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Nitrous oxide emissions from urea fertiliser and effluent with and without inhibitors applied to pasture

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ABSTRACT

There is currently a limited number of New Zealand studies quantifying nitrous oxide (N_2O) emission factors (EF_1, N_2O emissions as a percentage of N applied) for farm dairy effluent (FDE) and urea fertiliser. Therefore, two experiments were conducted in four regions of New Zealand to determine EF_1 for FDE and urea fertiliser applied to pastures with contrasting soils and climatic conditions. Experiment 1 included urease and nitrification inhibitors to determine their effect on EF_1. Urea treatments included (i) standard urea; (ii) urea amended with the nitrification inhibitor dicyandiamide (DCD) at 0.02 kg DCD kg^{-1} nitrogen (N) and (iii) urea amended with the urease inhibitor *N*-(*n*-butyl) thiophosphoric triamide (*n*BTPT) at 250 mg *n*BTPT kg^{-1} urea, while FDE was applied with or without DCD, at 10 kg DCD ha^{-1}. Experiment 2 focused solely on FDE, which was applied to pastures that had either never received FDE or had a history of repeated application of FDE over several years. Urea fertiliser produced a large variation in EF_1 values, ranging from 0.03% to 1.52%. Application of FDE resulted in EF_1 ranging from 0.06% to 0.94% across both experiments. The urease and nitrification inhibitors had little or no effect on reducing EF_1 from urea fertiliser and FDE application. The history of repeated applications of FDE to pasture also had no effect on EF_1.

1. Introduction

Nitrous oxide (N_2O) is a potent greenhouse gas and contributor to stratospheric ozone depletion, making it a global pollutant of growing concern (Sutton et al., 2014). Agriculture is the largest source of anthropogenic N_2O emissions representing 60% of such emissions (Syakila and Kroeze, 2011), with increasing use of synthetic N fertiliser being one of the important factors, leading to the rapid increase of atmospheric N_2O concentration in recent decades (Davidson, 2009). Synthetic fertilisers and animal manure are applied to pastures to promote growth for livestock feed. In New Zealand, the amount of N fertiliser applied to agricultural soils increased from 59 kt in 1990 to 359 kt in 2013, urea representing more than 80% of all synthetic N fertiliser in 2013 (Ministry for the Environment, 2015). Farm dairy effluent (FDE), a mixture of excreta and water with a total solids (TS) content of less than 5% (Longhurst et al., 2012), is the most common form of animal manure collected and applied to New Zealand pastoral soils (Laubach et al., 2015). Derived from the washdown of dairy milking sheds and associated yards, FDE represented 6% of lactating dairy cattle excreta a decade ago (Ledgard and Brier, 2004). However, this proportion is steadily increasing with increased intensification of dairying in New Zealand, leading to greater use of off-paddock facilities such as feedpads (Laubach et al., 2015), which are now present on approximately one-quarter of New Zealand dairy farms (Luo et al., 2013).

Repeated application of FDE onto pastoral soils may influence the magnitude of N_2O production and emissions due to continued addition of organic manure elevating soil labile C supply. This may raise both background and FDE emissions following FDE application compared to pastoral soils with no effluent irrigation history. Furthermore, apart from labile C influencing substrate supply for

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denitrifiers, it is also possible that nitrifying and denitrifying microbial activity may be influenced by the repeated application of effluent over several years.

To mitigate N_2O emissions from urea- and ammonium-based fertilisers and animal slurries/effluent the nitrification inhibitor dicyandiamide (DCD) has been used for several decades to retain soil N in the ammonium form, thereby improving their N use efficiency, and reduce N losses via nitrate (NO_3^-) leaching and N_2O emissions (Halvorson et al., 2014; Cahalan et al., 2015). Studies have shown that DCD can be effective at reducing N_2O emissions from N fertiliser application (McTaggart et al., 1997; Dobbie and Smith, 2003; Misselbrook et al., 2014; Gilsanz et al., 2016) and slurry and effluent application to grassland soils (Li et al., 2014, 2015; Cahalan et al., 2015; Gilsanz et al., 2016). In addition, urease inhibitors, such as *N*-(*n*-butyl) thiophosphoric triamide (*n*BTPT) that slow the conversion of urea to NH_4^+ by inhibiting soil urease activity and reducing NH_3 emissions can reduce the rate of nitrification and potentially the associated N_2O emissions. However results on the efficacy of urease inhibitors to reduce N_2O emissions have been inconsistent (Saggar et al., 2013). For example, Sanz-Cobena et al. (2012) conducted a two-year study comparing standard urea with *n*BTPT-treated urea for maize production and observed a 54% reduction in N_2O emissions in the first year, but no reduction in the following year.

