

## Supplementary Material

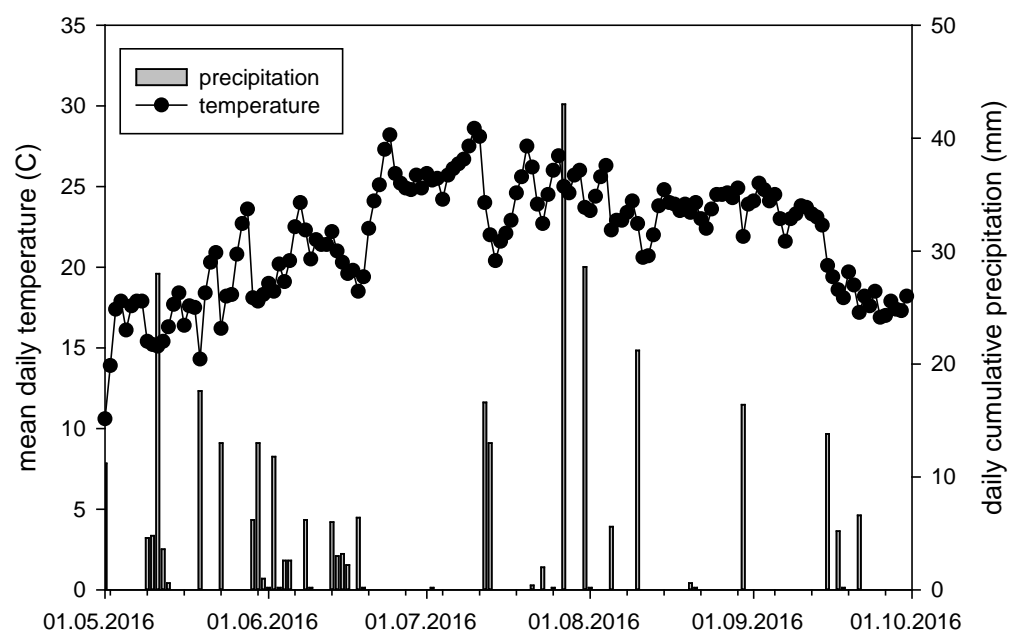


Figure S1. Mean daily air temperature and daily cumulative precipitation during the growing season. Data was retrieved from a weather station approximately 200 m from the field site, operated by the Agenzia Regionale per la Protezione dell'Ambiente-Lomardia (ARPA).

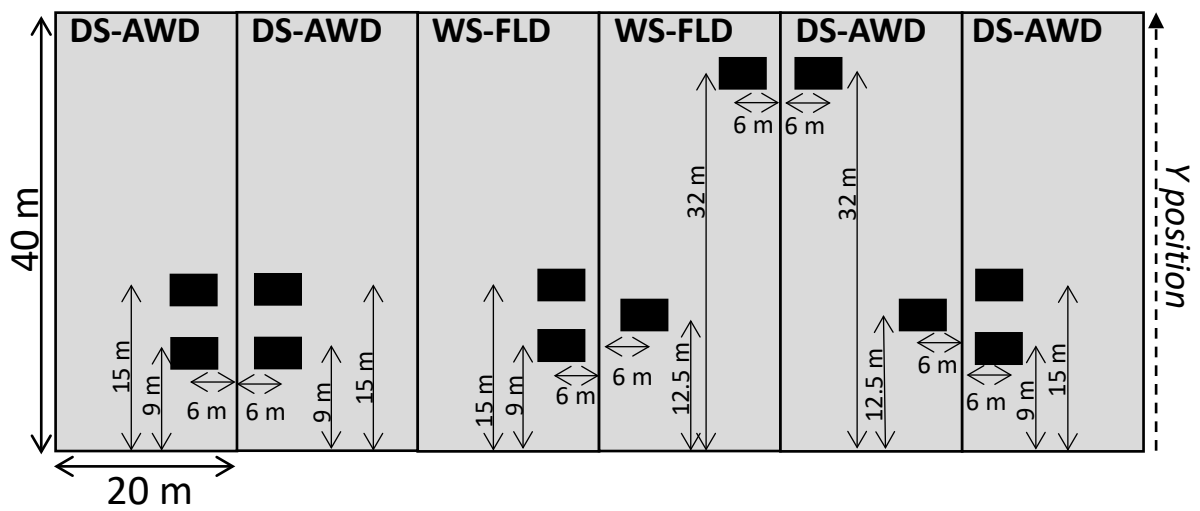


Figure S2. Experimental design and plot layout

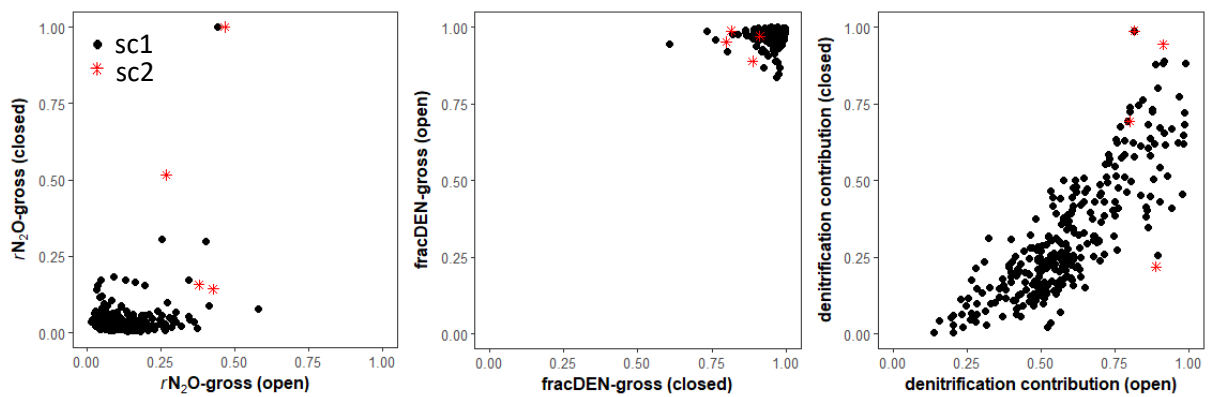


Figure S3. Comparison of modeled  $rN_2O$ ,  $fracDEN$ -gross, and  $DenContribution$  under open and closed system dynamics for scenario one (sc1) and scenario two (sc2).

