S1 Terms and abbreviations

GENERAL TERMS	
N_2O and N_2 isotopologues	molecules differing in mass due to isotopic substitution ($^{14}N^{14}N$ - $^{15}N^{14}N$ or $^{14}N^{14}N^{16}O$ - $^{15}N^{14}N^{16}O$)
N_2O isotopocules	molecules differing in either the number or positions of isotopic substitutions = isotopologues ($^{14}N^{14}N^{16}O$ - $^{15}N^{14}N^{16}O$ or $^{14}N^{14}N^{16}O$ - $^{14}N^{14}N^{18}O$) + isotopomers ($^{14}N^{15}N^{16}O$ - $^{15}N^{14}N^{16}O$)
Min soil	mineral arable soil with silt loam texture classified as a *Haplic Luvisol*
Org soil	organic grassland soil classified as *Histic Gleysol*
Exp1	Experiment 1 - soil incubations in He and He+O_2 atmosphere
Exp2	Experiment 2 – parallel soil incubations with and without ^{15}N addition
NA treatment	treatment without ^{15}N addition (Exp2) - natural abundance
^{15}N treatment	treatment with ^{15}N addition (Exp2) - ^{15}N labelled
WFPS	water-filled pore space
r_{N2O}	residual N_2O fraction
y_{N2}; y_{N2O}	mole fraction of N_2; N_2O in total gas background
f_F	fraction of N_2O from fungal denitrification or nitrification
n	nitrification rate pro soil amount and time
$DNRA$	rate of dissimilatory nitrate reduction to ammonium pro soil amount and time
m	minimal N mineralisation rate pro soil amount and time
i	N immobilisation rate pro soil amount and time
[N_2O] flux	N_2O released pro soil amount and time
[N_2O+N_2] flux	total N gases released pro soil amount and time
NATURAL ABUNDANCE ISOTOPIC ANALYSES	
$\delta^{18}O_{N2O}$	oxygen isotopic signature of N_2O
$\delta^{15}N^{bulk}_{N2O}$	nitrogen isotopic signature of N_2O - average value for both N atoms
$\delta^{15}N^{sp}_{N2O}$	site preference of nitrogen isotopic signature of N_2O - difference in $\delta^{15}N$ between central and peripheral N atom
δ_0	initial isotopic signature before N_2O reduction
δ_r	isotopic signature of residual N_2O after reduction
η_{red}	net isotope effect associated with N_2O reduction
$\delta^{18}O_{NO3}$	oxygen isotopic signature of NO_3^-
$\delta^{15}N_{NO3}$	nitrogen isotopic signature of NO_3^-
$\delta^{15}N_{NH4}$	nitrogen isotopic signature of NH_4^+
^{15}N LABELLED ANALYSES	
a	^{15}N abundance: $a^{15}N$
$at\%$	atom percent of ^{15}N
a_{NO3-}	^{15}N abundances in NO_3^-
a_{NH4+}	^{15}N abundances in NH_4^+
f_P	gas fraction originating from the ^{15}N-labelled pool
f_{P_N2}	N_2 fraction originating from the ^{15}N-labelled pool
f_{P_N2O}	N_2O fraction originating from the ^{15}N-labelled pool
a_m	measured ^{15}N abundance in total gas mixture
a_{bgd}	^{15}N abundance of - non-labelled pool (atmospheric background or experimental matrix)
a_P	calculated ^{15}N abundance of ^{15}N-labelled pool
a_{P_N2}	calculated ^{15}N abundance of ^{15}N-labelled pool producing N_2
a_{P_N2O}	calculated ^{15}N abundance of ^{15}N-labelled pool producing N_2O
f_{N_N2O}	N_2O fraction originating from non-labelled natural abundance pools, like NH_4^+ or Norg
f_{H_N2}	N_2 fraction originating from hybrid pool
f_{H_N2O}	N_2O fraction originating from hybrid pool

S2 Results

S2.1 Experiment 1 (Exp 1)

Here we show all the detailed results of Helium incubation experiment (Exp1) for Min (Figure S1(a)) and Org soil (Figure S1(b)). Results description can be found in paper Section 3.1.