As the current country-specific values of EF_1 for FDE and urea are based on few studies, largely conducted in one region of New Zealand, we conducted two experiments across four regions to test the following hypotheses: (i) the nitrification inhibitor DCD can effectively reduce the EF_1 for FDE as well as urea, (ii) the urease inhibitor *n*BTPT can effectively reduce the urea EF_1, and (iii) repeated application of FDE will alter the FDE EF_1.

2. Methodology

2.1. Field sites

Two field experiments were conducted in 4 regions (Waikato, Manawatu, Canterbury and Otago) of New Zealand. The first experiment started in September 2013 and the second in September 2014. All the regions have temperate climates, with mean annual rainfall of 1240 mm and mean annual temperature of 14 °C in Waikato, 970 mm and 13 °C in Manawatu, 680 mm and 11.5 °C in Canterbury and 700 mm and 9 °C in Otago.

Table 1 describes soil characteristics at each site in Experiments 1 and 2. All of the sites support a predominately ryegrass (*Lolium perenne*)/white clover (*Trifolium repens*) pasture which is grazed. Animals were excluded from the experimental sites for at least two months prior to treatment application, based on previous experience (Luo et al., 2007).

2.2. Experimental design and treatments

Each experiment was laid down as a completely randomised block design, with 6 replicates of each treatment. Experiment 1 included five N treatments; (i) urea (50 kg N ha^{-1}), (ii) urea + DCD (0.02 kg DCD kg^{-1} N) (iii) urea + *n*BTPT (250 mg *n*BTPT kg^{-1} urea) (iv) FDE (52–58 kg total N ha^{-1}) and (v) FDE +DCD (10 kg DCD ha^{-1}) (Table 2), as well as an untreated control (C). Each experimental site included 36 plots of 2 × 2.5 m, within which an area of 2 × 2 m was treated for soil sampling, to ensure there was sufficient soil available for 12 months of field sampling. The remaining 0.5 × 2 m area was used for siting N_2O gas chambers. A single application of each treatment was made on 4 or 5 September 2013, depending on the region. In New Zealand urea application to pasture is typically split 75:25 between spring and autumn (Jeff Morton, Ballance Agri-Nutrients, pers. comm.). The majority of stored FDE is typically applied from spring through to mid-summer, with less applied in the latter half of the lactation season up to the end of autumn to ensure storage ponds are empty by the beginning of winter (Dave Houlbrooke, AgResearch, pers. comm.). In this study the rate of urea applied was the same for each treatment and similar to the typical rate used for pasture (30–50 kg N ha^{-1}; Roberts and Morton, 2012) while FDE was typically applied at between 30 and 150 kg N ha^{-1} (maximum N load; Houlbrooke et al., 2013). For the FDE-DCD treatment, DCD was dissolved in deionised water at a rate of 10 kg DCD (containing 0.7 kg N kg^{-1}) per 800 L and sprayed on to the pasture plots immediately before FDE application, resulting of addition of 7 kg DCD-N ha^{-1}. Because

Table 1
Soil characteristics and locations of each site used for Experiments 1 and 2. For paddock FDE history, the number of years each site had received FDE is shown in brackets.