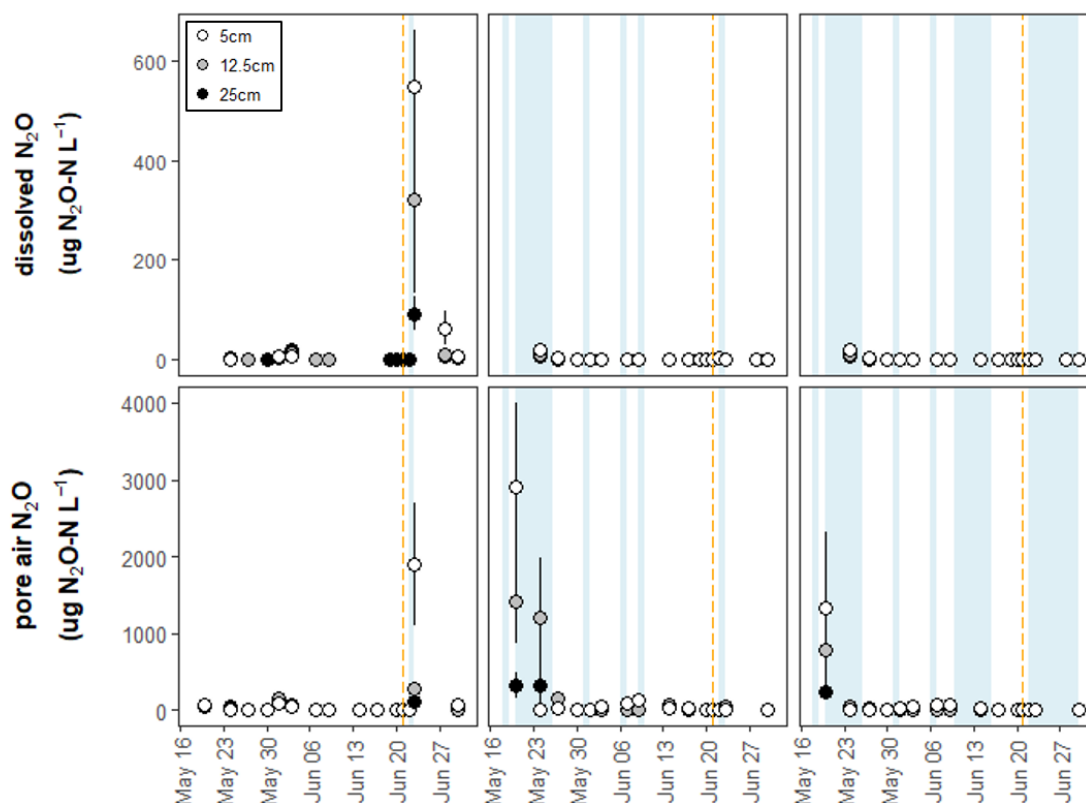


Figure S4. Dissolved and pore air  $\text{N}_2\text{O}$  throughout the experimental period in the three water management treatments (WS-FLD = wet-seeding + conventional flooding; WS-AWD = wet-seeding + alternate wetting and drying; DS-AWD = direct dry seeding + alternate wetting and drying). The dashed vertical line indicates the date of fertilization ( $60 \text{ kg urea-N ha}^{-1}$ ). Blue shaded areas represent periods of flooding, shaded areas that last only one day indicate a 'flush irrigation' = flooding for  $< 6 \text{ hrs}$ . The error bars represent the standard error of the mean.

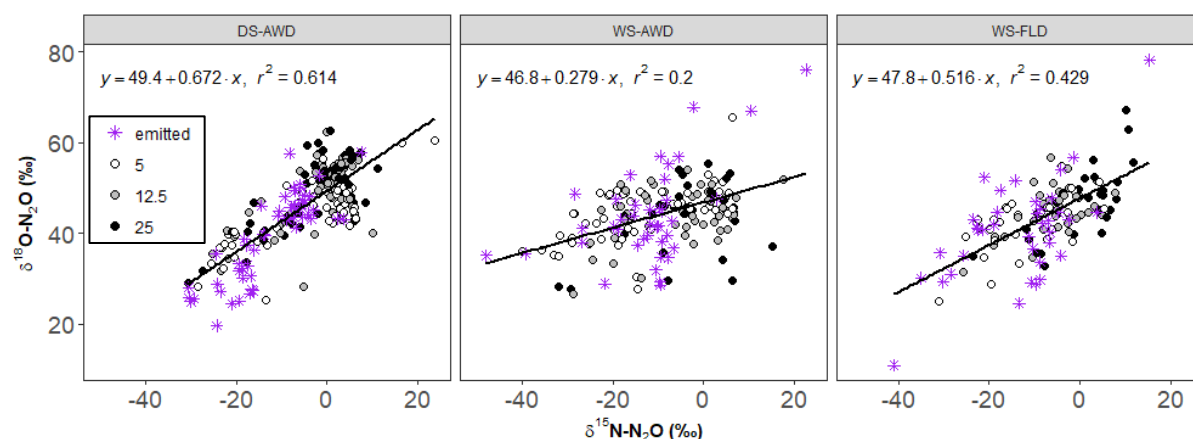


Figure S5. The relationship  $\delta^{18}\text{O}-\text{N}_2\text{O}$  with  $\delta^{15}\text{N}-\text{N}_2\text{O}$  in  $\text{N}_2\text{O}_{\text{emitted}}$  and  $\text{N}_2\text{O}_{\text{poreair}}$ .

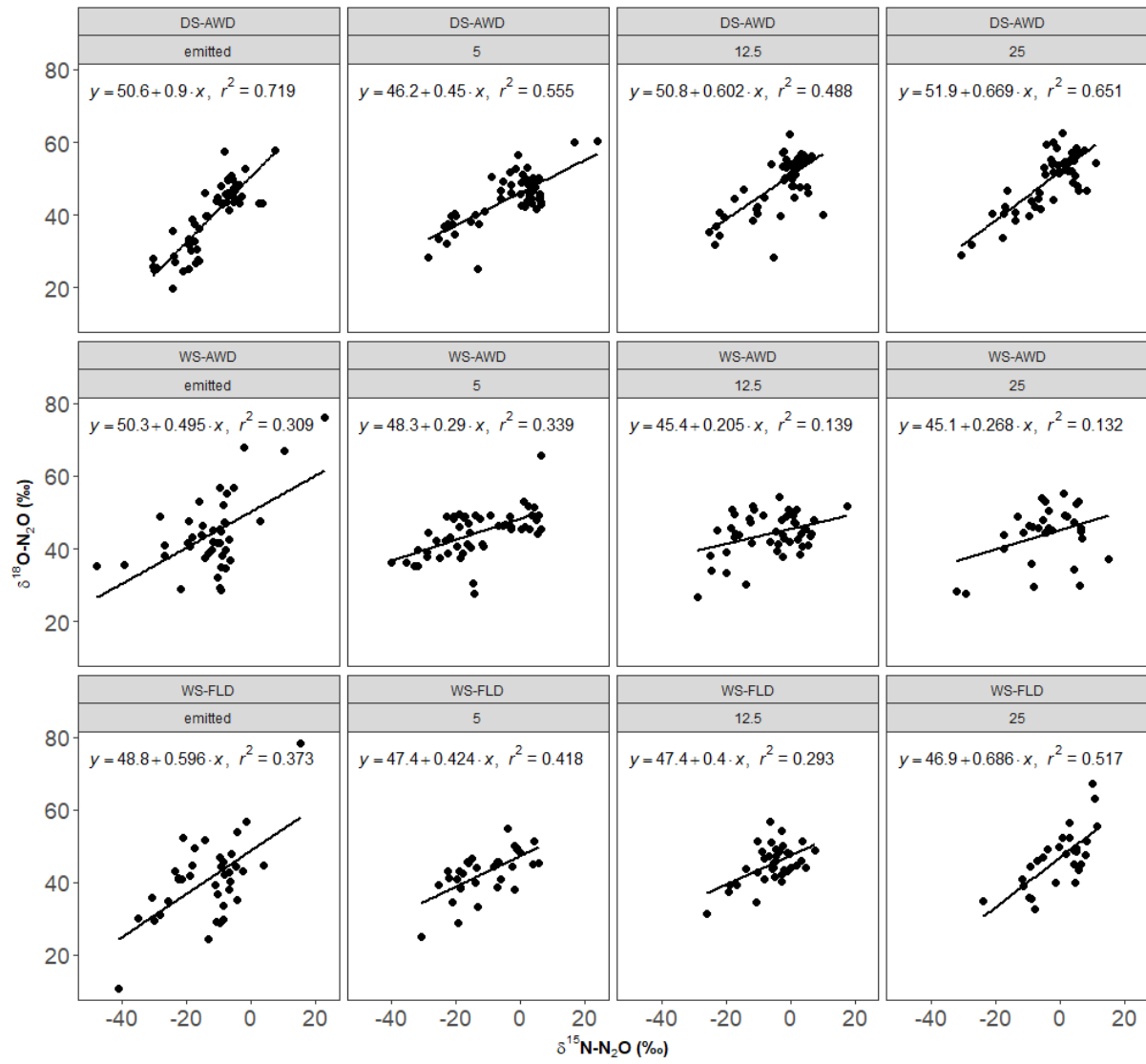


Figure S6. The relationship of  $\delta^{18}\text{O-N}_2\text{O}$  with  $\delta^{15}\text{N-N}_2\text{O}$  in  $\text{N}_2\text{O}_{\text{emitted}}$  and  $\text{N}_2\text{O}_{\text{poreair}}$ , differentiated by depth. Non-significant relationships are indicated by NS.

