the same order as the depletion rates, and usually the recovery rates are higher at the beginning of the reaeration stage, and then level off over time (i.e., O_2 recovery is a concave-down increasing function). Our observed average depletion rates are higher than the maximum depletion rates reported by Bachand et al. (2019) by up to ~0.1% $O_2 h^{-1}$. This is probably because their water application was more conservative compared with this study (i.e., less water was applied over longer periods).

4.2.3 | Dissolved oxygen

Under waterlogged conditions the galvanic gas-phase soil O_2 sensors might malfunction (see details in Section 2), returning low or zero O₂ readings, whereas the actual DO of the pore water might be higher. An example for this condition was observed at NSL, where we measured sporadically DO in water samples that were extracted from the air samplers at depths of 15, 30, and 50 cm (we took advantage of the fact that some of the air samplers were filled with pore water). In addition, we also measured a few DO samples of ponded and irrigation water. Although the total sampling amount was relatively small (n = 33), it better represents the aeration status for some trees. For example, at Tree 3W, 15-cm depth, the DO is always higher than 0.5 O_2 saturation (>4 in mg L⁻¹) or > 10 in $\%O_2$; Figure 9a; where O_2 saturation = measured DO [mg L^{-1}]/DO [mg L^{-1}] at 100% saturation) compared with 0% O₂ obtained with the galvanic soil O₂ sensor (Supplemental Figure S1b). These measurements also demonstrate

the impact of air injection on DO, as the trend of increasing DO during air injection periods is evident for all measured trees (Figure 10a). At CT, we were able to extract more DO samples using dedicated pore-water samplers. Dissolved O_2 levels fluctuated according to water application events and for the air-injection treatment also by the duration of air injection (Figure 10b).

Under flooded conditions, it is difficult to monitor the gas phase in the soil (due to technical limitation as well as the heterogeneity of the air-filled pores), and therefore DO measurements might be more suitable as soil aeration quantifier in Ag-MAR. Reliable in situ DO measurements can be achieved using optic sensors; however, its spatial resolution is still limited due to the relatively high costs of these sensors (Bhattarai et al., 2006).

4.3 | Plant response

The almond yield at KARE showed no statistical difference between the treatments, except for the Nonpareil variety that showed higher yield for the air treatment compared to the noair treatment (Figure 7a). This result is encouraging, but it should be taken with caution as it is based on only a few trees, and it might not correlate directly with the impact of Ag-MAR flooding, because yield in almond trees is commonly determined by the nutrient and water management practices of the previous growing seasons (Esparza et al., 2001).

The impact of flooding on almond yield was not studied systemically previously, although few studies on deficit irrigation showed yield reduction either by insufficient or excess irrigation (Collin et al., 2019; Goldhamer & Fereres, 2017). Still, these reported yield reductions are due to overirrigation throughout the entire growing season and not due to occasional flooding. In this study, the yield results of the air treatment at NSL (Figure 7a-7b) demonstrate the potential negative impact that Ag-MAR may have on almond yield in poorly aerated soils. Previous studies on flooding in almond seedlings (Wicks & Lee, 1985), and 1-yr-old almond trees (Sanchez-Blanco et al., 1994) demonstrated sensitivity to waterlogging which can lead to tree mortality. This sensitivity, also related to root diseases such as Phytophthora, varies among different almond varieties and Prunus rootstocks (Micke, 1996).

At CT, the decrease in plant indices for the no-air-injection treatment compared with the other treatments was due to a reduction in the dry root weight of the cover crop after flooding. Although these changes were not statistically significant, they agree with several studies that showed a reduction of root weight in bell beans under water-logged soils. This reduction is related to the formation of adventitious roots and aerenchyma with higher root porosity, which helps the plant to transport O_2 from the soil surface and the stem, in order



FIGURE 10 Dissolved O_2 manual measurements. (a) Air-injection treatment at Nickels Soil Laboratory (NSL). (b) Three profiles of air and no-air treatments at Campbell Tract (CT)

to reduce flooding injury (Munir et al., 2019; Pampana et al., 2016; Solaiman et al., 2007).