Region	Soil order	Soil type	Paddock FDE history (number of years receiving FDE)	Soil properties					
				Olsen P (mg L^{-1})	pH	Organic C (g kg^{-1} soil)	TKN (g kg^{-1} soil)	Bulk density (Mg m^{-3})	Total porosity (m^3 m^{-3})
Experiment 1: September 2013									
Waikato	Typic, orthic allophanic	Horotiu silt loam	No FDE history	44	6.0	59	6.7	0.84	0.68
Manawatu	Weathered, fluvial, recent	Karapoti fine sandy loam	No FDE history	27	5.7	25	2.6	1.08	0.59
Canterbury	Immature pallic	Templeton fine sandy loam	No FDE history	25	6.5	28	2.2	1.16	0.56
Otago	Mottled-weathered fluvial recent	Wingatui deep silt loam	No FDE history	32	6.0	49	4.8	0.90	0.66
Experiment 2: September 2014									
Waikato	Typic orthic allophanic	Horotiu silt loam	No FDE history	97	6.1	67	6.7	0.85	0.63
			FDE history (20)	114	6.4	72	7.3	0.83	0.64
Manawatu	Typic fluvial recent	Recent sandy[a]	No FDE history	53	6.9	14	1.4	1.26	0.52
			FDE history (25[b])	57	5.9	25	2.6	1.16	0.55
Canterbury	Immature pallic	Templeton fine sandy loam/silt loam.	No FDE history	26	5.8	37	3.5	1.12	0.56
			FDE history (14)	20	6.0	37	3.3	1.06	0.59
Otago	Acidic orthic gley	Koau deep silty clay loam	No FDE history	21	6.2	93	8.3	0.75	0.69
			FDE history (10)	65	6.5	108	9.9	0.73	0.69

[a] The 'No FDE history' site was classified as a sandy loam soil, whilst the 'FDE history' site was classified as a loamy silt soil.
[b] Estimated by the farmer as "20–30 years", therefore we have assumed a mid-point of 25 years.

Table 2
Treatments, N load (kg N ha^{-1}) and measurement period for Experiments 1 and 2.

Region	Treatment	N load (kg N ha^{-1})	Measurement period
Experiment 1: September 2013			
Waikato	Urea	50	157 days, up to 8 January 2014
	Urea + DCD (0.02 kg DCD kg^{-1} N)	51	
	Urea + *n*BTPT (250 mg *n*BTPT kg^{-1} urea)	50	
	FDE	58	370 days, up to 9 September 2014
	FDE + DCD (10 kg DCD ha^{-1})	65	
Manawatu	Urea	50	81 days, up to 26 November 2013
	Urea + DCD (0.02 kg DCD kg^{-1} N)	51	
	Urea + *n*BTPT (250 mg *n*BTPT kg^{-1} urea)	50	
	FDE	52	366 days, up to 5 September 2014
	FDE + DCD (10 kg DCD ha^{-1})	59	
Canterbury	Urea	50	97 days, up to 10 December 2013
	Urea + DCD (0.02 kg DCD kg^{-1} N)	51	
	Urea + *n*BTPT (250 mg *n*BTPT kg^{-1} urea)	50	
	FDE	56	366 days, up to 4 September 2014
	FDE + DCD (10 kg DCD ha^{-1})	63	
Otago	Urea	50	96 days, up to 11 December 2013
	Urea + DCD (0.02 kg DCD kg^{-1} N)	51	
	Urea + nBTPT (250 mg *n*BTPT kg^{-1} urea)	50	
	FDE	57	367 days, up to 8 September 2014
	FDE + DCD (10 kg DCD ha^{-1})	64	
Experiment 2: September 2014			
Waikato	FDE	54	105 days, up to 27 January 2015
Manawatu	FDE	28	106 days, up to 28 January 2015
Canterbury	FDE	43	126 days, up to 17 February 2015
Otago	FDE	46	103 days, up to 11 January 2015

the DCD treatment was equivalent to a shallow depth of only 0.08 mm water, no equivalent water was applied to the control plots. The DCD-treated urea contained a loading of 0.02 kg DCD kg^{-1} urea-N. In the urea + *n*BTPT treatment, *n*BTPT was added at the recommended rate of 250 mg kg^{-1} urea, akin to the commercially formulated fertiliser product called SustaiN (Saggar et al., 2013). The fertiliser products were manufactured by Ballance Agri-Nutrients, Mt. Manganui, New Zealand.