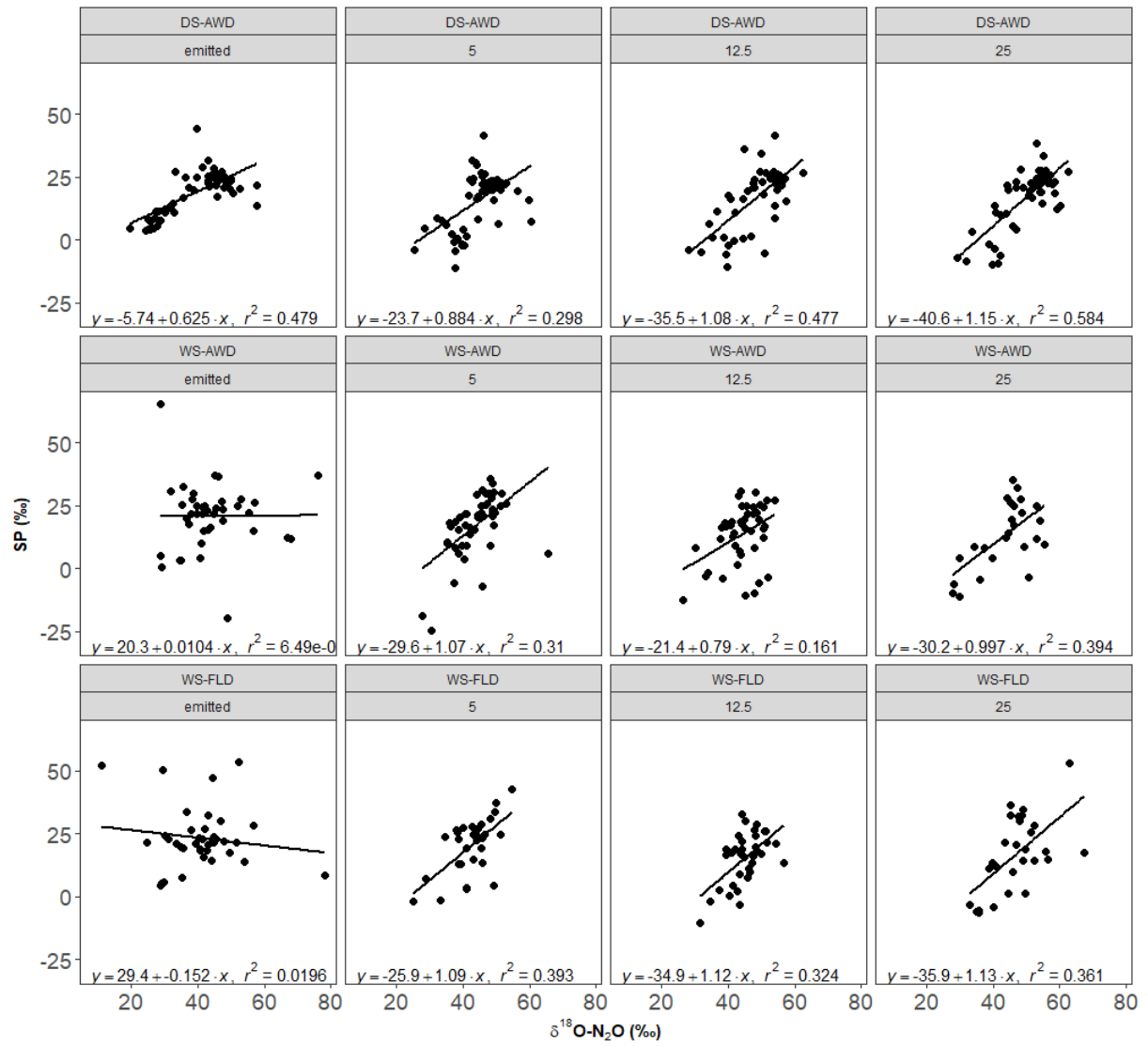


Figure S7. The relationship of SP with  $\delta^{18}\text{O-N}_2\text{O}$  in  $\text{N}_2\text{O}_{\text{emitted}}$  and  $\text{N}_2\text{O}_{\text{poreair}}$ , differentiated by depth. Non-significant relationships are indicated by NS.

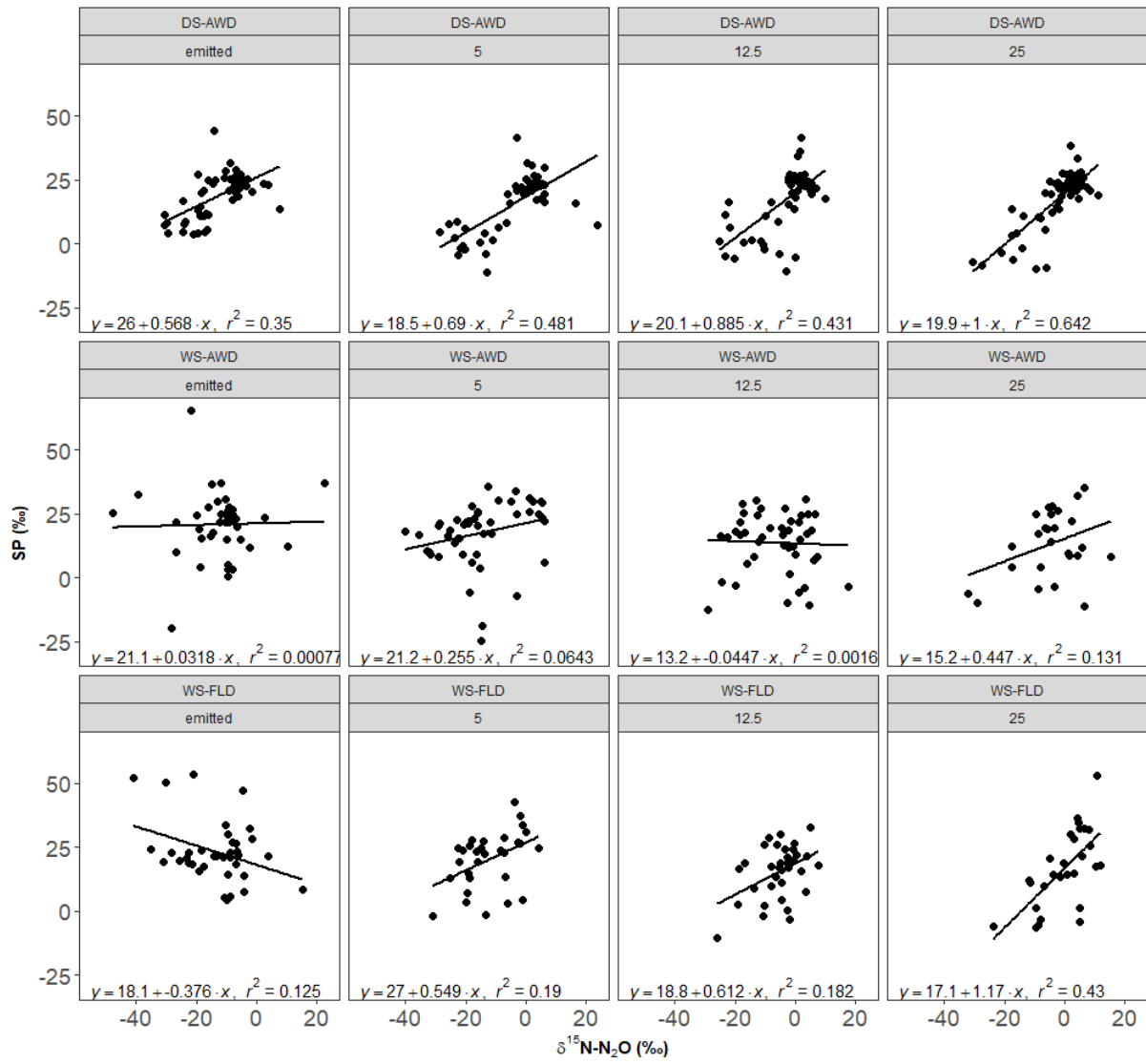


Figure S8. The relationship of SP relative to  $\delta^{15}\text{N-N}_2\text{O}$  in  $\text{N}_2\text{O}_{\text{emitted}}$  and  $\text{N}_2\text{O}_{\text{poreair}}$ , differentiated by depth. Non-significant relationships are indicated by NS.