S1(a): Min soil

S1(b): Org soil

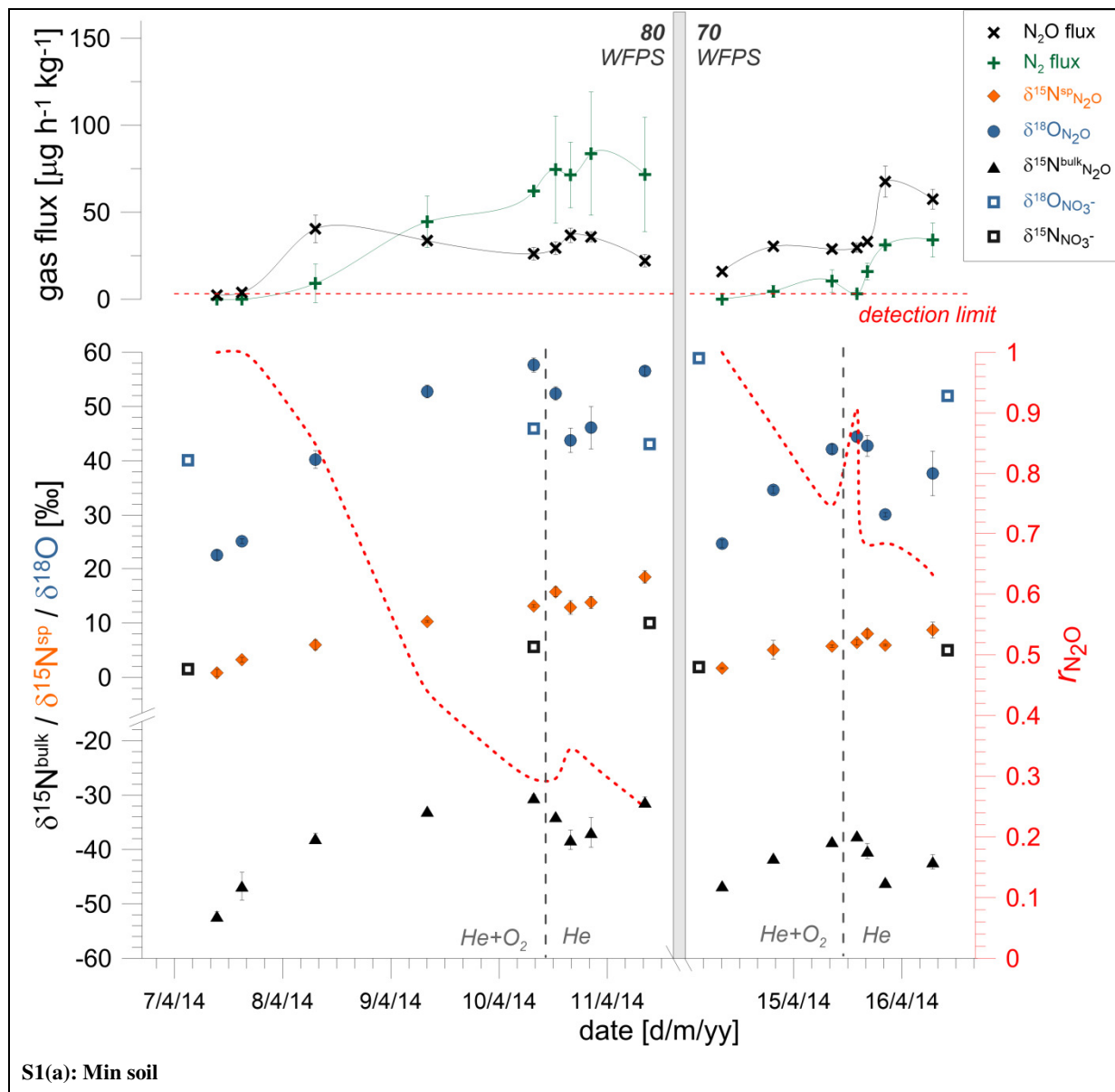
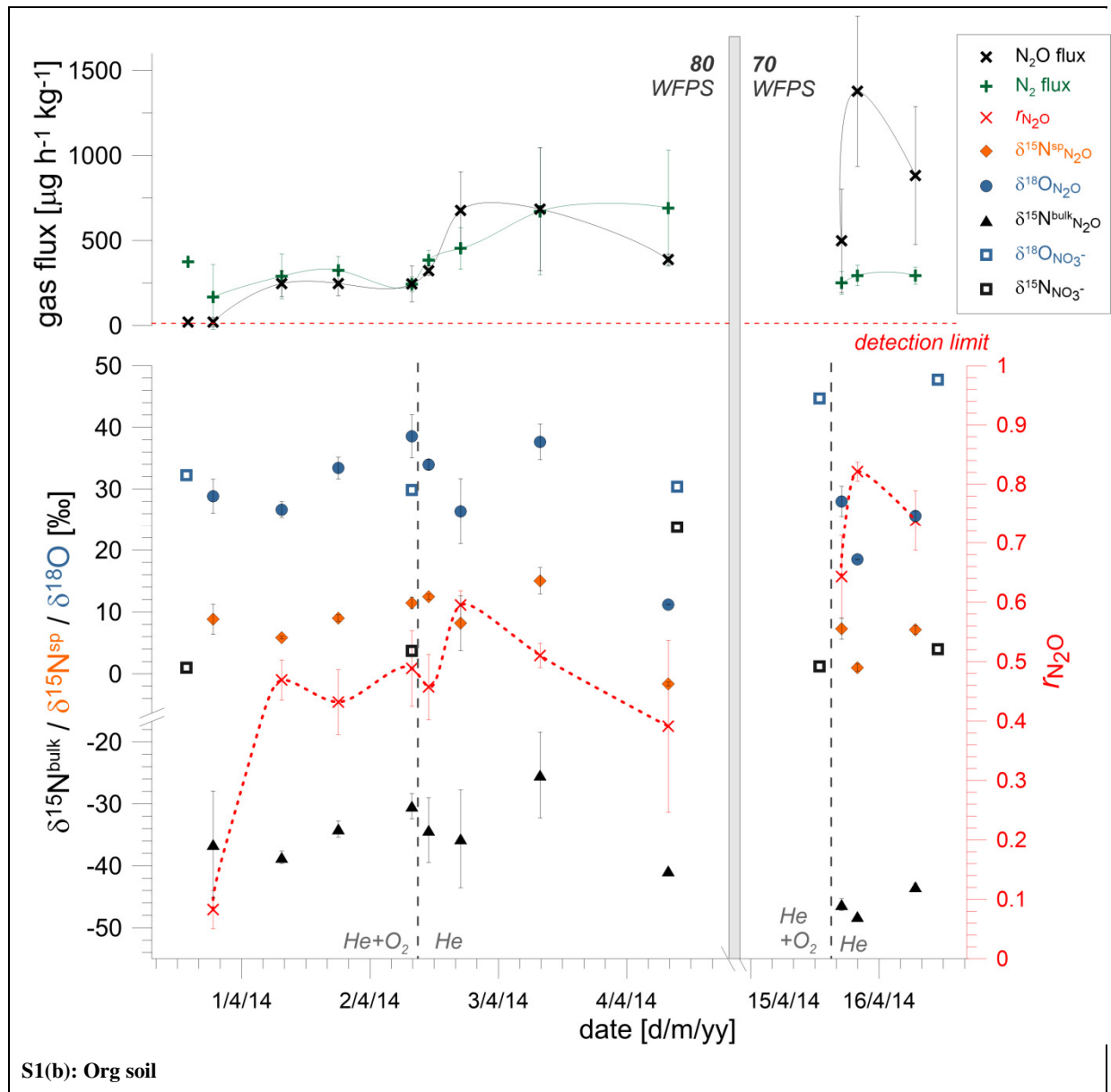



Figure S1: Measured N_2 and N_2O gas fluxes (green and black crosses, upper graph), calculated N_2O residual fraction (r_{N2O}) (red crosses, lower graph), N_2O isotopocules ($\delta^{18}O$ - blue circles; $\delta^{15}N^{sp}$ - orange diamonds; $\delta^{15}N^{bulk}$ - black triangles) from Exp1 for Min soil (a) and Org soil (b). Mean values and standard deviations (n=3) are shown. $\delta^{15}N$ and $\delta^{18}O$ of extracted soil nitrate (black and blue squares) were determined at the beginning and at the end of the experiment.