4.4 | Impact of forced aeration

Based on the results of the soil aeration quantifiers at CT, forced aeration by air injection can improve the soil aeration status during Ag-MAR. However, based on the same quantifiers, the results from KARE and NSL show a minor impact of air injection. This discrepancy can be explained by (a) the SDI system that delivered the injected air, (b) emitter density, and (c) the location of the soil sensors relative to the emitters. The ad-hoc SDI that we installed at KARE and NSL was suffering from the "chimney-effect," a well-known phenomenon in air sparging where air (a buoyant, nonwetting fluid) flows quickly upward to the soil surface through large pores without penetrating laterally into smaller pores (Ben-Noah & Friedman, 2016; Elder & Benson, 1999). Suggested methods to overcome the "chimney effect" include increasing the injection depth and pulse-mode injection (Ben Neriah & Paster, 2017, 2019; Ben-Noah & Friedman, 2019; Ben-Noah et al., 2020). At CT, the SDI was already established for several years and emitter density was higher compared with KARE and NSL. In addition, soil sensors at CT were installed closer to the emitters compared with KARE and NSL, and therefore were closer to the zone of influence (ZOI) of the emitter. As the injected air does not spread homogenously in saturated soil, the ZOI comprises an ensemble of discrete air channels extended from the injection point upwards, separated by zones fully saturated with water, which together form a parabolic plume shape (Selker et al., 2007). The ZOI depends on the soil type, air-injection depth, and flow rate (Ben Neriah & Paster, 2017; Ben-Noah & Friedman, 2019; Hu et al., 2010; Selker et al., 2007). Generally, fine soils, deep injection depths, and high flow rates increase the ZOI compared with coarse soils, shallow injection depths, and low flow rates. In this study (and whenever a pre-installed SDI is used for air injection), these parameters were given by the soil texture at each site and the design of the installed SDI system. For an injection depth of 30 cm in fine sand, the ZOI has the range of several centimeters and up to ~50 cm (Ben Neriah & Paster, 2017; Hein et al., 1997; Hu et al., 2010; Ji et al., 1993; Selker et al., 2007; Semer et al., 1998), which explains why at KARE and NSL the effect of air injection was barely detected by the soil sensors (installed 40-60 cm from the emitters). Given this ZOI, even for a well-established SDI system, it is still questionable whether the density (120-cm spacing, double line) and depth (30 cm) of the emitters at KARE and NSL can support significant aeration through air injection. On the other hand, in an orchard originally planted with SDI, active roots will be found within the air-injection ZOI, as root density is expected to be higher next to the emitters (for efficient water uptake).

Our DO measurements at NSL and CT demonstrate that forced aeration by air injection can increase the DO in saturated soils (Figure 10). A similar approach is used in hydroponics and soilless media where active aeration of the nutrient solution is a common growing practice to avoid the decrease of DO below 3–4 mg L⁻¹, which inhibits root growth (Trejo-Téllez & Gómez-Merino, 2012). However, it is still unclear whether air injection can support root respiration of woody perennials under complete water-logged conditions.

In this study, air was injected into the soil after the water content reached saturation (or close to saturation). However, as discussed above, under these conditions the spreading of the injected air is limited, and O_2 diffusion rates are significantly reduced. Alternatively, injection of air during the infiltration stage (before the soil reaches saturation) and/or during the drainage stage, might be more effective in reducing and enhancing soil O_2 depletion and recovery rates, respectively. A similar approach resulted in increased yield of greenhouse cucumbers under both SDI and furrow irrigation, aerated by air injection after the irrigation cycles (Niu et al., 2013); however, further study is needed to evaluate the benefit of this approach in Ag-MAR.

Our soil O_2 results agree with the results of forced aeration air-injection experiments conducted in barrels with peppers (Ben-Noah & Friedman, 2016) and at a citrus orchard (Ben-Noah et al., 2021). Our DO results agree with studies that used aerated irrigation (oxygation) through SDI in several crops (Chen et al., 2011; Lei et al., 2016; Zhu et al., 2019). However, most aeration studies report only plant indices for assessing the impact of active aeration (see Table 3 in Ben-Noah & Friedman, 2018).