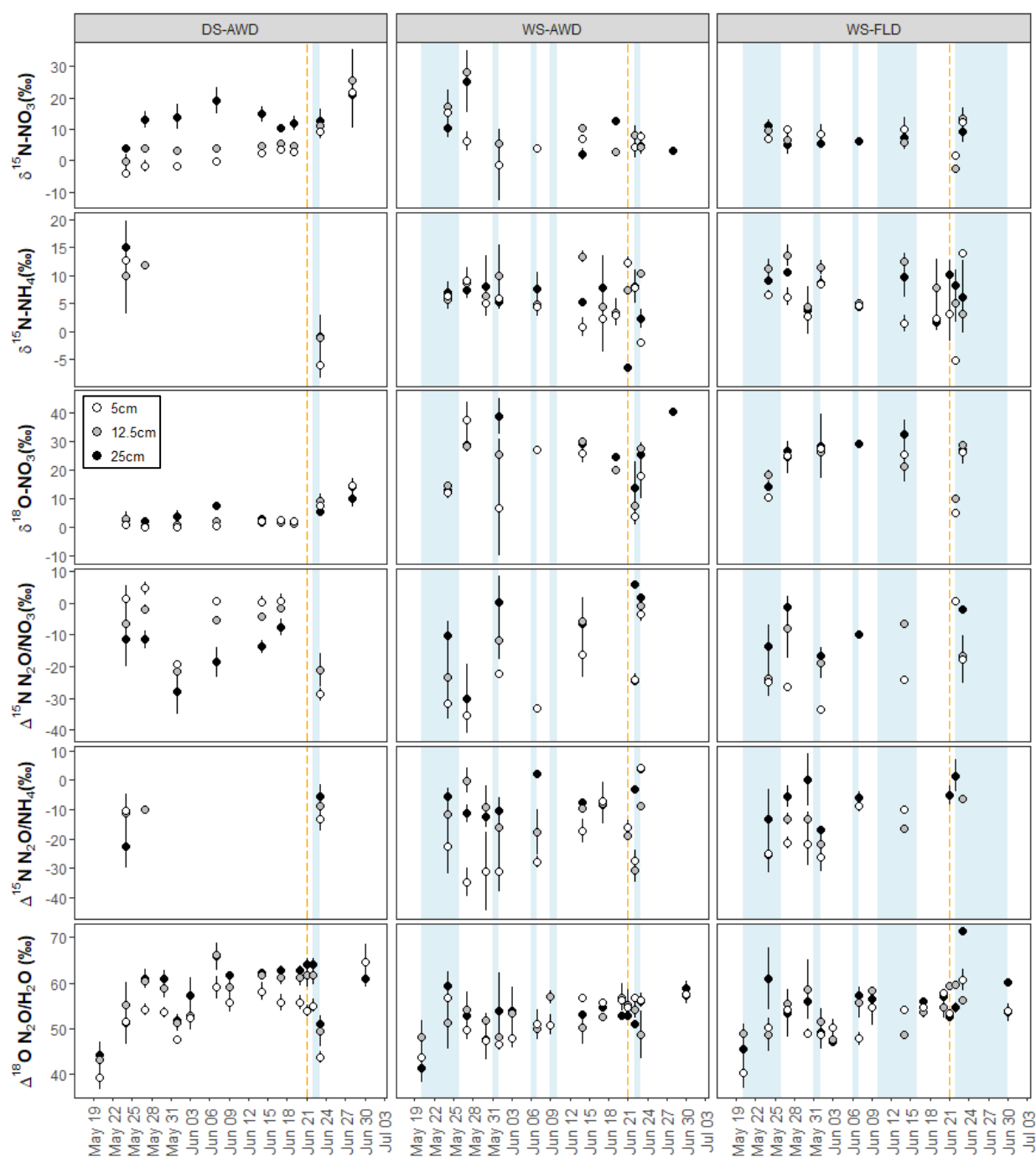


Figure S9.  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  of  $\text{NO}_3^-$ ,  $\text{NH}_4^+$  and the associated isotope effects calculated relative to  $\text{N}_2\text{O}_{\text{poreair}}$  at 5, 12.5 and 25 cm in the three water management treatments (WS-FLD = wet-seeding + conventional flooding; WS-AWD = wet-seeding + alternate wetting and drying; DS-AWD = direct dry seeding + alternate wetting and drying). The error bars represent the standard error of the mean.