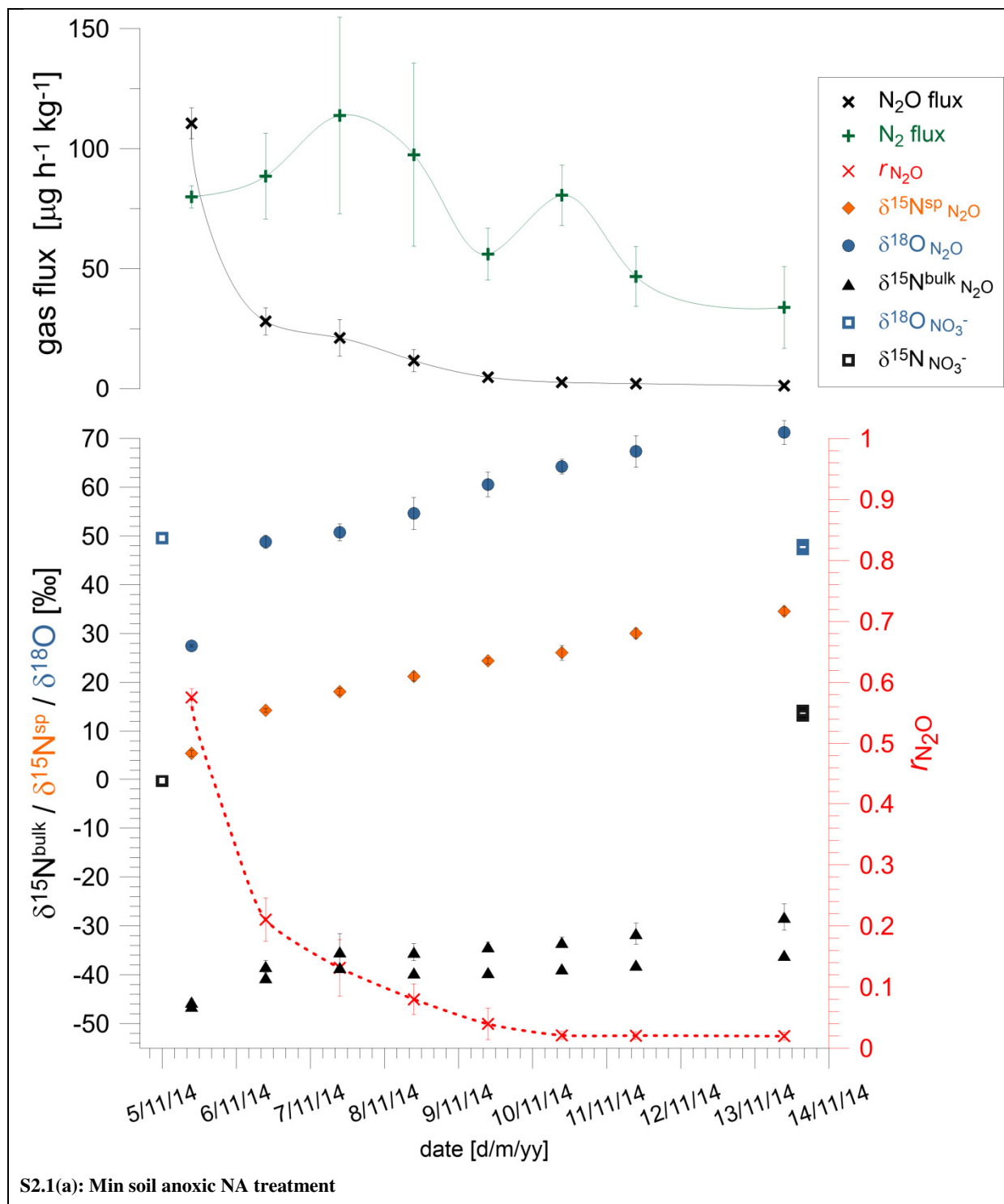
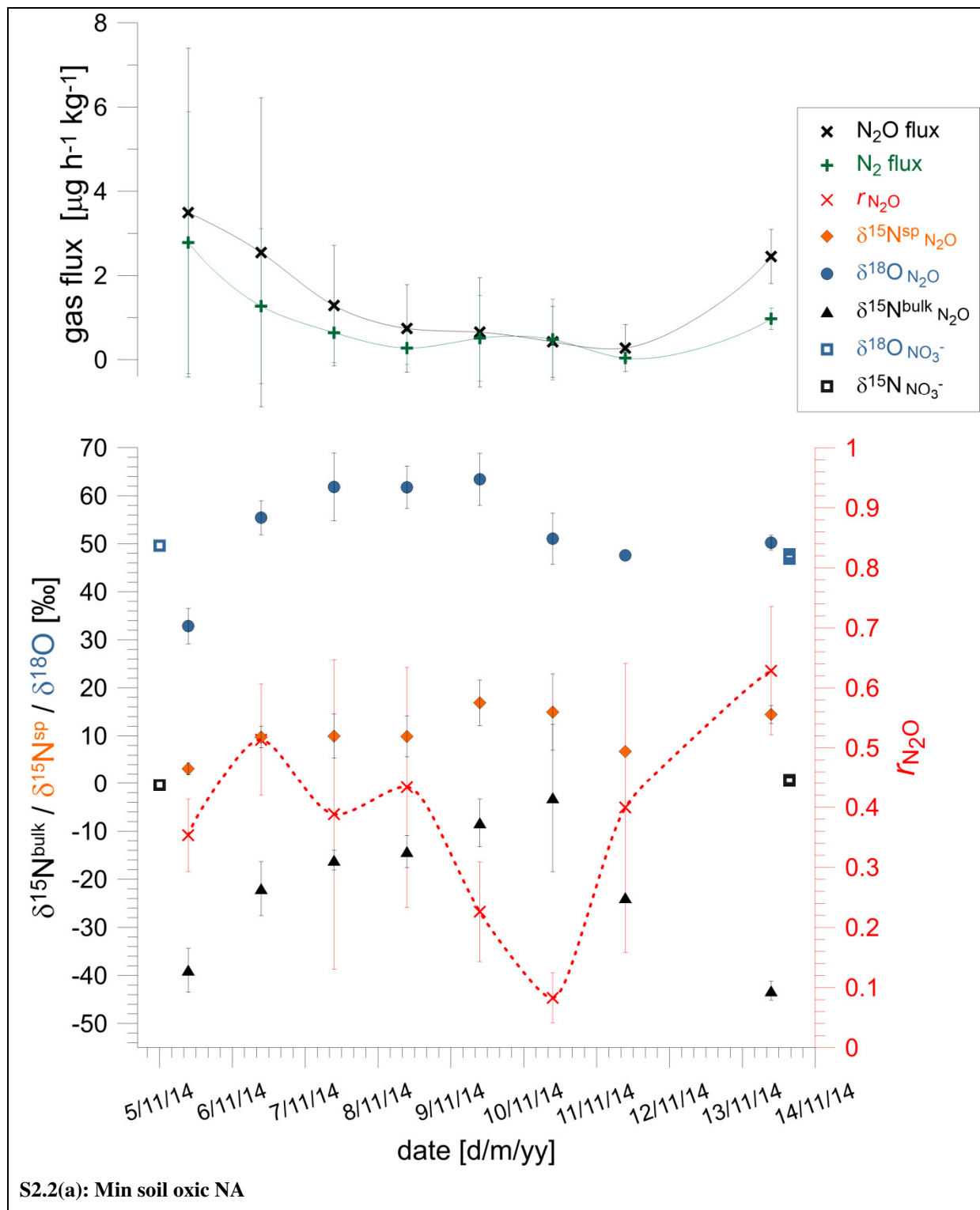
S2.1 Experiment 2 (Exp 2)

S2.1.1 Natural abundance (NA) treatment, Exp2

Here we show all the detailed results of the natural abundance treatment of Experiment 2 (Exp2) for Min (Figure S2(a)) and Org soil (Figure S2(b)) incubated under anoxic (S2.1) and oxic (S2.2) atmosphere. Results description can be found in paper Section 3.2.1.