Experiment 2 used different sites to Experiment 1 and included two treatments: (i) FDE (28–54 kg N ha^{-1}) applied to paddocks with no history of receiving effluent ('no FDE history') and (ii) FDE (28–54 kg N ha^{-1}) applied to paddocks that had previously received effluent over 10 years or more ('FDE history') (Table 2). An untreated control (no FDE) was also included in each paddock in each region. Within each paddock, the experimental site included 12 plots of 1×2 m each, within which an area of 1×1 m was treated for soil sampling and the remaining 1×0.5 m area used for siting N_2O gas chambers. Smaller soil sampling plots were used in Experiment 2 because of the shorter duration of up to 3–4 months sampling. A single application of each treatment was applied on 14 October 2014 in Waikato, Manawatu and Canterbury, and on 16 October 2014 in Otago. The paddocks with 'FDE history' had received at least one application of FDE annually for the past 20, 25, 14 and 10 years at the Waikato, Manawatu, Canterbury and Otago sites, respectively.

For both experiments, fresh FDE was collected either on the day of application or 1 day earlier from the sump of dairy milking shed yards on local dairy farms within each region to represent typical fresh FDE applied to pasture under spring conditions. In Experiment 1, the N concentration of the FDE was adjusted to ca 0.5 g N L^{-1} using dairy cattle urine collected from local dairy farms. This was achieved by analysing a sub-sample of FDE for total N content and adding urine where N content was <0.5 g N L^{-1}. The concentration of 0.5 g N L^{-1} was based on FDE data presented by Longhurst et al. (2000). In Experiment 2, a simpler approach was adopted to avoid influencing the ammoniacal-N:total N ratio, with no alteration of the N concentration. Instead, the N content of local dairy FDE ponds was analysed 2–3 weeks prior to the start of the experiment to identify ponds where N concentration was 0.3–0.5 g N L^{-1}.

On application day, an FDE subsample was collected from each region for analysis (total solids, pH, total carbon, total nitrogen, ammoniacal-N content, nitrate-N content) to characterise the FDE that was applied to the plots (Table 3). These characteristics are

Table 3
Characteristics of FDE applied to plots in Experiments 1 and 2.

Region	Total solids (%)	pH	Total C concentration (g L^{-1})	Total N concentration (g L^{-1})	NH_4–N (mg L^{-1})	TAN[a] as % of Total N (%)	NO_3–N (mg L^{-1})
Experiment 1: September 2013							
Waikato	0.2	7.8	2.2	0.58	311	54	<5
Manawatu	0.4	7.3	1.6	0.52	145	28	<5
Canterbury	0.2	8.8	1.8	0.56	370	66	<5
Otago	0.4	7.7	2.2	0.57	312	55	<5
Experiment 2: September 2014							
Waikato	0.7	8.0	2.3	0.54	229	42	<5
Manawatu	2.1	7.5	1.8	0.28	169	60	<5
Canterbury	0.3	8.3	0.9	0.43	210	49	<5
Otago	0.8	7.4	2.2	0.46	285	62	<5

[a] TAN = total ammoniacal N.

typical of FDE applied to New Zealand pastures. FDE was applied to the pasture plots at a depth of 10 mm, following the guidelines for application to soils with impeded or low infiltration rates to minimise overland flow of land-applied FDE (Houlbrooke et al., 2013). The volume of FDE applied ranged between 9.4 and 10.2 L m^{-2} depending on the N content. While many of the sites used in the study were located on well-draining soils, we maintained this depth of application for consistency in the wetting up of soils by FDE application.

Urea and FDE treatments were applied to the gas chamber areas (between 0.05 m^2 and 0.07 m^2, varying between the regions). Adjacent to each N_2O sampling area a set of separate plots for destructive soil sampling received the same treatments at the same rates as for the N_2O measurements. Pasture growth was managed by cutting herbage when the pasture was about 12 cm height to approximately 3–5 cm height (or about 1400 kg DM ha^{-1}) in the study areas.