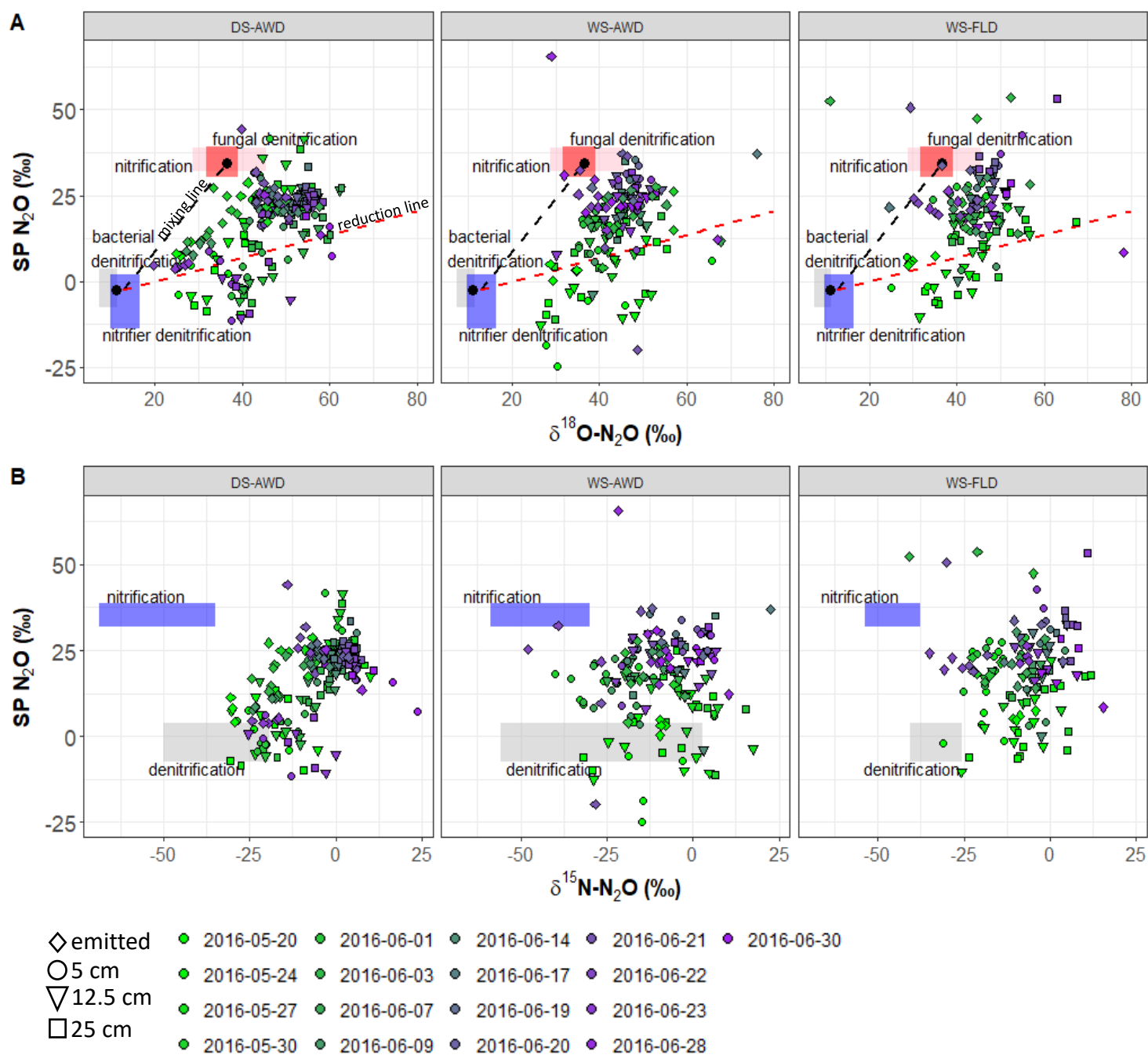


Figure S10. Graphical two-end member mixing plot shaded by sampling date. Following Lewicka-Szcebak *et al.* (2017), sample values are plotted in SP x  $\delta^{18}\text{O}-\text{N}_2\text{O}$  space (A) after Toyoda *et al.* (2011) where sample values are plotted in SP x  $\delta^{15}\text{N}-\text{N}_2\text{O}$  space (B). For further explanation and derivation of endmember values and process boxes the reader is referred to the main text, Fig. 3, Supplementary Table 1.4 and section 2.7.



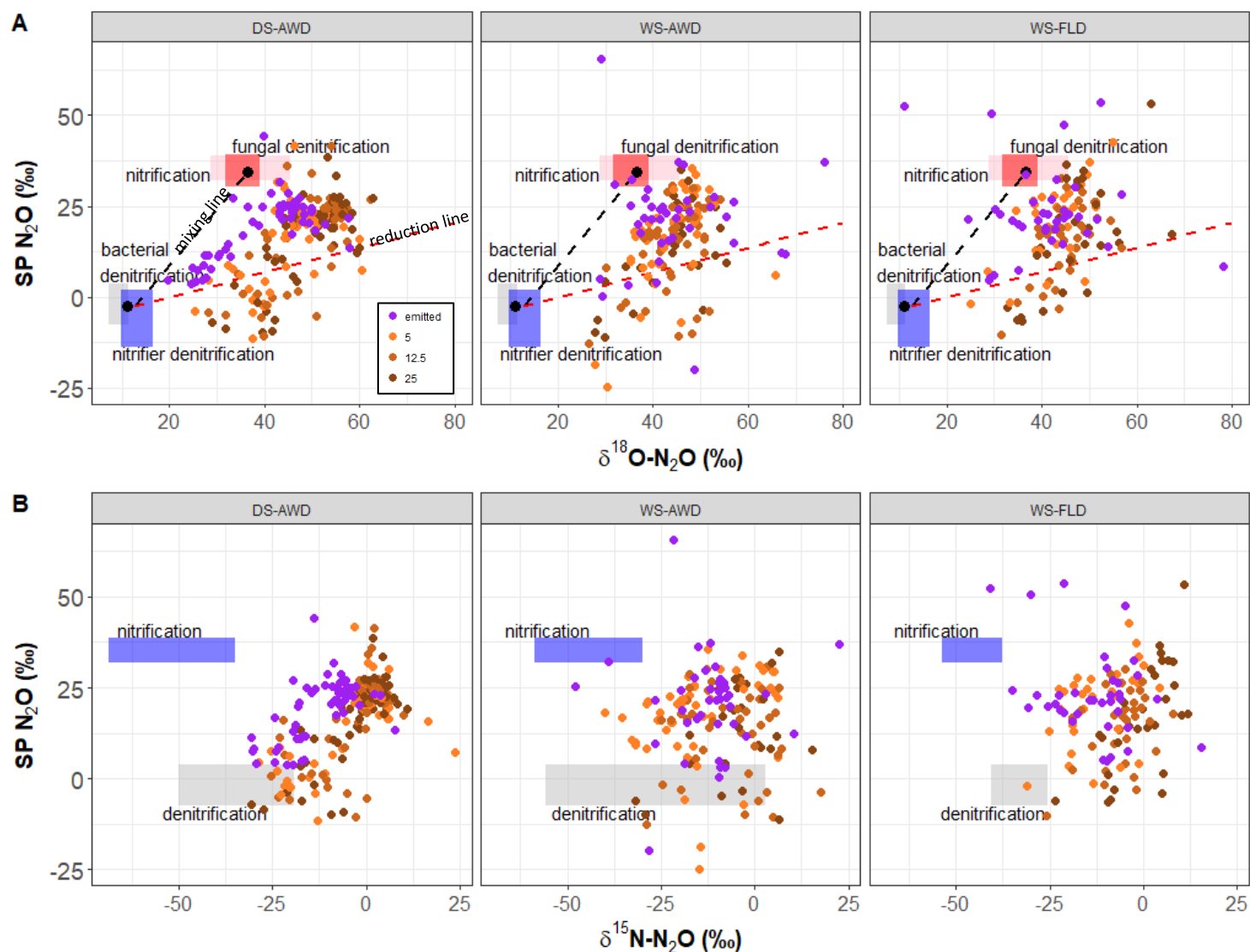


Figure S11. Graphical two-end member mixing plot shaded by depth. Following Lewicka-Szcebak *et al.* (2017), sample values are plotted in  $\text{SP} \times \delta^{18}\text{O-N}_2\text{O}$  space (A) after Toyoda *et al.* (2011) where sample values are plotted in  $\text{SP} \times \delta^{15}\text{N-N}_2\text{O}$  space (B). For further explanation and derivation of endmember values and process boxes the reader is referred to the main text, Fig. 3, Supplementary Table 1.4 and section 2.7.