S2.1(a): Min soil anoxic NA treatment

S2.2(a): Min soil oxic NA

S2.1(b): Org soil anoxic NA

S2.2(b): Org soil oxic NA

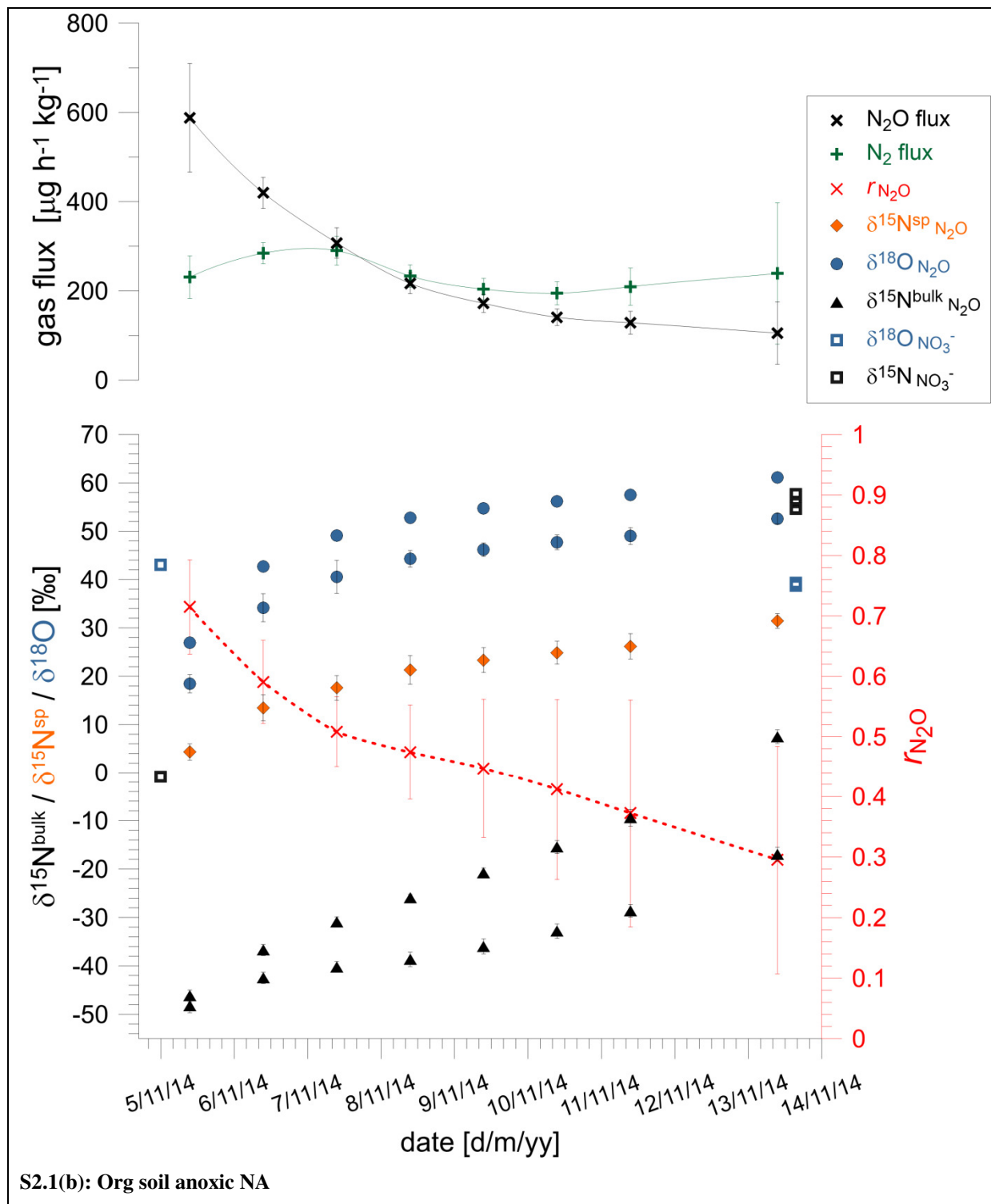
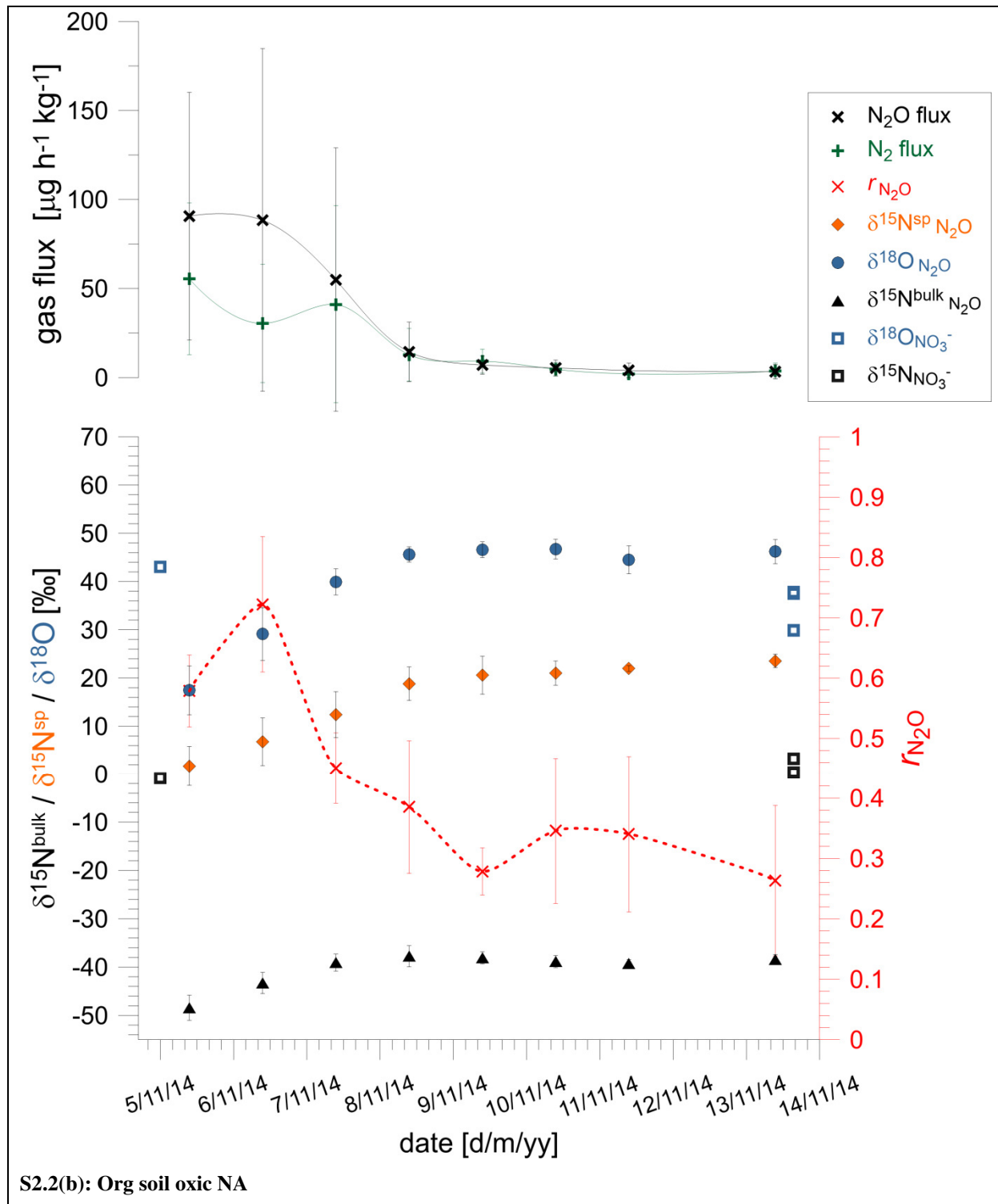



Figure S2: Data of natural abundance (NA) treatments for Min (A) and Org soil (B) incubated under anoxic (2.1) and oxic (2.2) atmosphere in Exp2. Mean values and standard deviations (n=4; n=3 for Org soil oxic treatment) are shown. Measured N_2O gas fluxes (black crosses, upper graphs) with calculated N_2 fluxes (green crosses, upper graphs) from the residual N_2O fraction determined with ^{15}N method, Eq. 6 (r_{N2O}) (red crosses, lower graphs).
N_2O isotopic signatures ($\delta^{18}O$ - blue circles; $\delta^{15}N^{sp}$ - orange diamonds; $\delta^{15}N^{bulk}$ - black triangles) measured daily; $\delta^{15}N$ and $\delta^{18}O$ of extracted soil nitrate (black and blue squares) determined at the beginning and at the end of the experiment.