The impact of air injection on plant indices was not statistically different at all sites (excluding the positive impact in the Nonpareil variety at KARE). However, this finding is based on only one growing season with air-injection treatment. At CT, Ag-MAR flooding was applied daily, generating flood/drainage cycles that probably reduced the flood-related stress of the cover crops.

4.5 | Implications

Regulating the aeration conditions of the soil during Ag-MAR can be achieved by natural aeration (i.e., controlling flood and drainage duration) and by forced aeration methods. Controlling the flood/drainage duration is an efficient and inexpensive way to ensure adequate soil aeration during Ag-MAR. However, maintaining even flooding in a fieldscale Ag-MAR project is a major challenge due to surface irregularities (topography) and soil heterogeneity, which is found in most agricultural fields (the NSL site in this study demonstrates how field slope negatively affects soil aeration and yield). For these reasons, careful inspection of the potential Ag-MAR site must be made before initiating Ag-MAR project, and a small-scale pilot is recommended. In many cases, nonuniform infiltration is expected (Ulrich et al., 2017; Wang et al., 2003) that will lead to nonuniform soil aeration conditions and can result in hypoxic or anoxic zones. As observed at the NSL site, these zones are a limiting factor for implementing large-scale Ag-MAR projects and may benefit from a local forced aeration treatment. Hence, air injection, even for a short duration of a few hours, can be beneficial and easily implement in field-scale Ag-MAR projects (e.g., using a mobile compressor to cover large acreage).

Implementing forced aeration by air injection requires agricultural fields with pre-installed SDI, which are less abundant in some crops. In California, SDI is commonly used in annual crops (e.g., tomato [*Solanum lycopersicum* L.], corn [Zea mays L.]) and to a lesser extent in perennial crops (Ayars et al., 2015). When SDI is unavailable other forced aeration methods can be used. For example, we are currently testing the application of peroxide fertilizers during Ag-MAR, because O_2 (and H_2O_2) is released when solid peroxides react with water. An example of O_2 response to an application of CaO₂ was shown in this study for one tree at the end of the experiment at NSL. The main limitations of this aeration method are its high costs and the limited control of its decomposition rate (Ben-Noah & Friedman, 2018).

5 | SUMMARY

Soil aeration is an important parameter in Ag-MAR, as prolonged flooding may result in yield loss due to soil O₂ deficiency. In this study, we tested whether forced soil aeration by air injection improves the soil aeration status compared with natural soil aeration during Ag-MAR flood experiments in three sites differs by their soil drainage grade and SAGBI index. Our results show that forced aeration increases soil O₂ content by up to 2% O₂ (and Eh of up to ~75 mV), but without a significant impact on yield. We suggest that adequate soil aeration during Ag-MAR should be regulated by flood duration, which can be estimated based on soil O_2 depletion rates but recognize that data of O₂ depletion rates during flooding for various soils and crops is currently limited. Forced aeration methods might be useful to mitigate local hypoxic/anoxic conditions that are expected to form during large-scale Ag-MAR projects due to surface irregularities and spatial variability of drainage properties. However, this study was only an initial attempt to apply forced aeration during Ag-MAR, and further research is needed to determine whether it is beneficial for Ag-MAR projects in terms of other forced aeration methods, timing and duration, costs, and applicability.

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AUTHOR CONTRIBUTIONS

Yonatan Ganot: Conceptualization; Data curation; Formal analysis; Funding acquisition; Investigation; Methodology; Visualization; Writing-original draft; Writing-review & editing. Helen E. Dahlke: Conceptualization; Funding acquisition; Methodology; Resources; Supervision; Writingreview & editing

CONFLICT OF INTEREST

The authors declare no conflict of interest.

DATA AVAILABILITY STATEMENT

The data of this study is available upon request from the first author via email (yganot@ucdavis.edu).

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

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