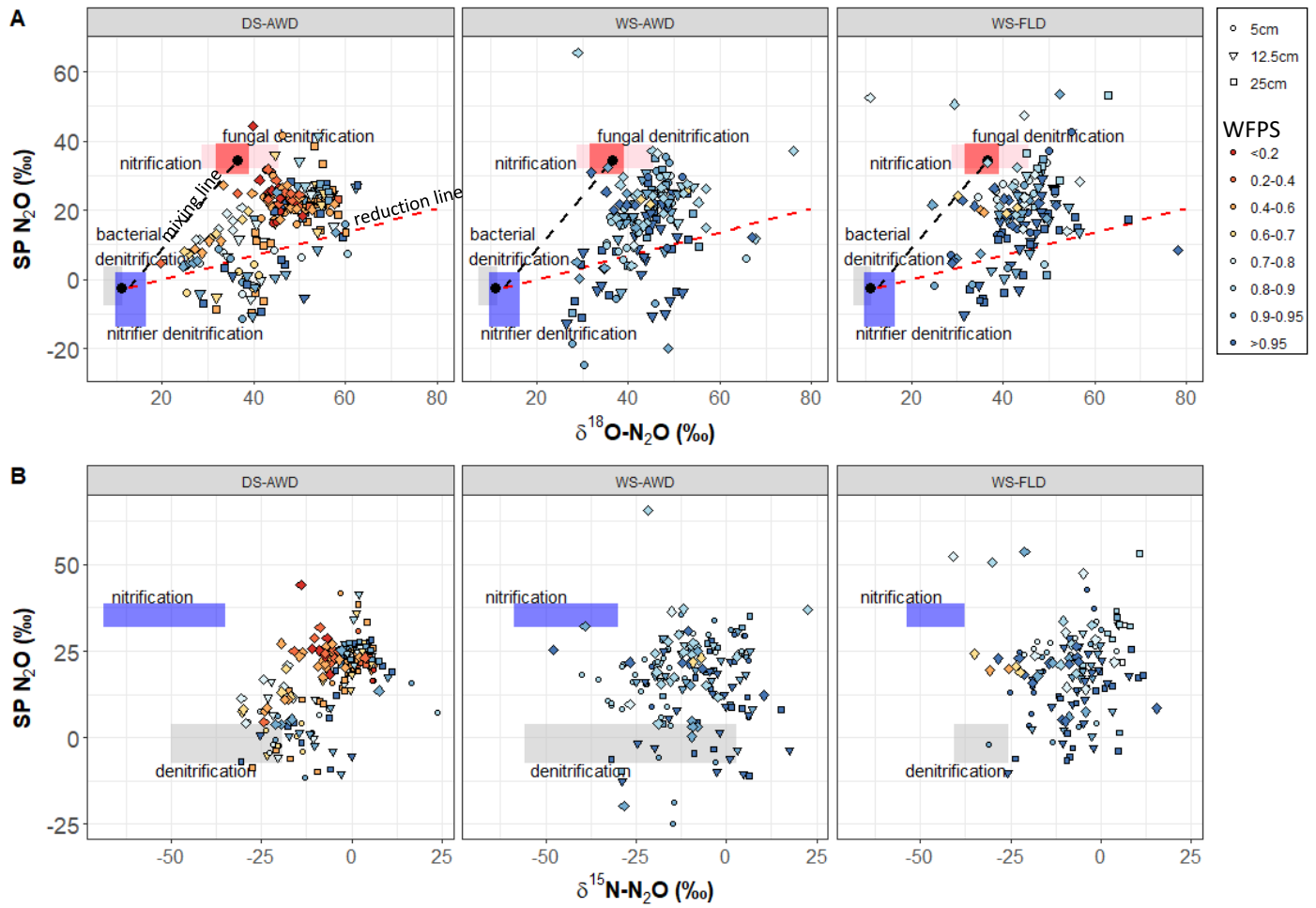


Figure S12. Graphical two-end member mixing plot shaded by WFPS. Following Lewicka-Szczebak *et al.* (2017), sample values are plotted in SP x  $\delta^{18}O-N_2O$  space (A) after Toyoda *et al.* (2011) where sample values are plotted in SP x  $\delta^{15}N-N_2O$  space (B). For further explanation and derivation of endmember values and process boxes the reader is referred to the main text, Fig. 3, Supplementary Table 1.4 and section 2.7.

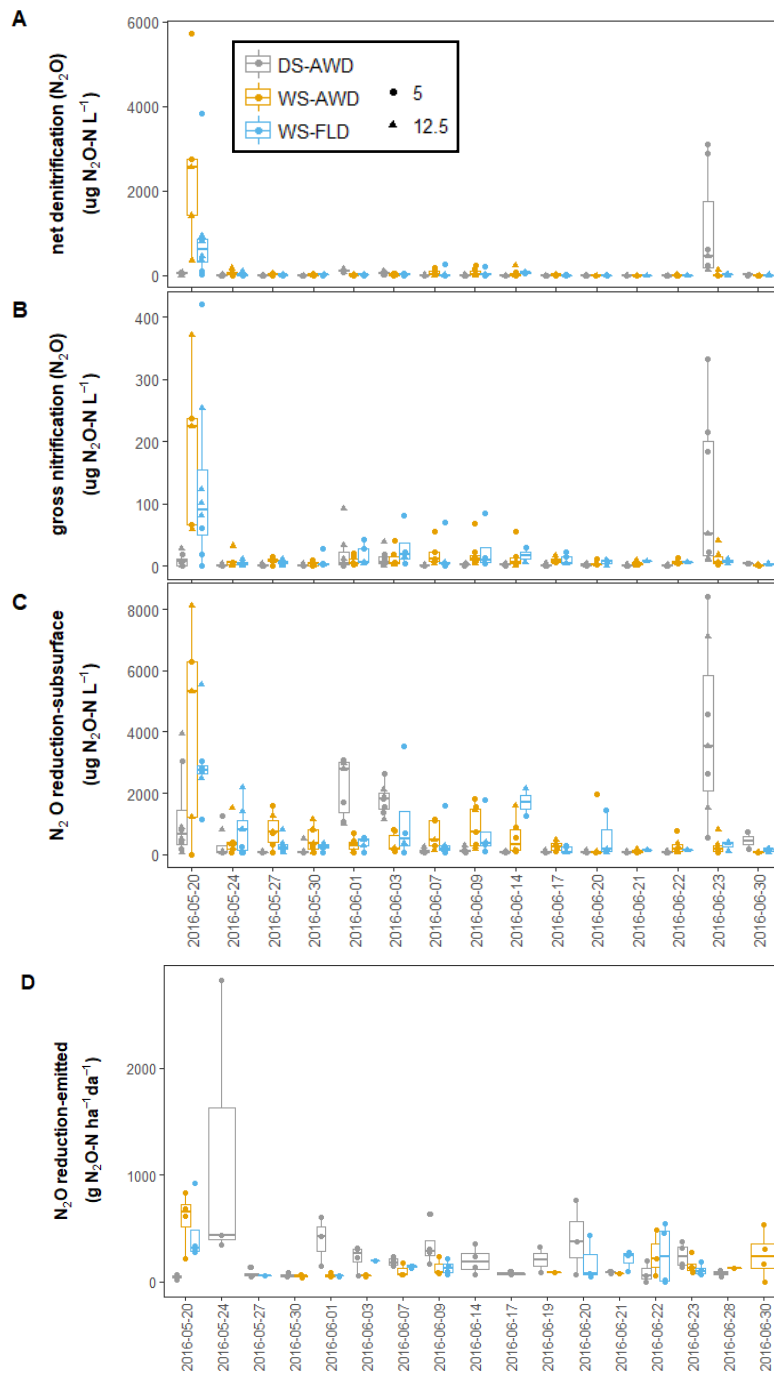
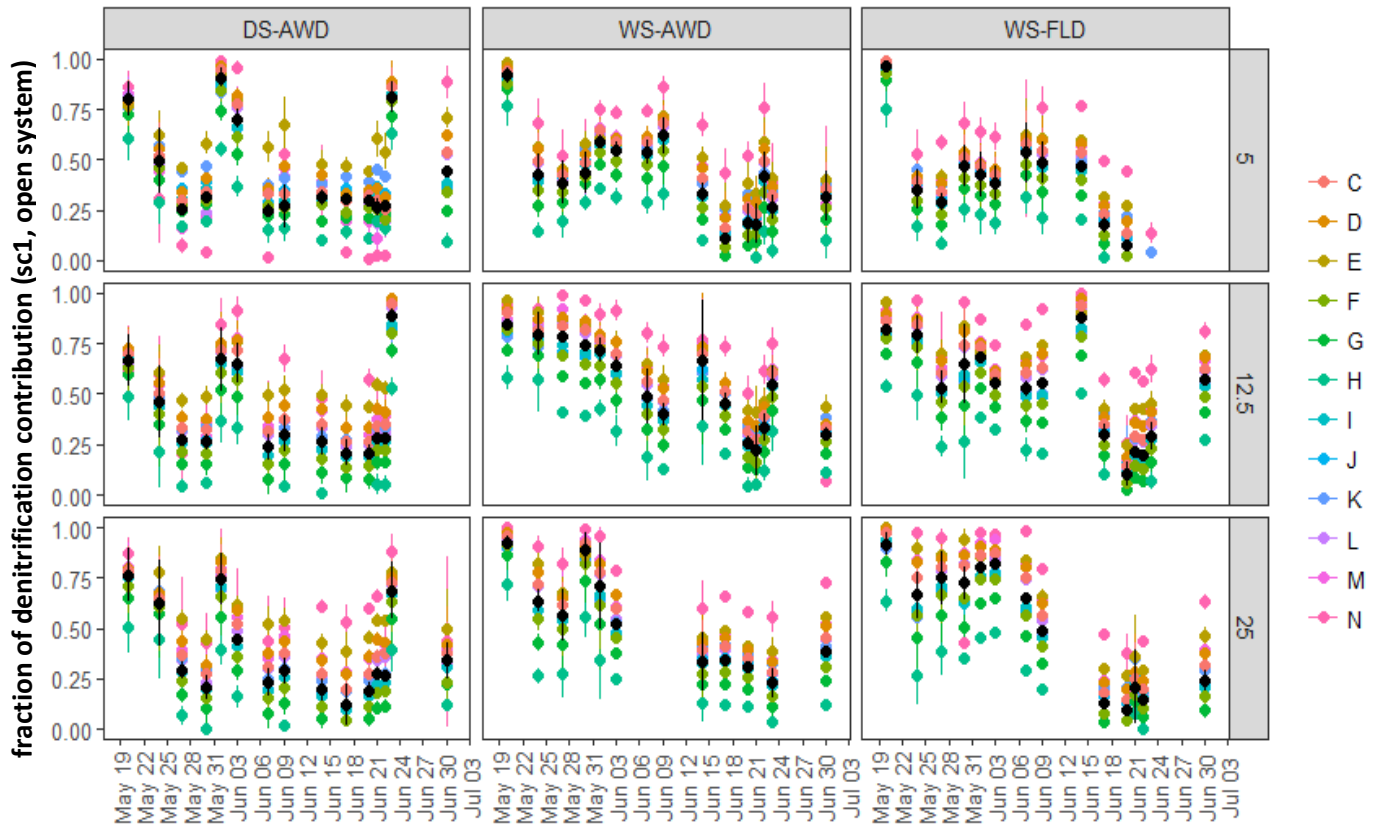