S2.1.2 ^{15}N treatment, Exp2

Here we show all the detailed results of the ^{15}N treatment of Experiment 2 (Exp2) for Min (Figure S3(a)) and Org soil (Figure S3(b)) incubated under anoxic (S3.1) and oxic (S3.2) atmosphere. Results description can be found in paper Section 3.2.2.

S3.1(a): Min soil anoxic ^{15}N

S3.2(a): Min soil oxic ^{15}N

S3.1(b): Org soil anoxic ^{15}N

S3.2(b): Org soil oxic ¹⁵N

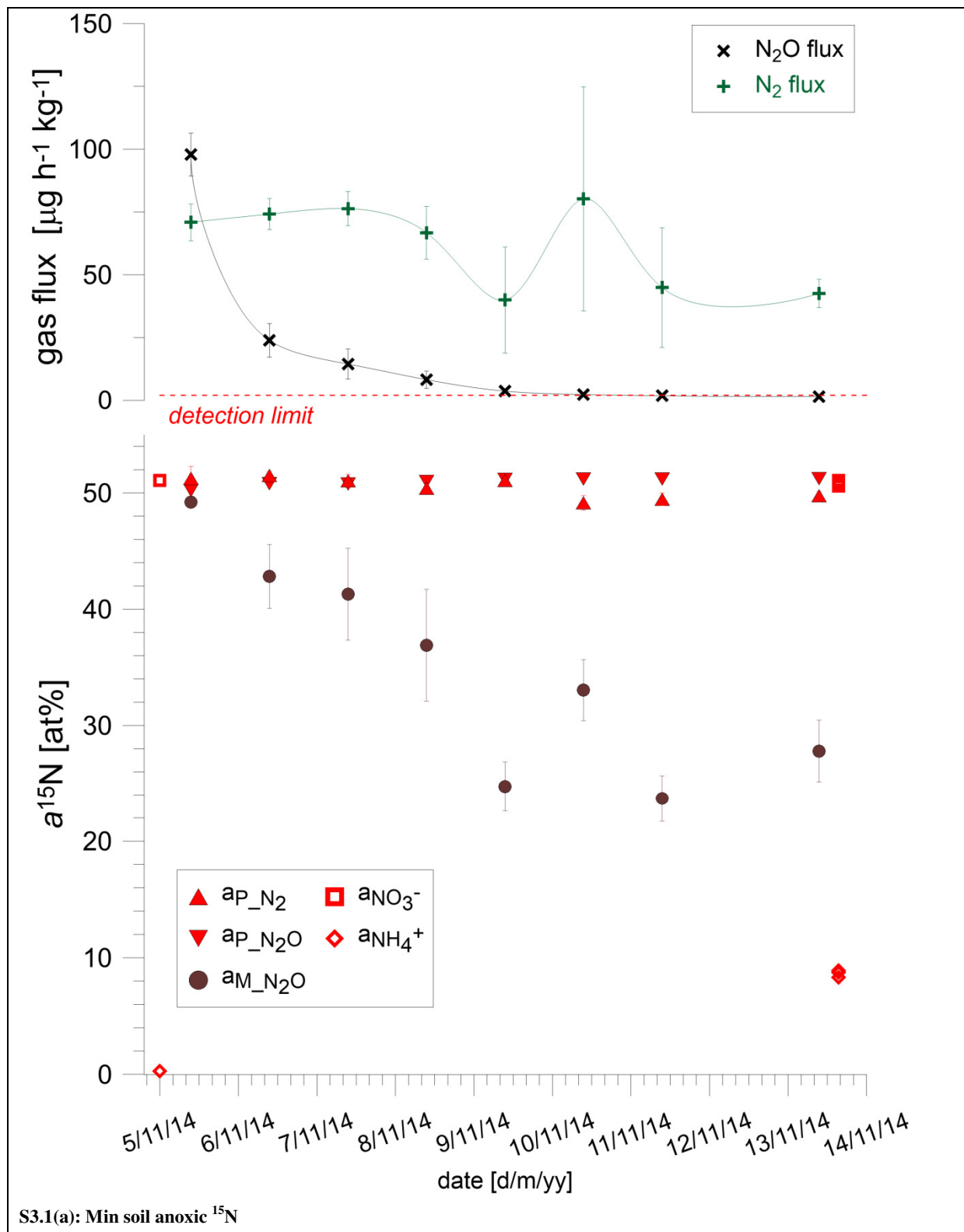
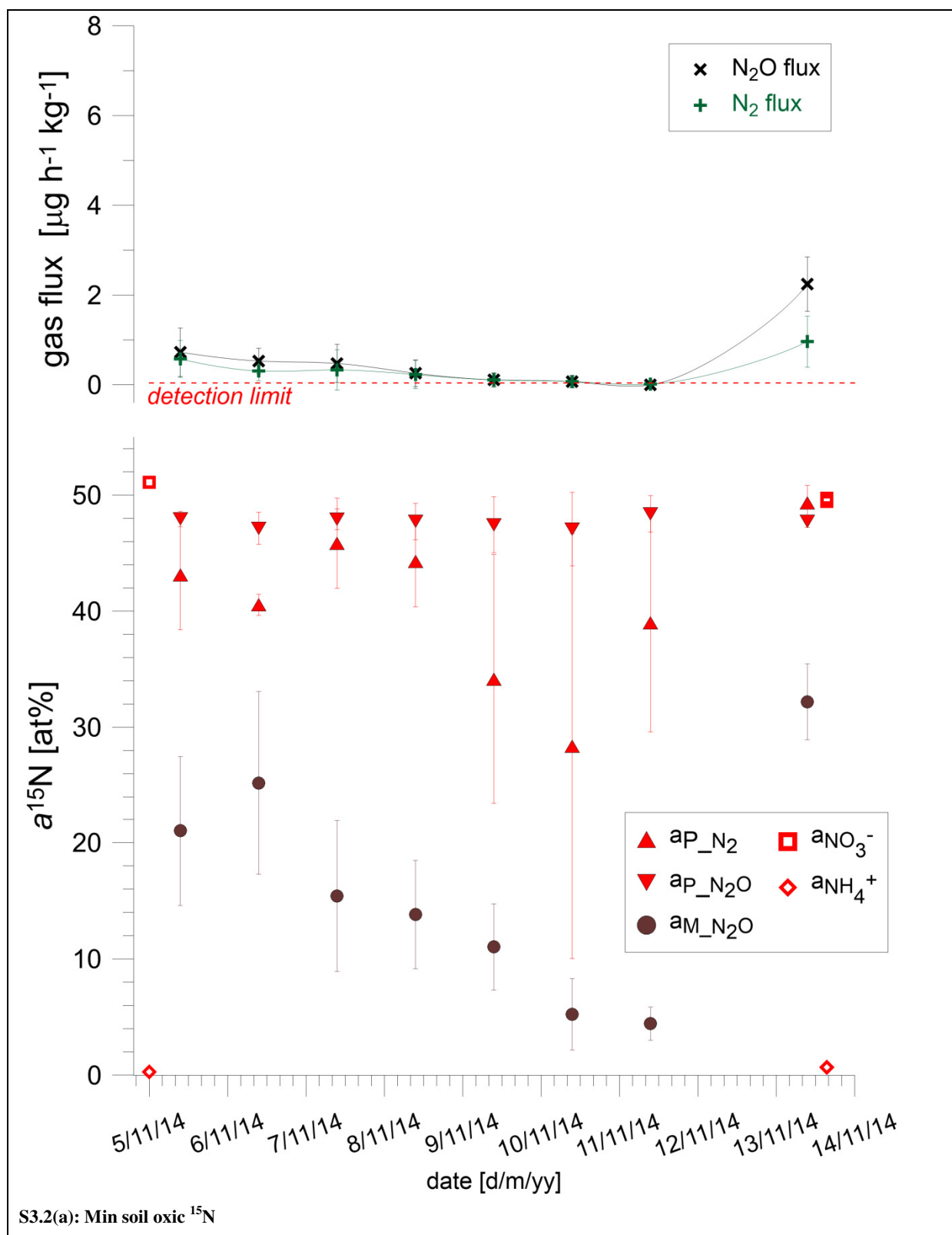
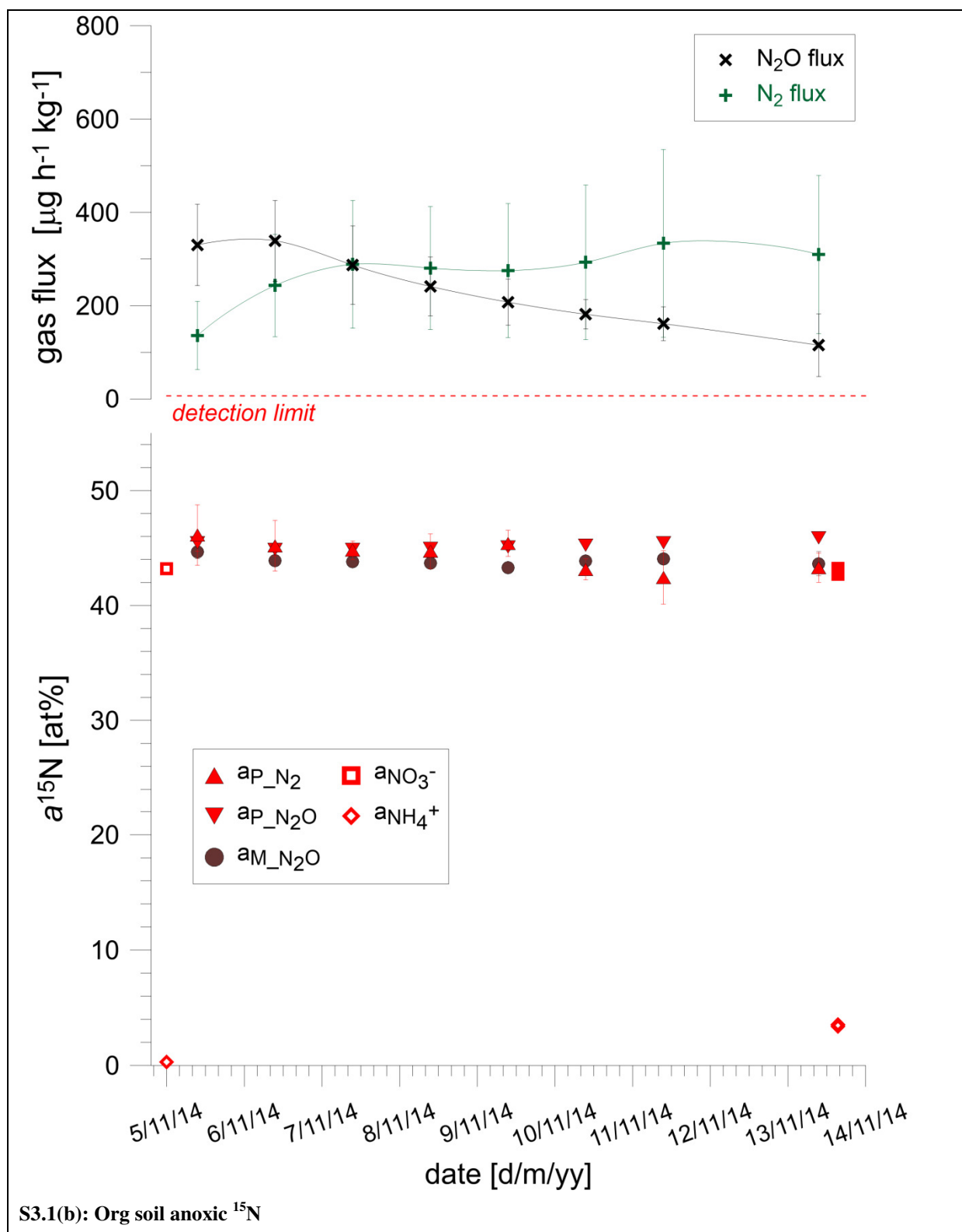
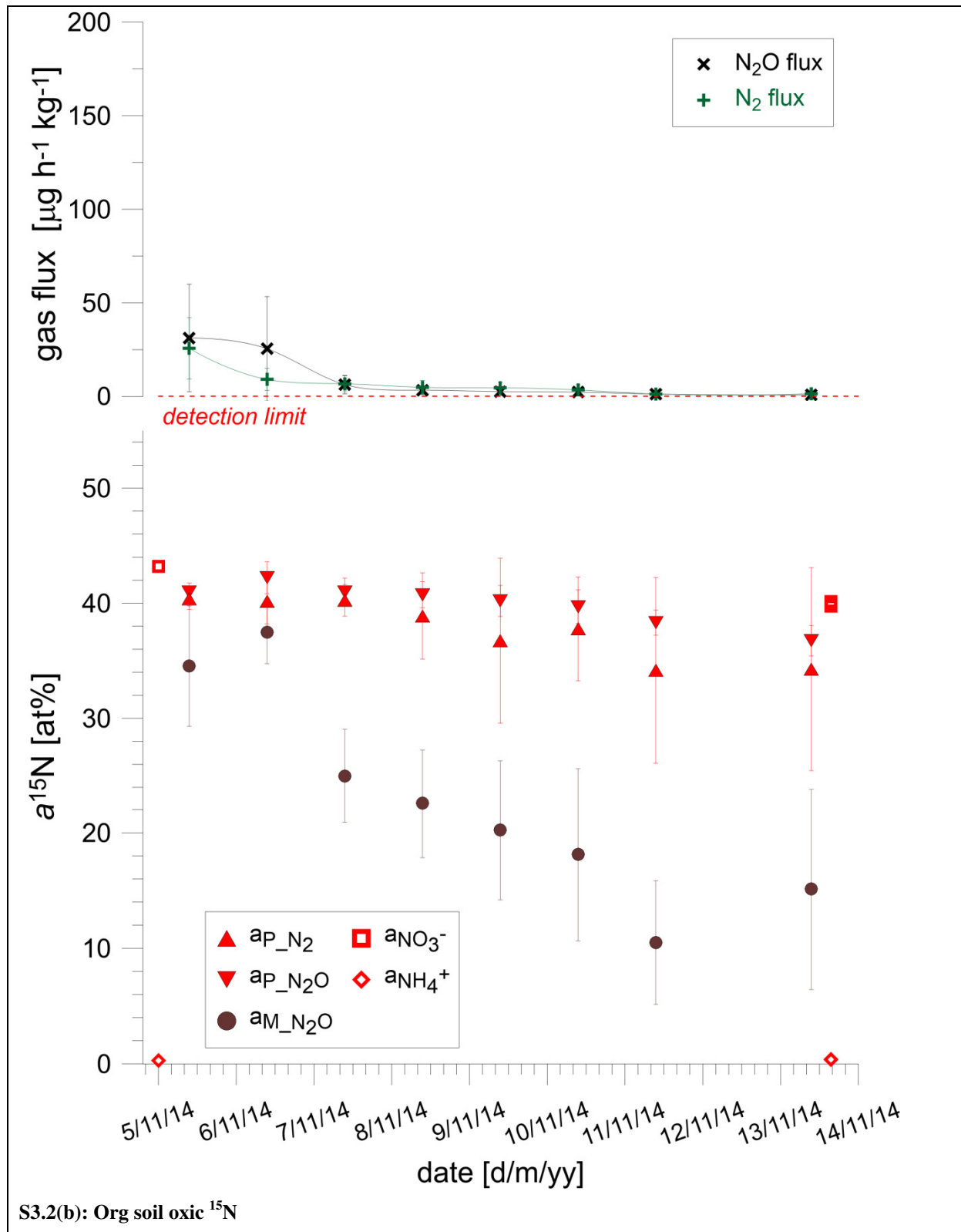



Figure S3: Data of ¹⁵N treatments for Min (A) and Org soil (B) incubated under anoxic (3.1) and oxic (3.2) atmosphere in Exp2. Mean values and standard deviations (n=4; n=3 for Org soil oxic treatment) are shown. Measured N_2O gas fluxes (black crosses, upper graphs) with calculated N_2 fluxes (green crosses, upper graphs) from the calculated residual N_2O fraction, Eq.6 (r_{N2O}) (red crosses, lower graphs).
¹⁵N atom fractions ($a^{15}N$): in total emitted N_2O representing the mixture of ¹⁵N-labelled and non-labelled N_2O (a_{N2O} - brown circles); in ¹⁵N-pool derived N_2O representing ¹⁵N enrichment of active ¹⁵N-labelled pool producing N_2O (a_{P_N2O} - red triangles), and in ¹⁵N-pool derived N_2 representing ¹⁵N enrichment of active ¹⁵N-labelled pool producing N_2 (a_{P_N2} - red reversed triangles). ¹⁵N abundance measured in extracted mineral N: soil nitrate (a_{NO3} - red squares) and ammonium (a_{NH4} - red diamonds), at the beginning and at the end of the experiment.

Table S1: Contents and isotopic signatures of mineral nitrogen pools of Exp 2. Rates of nitrification (*n*), mineralisation (*m*), *DNRA* and immobilisation (*i*) as calculated from mass balances (for NA treatment) and ^{15}N pool dilution (for ^{15}N treatment), Eqs. (15) - (18). All pools are expressed as mg N per kg dry soil, and rates as mg N per kg dry soil per 24 h. Values for natural abundance (NA) treatments and ^{15}N treatments are presented.

treatment	NO$_3^-$ initial			NO$_3^-$ Final			NH$_4^+$ initial	NH$_4^+$ final		N-transformations: calculated rates					
										n	f_{N_N2O}* [N$_2$O]	*DNRA*	*m*	[N$_2$+ N$_2$O]	*i*
NA	$c_{NO3\ 0}$ [mg N kg^{-1}]	$\delta^{15}N_{NO3\ 0}$ [‰]	$\delta^{18}O_{NO3\ 0}$ [‰]	$c_{NO3\ t}$ [mg N kg^{-1}]	$\delta^{15}N_{NO3\ t}$ [‰]	$\delta^{18}O_{NO3\ t}$ [‰]	$c_{NH4\ 0}$ [mg N kg^{-1}]	$c_{NH4\ t}$ [mg N kg^{-1}]		[mg N kg^{-1}]	[mg N kg^{-1}]	[mg N kg^{-1}]	[mg N kg^{-1}]	[mg N kg^{-1}]	[mg N kg^{-1}]
Min Soil															
oxic	117.3	-0.3	49.6	98.7	0.7	47.4	0.1	0.0			0.02			0.05	1.81
anoxic	117.3	-0.3	49.6	80.5	13.7	47.8	0.1	0.9			0.05			2.29	1.39
Org Soil															
oxic	261.6	-0.9	43.0	236.1	1.3	35.1	0.2	0.1			0.15			0.96	1.59
anoxic	261.6	-0.9	43.0	76.3	55.8	39.0	0.2	11.6			0.13			11.01	7.52
^{15}N	$c_{NO3\ 0}$ [mg N kg^{-1}]	$a^{15}N_{NO3\ 0}$ [%]		$c_{NO3\ t}$ [mg N kg^{-1}]	$a^{15}N_{NO3\ t}$ [%]		$c_{NH4\ 0}$ [mg N kg^{-1}]	$c_{NH4\ t}$ [mg N kg^{-1}]	$a^{15}N_{NH4\ t}$ [%]						
Min Soil															
oxic	111.8	51.1		92.8	49.6		0.0	0.0	b.d.	0.30	0.01		0.31	0.02	2.18
anoxic	111.8	51.1		70.3	50.8		0.0	1.0	8.7	0.05	0.04	0.02	0.15	1.67	2.51
Org Soil															
oxic	270.9	43.2		223.8	40.0		0.2	0.1	b.d.	1.93	0.07		1.99	0.34	6.29
anoxic	270.9	43.2		71.1	43.0		0.2	11.9	3.5	0.06	0.13	0.10	1.25	10.42	9.53

S3 Discussion: Relations between isotopic signatures

Here we show the relations between N$_2$O isotopic signatures: $\delta^{15}N^{sp}/\delta^{18}O$ (Fig. S4.1), $\delta^{15}N^{sp}/\delta^{15}N^{bulk}$ (Fig. S4.2), $\delta^{18}O/\delta^{15}N^{bulk}$ (Fig. S4.3). The results from these graphs, *i.e.*, the calculated slopes are summarised in the paper in Table 3 and discussed in Section 3.4.3. On the graphs below we show the correlations slopes for calculated δ_0 values in black and for measured δ values in grey.