Figure S13. Model estimates of net subsurface denitrification/nitrifier-denitrification (a) and gross subsurface denitrification/nitrifier-denitrification N<sub>2</sub>O production (b) and N<sub>2</sub> production in the subsurface (c) and N<sub>2</sub> emissions (d). Subsurface values from 25 cm were omitted due to poor data availability.  $n \leq 4$ , as rates could not be estimated for all treatment x depth combinations.



Identification	Description	$\delta_0^{18}\text{O}-\text{N}_2\text{O}_{\text{nit}}$	$\delta_0^{18}\text{O}-\text{N}_2\text{O}_{\text{den}}$
"A"	Default values (DF) derived from Lewicka-		
black dots	Szczebak <i>et al.</i> (2017)	36.5	12.7
C	$\text{N}_2\text{O}_{\text{nit}}$ fixed, $\text{N}_2\text{O}_{\text{den}}+5$	36.5	17.7
D	$\text{N}_2\text{O}_{\text{nit}}$ fixed, $\text{N}_2\text{O}_{\text{den}}+10$	36.5	22.7
E	$\text{N}_2\text{O}_{\text{nit}}$ fixed, $\text{N}_2\text{O}_{\text{den}}+20$	36.5	32.7
F	$\text{N}_2\text{O}_{\text{nit}}$ fixed, $\text{N}_2\text{O}_{\text{den}}-5$	36.5	7.7
G	$\text{N}_2\text{O}_{\text{nit}}$ fixed, $\text{N}_2\text{O}_{\text{den}}-10$	36.5	2.7
H	$\text{N}_2\text{O}_{\text{nit}}$ fixed, $\text{N}_2\text{O}_{\text{den}}-20$	36.5	-7.3
I	$\text{N}_2\text{O}_{\text{den}}$ fixed, $\text{N}_2\text{O}_{\text{nit}}+5$	41.5	12.7
J	$\text{N}_2\text{O}_{\text{den}}$ fixed, $\text{N}_2\text{O}_{\text{nit}}+10$	46.5	12.7
K	$\text{N}_2\text{O}_{\text{den}}$ fixed, $\text{N}_2\text{O}_{\text{nit}}+20$	56.5	12.7
L	$\text{N}_2\text{O}_{\text{den}}$ fixed, $\text{N}_2\text{O}_{\text{nit}}-5$	31.5	12.7
M	$\text{N}_2\text{O}_{\text{den}}$ fixed, $\text{N}_2\text{O}_{\text{nit}}-10$	26.5	12.7
N	$\text{N}_2\text{O}_{\text{den}}$ fixed, $\text{N}_2\text{O}_{\text{nit}}-20$	16.5	12.7

Figure S1. Denitrification contribution results for sc1, open system modeling across a range of  $\delta_0^{18}\text{O}-\text{N}_2\text{O}_{\text{nit}}$  and  $\delta_0^{18}\text{O}-\text{N}_2\text{O}_{\text{den}}$  values; values are given in the table. The values actually used in the manuscript results are from "A" (black dots). From this analysis we chose values derived from Lewicka-Szczebak *et al.* 2017 for consistency and because they represented the mean. The ranges changed with varying  $\delta_0^{18}\text{O}$  values but the relative patterns were conserved.

Table S1. Dates of sampling for the various parameters

date	N <sub>2</sub> O emitted	pore water	pore air	NH <sub>3</sub>	<sup>15</sup> N-NO <sub>3</sub> <sup>-</sup> , NH <sub>4</sub> <sup>+</sup>
20-May	X		X		
24-May	X	X	X		X
25-May				X	
27-May	X	X	X		X
30-May	X	X	X		
31-May				X	
1-Jun	X	X	X		X
3-Jun	X	X	X		
7-Jun	X	X	X		X
9-Jun	X	X	X		
14-Jun	X	X			X
17-Jun	X	X	X		X
19-Jun	X	X			X
20-Jun	X	X	X	X	
21-Jun	X	X	X	X	
22-Jun	X	X	X		X
23-Jun	X	X		X	X
28-Jun	X	X		X	X
30-Jun	X	X	X		

Table S2. Percent of observations meeting data quality criteria for open and closed mixing models under *scenario one* and *scenario two*. Observations were considered not plausible and were eliminated if the modeled fraction was  $< 0$  or  $> 1$ . The open system model was solved by solving a series of equations for the minimal sum of squares (minSS). In this case, an additional criteria of a  $\text{minSS} < 500$  was also used. Gross  $\text{frac}_{\text{DEN}}$  is the fraction of  $\text{N}_2\text{O} + \text{N}_2$  attributed to denitrification; gross  $r\text{N}_2\text{O}$  is the fraction of residual  $\text{N}_2\text{O}$  not reduced; DenContribution is the fraction of  $\text{N}_2\text{O}$  attributed to denitrification.

dataset		scenario one		scenario two	
		open	closed	open	closed
$\text{N}_2\text{O}_{\text{poreair}}$ (381 obs)	gross $\text{frac}_{\text{DEN}} > 1$	0%	20%	0%	20%
	gross $\text{frac}_{\text{DEN}} < 0$	0%	1%	0%	1%
	gross $\text{frac}_{\text{DEN}} = 1$	6%	1%	3%	0%
	gross $r\text{N}_2\text{O} > 1$	0%	0%	0%	0%
	gross $r\text{N}_2\text{O} < 0$	0%	0%	0%	0%
	DenContribution $> 1$	1%	20%	3%	20%
	DenContribution $< 0$	5%	1%	89%	1%
	minSS $> 500$	8%	NA	3%	NA
$\text{N}_2\text{O}_{\text{emitted}}$ (128 obs)	gross $\text{frac}_{\text{DEN}} > 1$	0%	9%	0%	8%
	gross $\text{frac}_{\text{DEN}} < 0$	0%	2%	0%	6%
	gross $\text{frac}_{\text{DEN}} = 1$	2%	1%	0%	0%
	gross $r\text{N}_2\text{O} > 1$	0%	0%	0%	0%
	gross $r\text{N}_2\text{O} < 0$	0%	2%	0%	0%
	DenContribution $> 1$	0%	6%	6%	8%
	DenContribution $< 0$	6%	5%	4%	6%
	minSS $> 500$	5%	NA	4%	NA

Table S3. ANCOVA results of  $\text{N}_2\text{O}$  emissions ( $\text{N}_2\text{O}_{\text{emitted}}$ ),  $\text{N}_2\text{O}_{\text{poreair}}$  concentrations, inorganic N, DOC, WFPS and Eh.