S4.1(a): Min soil

S4.1(b): Org soil

S4.2(a): Min soil

S4.2(b): Org soil

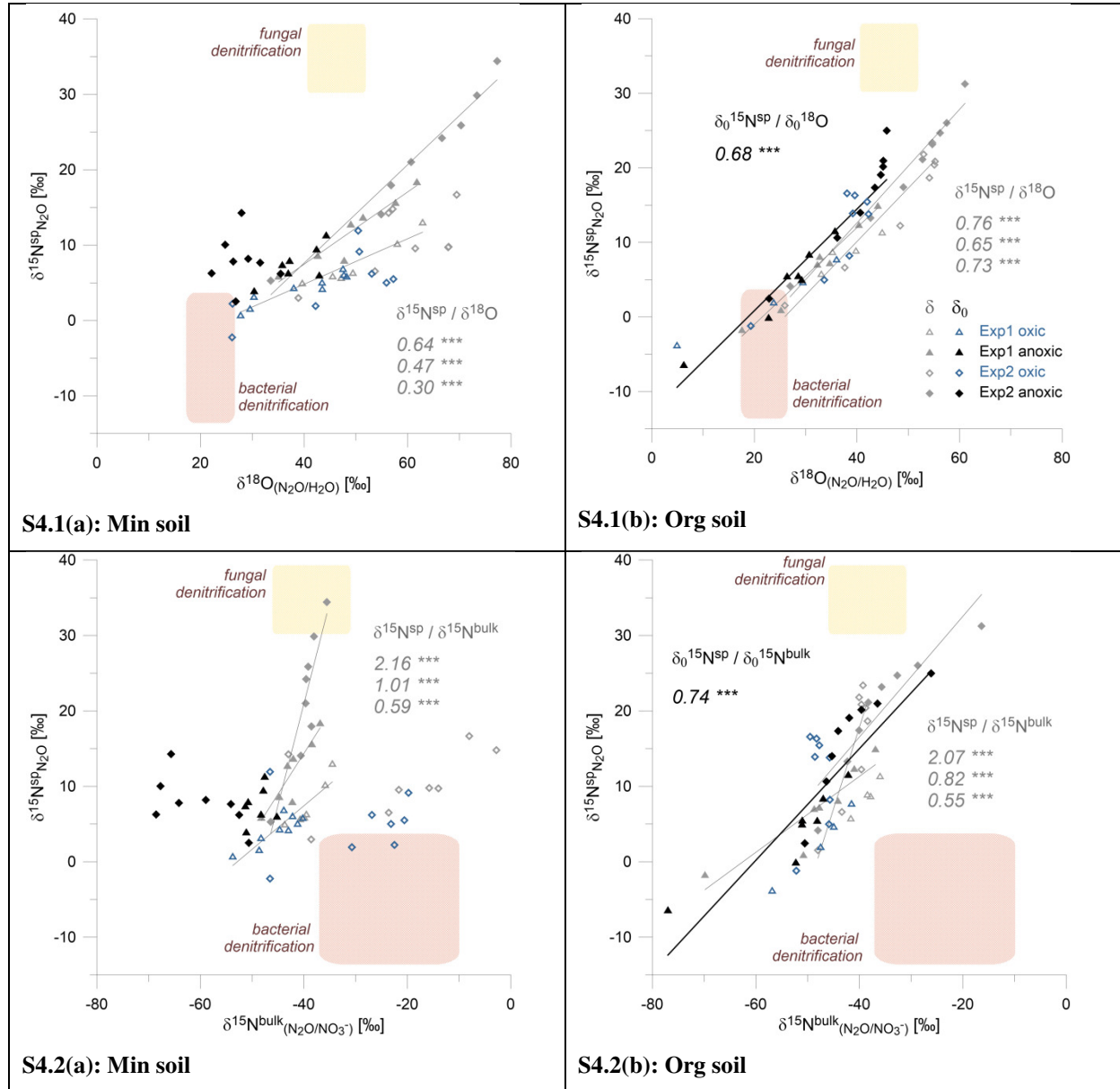
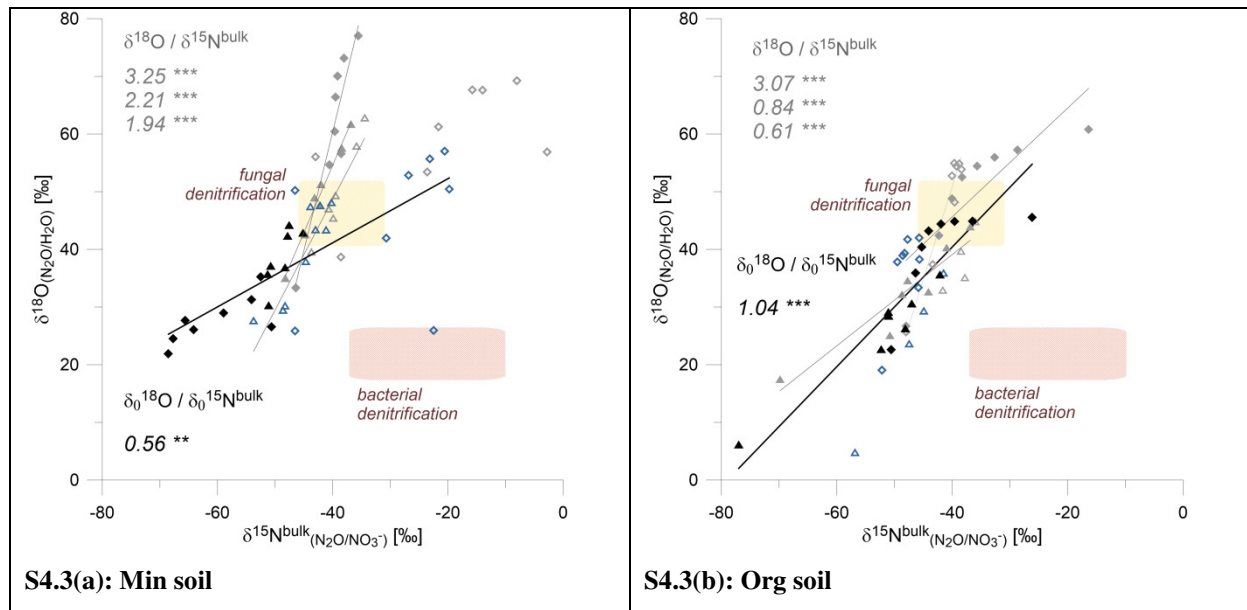



Figure S4: Correlations between isotopic signatures for measured δ values of residual N₂O after reduction (grey points) and for calculated δ₀ values after correction for N₂O reduction according to Eq. (13) (black points for anoxic treatments, blue points for oxic treatments). The slopes of linear regression lines are given for statistically significant correlations: for calculated δ₀ values (black font - slope for all samples jointly) and for measured δ values (grey font - slopes for individual treatments). Min soil (a) and Org soil (b) shown. Given ranges are based on bacterial and fungal pure culture studies (Barford et al., 1999; Frame and Casciotti, 2010; Rohe et al., 2014b; Sutka et al., 2006; Toyoda et al., 2005) summarised by Toyoda et al. (2015) and controlled soil studies (Lewicka-Szczebak et al., 2016).

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