	$\text{N}_2\text{O}_{\text{emitted}}$	$\text{N}_2\text{O}_{\text{poreair}}$	$\text{NO}_3^-$	$\text{NH}_4^+$	DOC	WFPS	Eh
treatment	<b>&lt;0.001</b>	0.08	<b>&lt;0.001</b>	<b>&lt;0.001</b>	0.22	0.001	<b>&lt;0.001</b>
date	<b>&lt;0.001</b>	<b>&lt;0.001</b>	<b>&lt;0.001</b>	<b>&lt;0.001</b>	<b>&lt;0.001</b>	<b>&lt;0.001</b>	<b>&lt;0.001</b>
depth		0.43	0.01	0.01	0.15	0.01	0.00
Y position	0.82	0.08	0.86	0.79	0.56	0.92	0.20
treatment x date	<b>&lt;0.001</b>	<b>&lt;0.001</b>	<b>&lt;0.001</b>	<b>&lt;0.001</b>	<b>&lt;0.001</b>	<b>&lt;0.001</b>	<b>&lt;0.001</b>
treatment x depth		0.55	0.02	0.31	0.33	0.42	0.01
date x depth		<b>&lt;0.001</b>	0.05	<b>&lt;0.001</b>	0.61	<b>&lt;0.001</b>	<b>&lt;0.001</b>
treatment x date x depth		<b>&lt;0.001</b>	0.09	<b>&lt;0.001</b>	0.01	<b>&lt;0.001</b>	<b>&lt;0.001</b>

Table S4. ANCOVA table of modeled net denitrification/nitrifier-denitrification N<sub>2</sub>O, gross nitrification/fungal denitrification N<sub>2</sub>O and N<sub>2</sub>O reduction. Subsurface data from 25 cm was not included in the analysis due to poor data availability.

	NumDF	net denitrification/ nitrifier- denitrification	gross nitrification/ fungal denitrification	N <sub>2</sub> O reduction
<i>subsurface</i>				
trmt	2	0.285	<b>0.005</b>	0.431
day	14	<b>&lt; 0.001</b>	<b>&lt; 0.001</b>	<b>&lt; 0.001</b>
depth	1	0.378	0.485	0.228
Yposition	1	0.307	0.467	0.757
Trmt:day	28	<b>&lt; 0.001</b>	<b>&lt; 0.001</b>	<b>&lt; 0.001</b>
trmt:depth	2	0.959	0.182	0.773
day:depth	14	<b>&lt; 0.001</b>	0.476	<b>0.002</b>
trmt:day:depth	23	<b>&lt; 0.001</b>	<b>&lt; 0.001</b>	<b>0.001</b>
<i>surface</i>				
trmt	2	<b>&lt; 0.001</b>	<b>0.017</b>	0.858
day	16	<b>&lt; 0.001</b>	<b>&lt; 0.001</b>	<b>0.008</b>
Yposition	1	0.650	0.516	0.534
trmt:day	19	<b>&lt; 0.001</b>	<b>&lt; 0.001</b>	<b>0.005</b>

Table S5. Mean, minimum and maximum observed  $\delta^{15}\text{N-NO}_3^-$  and  $\delta^{15}\text{N-NH}_4^+$  values. The estimated range of  $\delta^{15}\text{N-N}_2\text{O}$  derived from denitrification and nitrification, used in Fig. 3B and Supplementary Fig. 1.9B-1.11B, was calculated using the mean isotope effects for  $\text{N}_2\text{O}$  produced from  $\text{NO}_3^-$  and  $\text{NH}_4^+$ , respectively, reported in Denk *et al.*, (2017) plus the minimum and maximum observed  $\delta^{15}\text{N-NO}_3^-$  and  $\delta^{15}\text{N-NH}_4^+$ .

	DS-AWD	WS-AWD	WS-FLD
	‰		
$\delta^{15}\text{N-NO}_3^-$ (mean)	6.0	9.5	8.5
$\delta^{15}\text{N-NH}_4^+$ (mean)	4.4	6.8	9.4
$\delta^{15}\text{N-NO}_3^-$ (min)	-7.2	-12.9	2.2
$\delta^{15}\text{N-NH}_4^+$ (min)	-11.9	-2.0	3.0
$\delta^{15}\text{N-NO}_3^-$ (max)	23.7	45.9	17.2
$\delta^{15}\text{N-NH}_4^+$ (max)	21.7	26.6	18.8
literature mean <sup>a</sup> $\epsilon^{15}\text{N}_{\text{N}_2\text{O}/\text{NO}_3}$ (denitrification)	-42.9	-42.9	-42.9
literature mean <sup>a</sup> $\epsilon^{15}\text{N}_{\text{N}_2\text{O}/\text{NH}_4}$ (nitrification)	-56.6	-56.6	-56.6
estimated denitrification $\delta^{15}\text{N-N}_2\text{O}$ range (min)	-19.2	3.0	-25.7
estimated denitrification $\delta^{15}\text{N-N}_2\text{O}$ range (max)	-50.1	-55.8	-40.7
estimated nitrification $\delta^{15}\text{N-N}_2\text{O}$ range (min)	-34.9	-30.0	-37.8
estimated nitrification $\delta^{15}\text{N-N}_2\text{O}$ range (max)	-68.5	-58.6	-53.6
$\delta^{15}\text{N-NO}_3^-$ (n)	97	58	46
$\delta^{15}\text{N-NH}_4^+$ (n)	19	89	92

<sup>a</sup> Denk *et al.*, (2017)

Table S6. Estimated  $\epsilon^{15}\text{N}_{\text{N}_2\text{O}/\text{NO}_3}$  considering  $\text{N}_2\text{O}$  reduction effects on measured  $\delta^{15}\text{N-N}_2\text{O}$  values. Values were calculated by using measured  $^{15}\text{N-N}_2\text{O}$  values and modeled  $r\text{N}_2\text{O}$  values in the Rayleigh equation.

depth	treatment	mean $\epsilon^{15}\text{N}_{\text{N}_2\text{O}/\text{NO}_3}$ (se)
emitted	DS-AWD	-28.6 (1.3)
5	DS-AWD	-25.0 (2.3)
12.5	DS-AWD	-28.9 (2.1)
25	DS-AWD	-36.5 (2.2)
emitted	WS-AWD	-42.3 (3.7)
5	WS-AWD	-39.4 (2.7)
12.5	WS-AWD	-33.1 (5.4)
25	WS-AWD	-32.6 (5.1)
emitted	WS-FLD	-37.6 (3.3)
5	WS-FLD	-51.1 (9.4)
12.5	WS-FLD	-36.8 (3.7)
25	WS-FLD	-29.0 (3.9)