2.3. Gas measurements

The direct N_2O emissions were measured using a standardised static cover technique (de Klein et al., 2014). Measurements were taken twice a week for the first 6 weeks after treatment application and then once a week, with an additional sampling taken within 1–2 days when rainfall exceeded 10 mm in 24 h (van der Weerden et al., 2013). On each sampling day, sampling was done once between 10 a.m. and 12 p.m. standard time to estimate the mean emissions (van der Weerden et al., 2013). Headspace gas samples were taken during a cover period of 40 min at times t_0,t_{20} and t_{40} for the first 13 gas sampling occasions and during a cover period of 40 min at times t_0 and t_{40} for the remainder of the sampling occasions. On each sampling day at each site, 2 background atmosphere samples were taken. Gas samples were analysed by gas chromatography, with samples collected in Waikato, Canterbury and Otago analysed at Lincoln University, Canterbury, using an SRI Instruments 8610 gas chromatograph (San Francisco, CA, USA), where N_2O was quantified using an ^{63}Ni electron capture detector operated at 320 °C. Samples collected from Manawatu were analysed by Landcare Research, Palmerston North using a Shimadzu GC-17 gas chromatograph (Kyoto, Japan), where N_2O was quantified using a ^{63}Ni electron capture detector operated at 280 °C.

Gas and soil sampling from the urea fertiliser treatments in Experiment 1 were carried out over a 3 month period, by which time N_2O emissions had returned to background levels (as measured from the control treatment). Sampling from the FDE (and control) treatments was carried out over 12 months, thereby ensuring emissions and soil mineral N content had returned to background levels. For Experiment 2, gas and soil sampling from the FDE treatments (and controls) were carried out over a 3–4 month period, until N_2O emissions and soil mineral N content had returned to background levels (as measured from the control treatment). Data from Experiment 1 suggested N_2O emissions from FDE were complete after 3–4 months following FDE application at ca 50 kg N ha^{-1}.

The hourly N_2O emissions (mg N m^{-2} h^{-1}) were calculated from the linear increase in head space N_2O over the sampling time (de Klein et al., 2014; de Klein and Harvey, 2012).

$$N_2O\ \text{flux} = \frac{\delta N_2O}{\delta T} \times \frac{M}{V_m} \times \frac{V}{A} \quad (1)$$

where, δN_2O is the increase in head space N_2O over time (μL L^{-1}); δT is the enclosure period (h); M is the molar weight of N in N_2O; V_m is the molar volume of gas at the sampling temperature (L mol^{-1}); V is the headspace volume (m^3); and A is the area covered (m^2).

These hourly emissions were subjected to a trapezoidal integration, for each chamber, to estimate the total emission over the measurement period. Any negative fluxes observed, including those within the minimum detection limit (MDL) of ±0.006 mg N m^{-2} h^{-1}, were included for calculating cumulative losses to avoid biasing the results. The direct N_2O emission factors (EF_1, N_2O–N emitted as a % of N applied) were then calculated by dividing the treatment-induced emission by the amount of N applied for each treatment (de Klein et al., 2014):

$$EF_1 = \frac{\text{Total FDE or fertiliser } N_2O - \text{Total Control } N_2O}{\text{FDE or fertiliser N applied}} \times 100\% \quad (2)$$

where EF_1 is emission factor (N_2O–N emitted as a % of N applied), Total FDE or fertiliser N_2O and total control N_2O are the cumulative N_2O emissions from the FDE, fertiliser and control plots, respectively (kg N ha^{-1}), and FDE or fertiliser N applied is the rate of N applied (kg N ha^{-1}). For Experiment 1, the urea fertiliser EF_1 values were calculated using the control treatments restricted to the same time period as the urea treatments within each region, whereas FDE EF_1 values were calculated using the 12-month cumulative emissions measured from the FDE and control plots.

2.4. Soil measurements

Soil bulk density measurements were taken at the start of each experiment. Soil cores (100 mm diameter × 75 mm height) were dried at 105 °C for 48 h and then dry soil recorded and bulk densities calculated (Mg m^{-3}).

On each gas sampling day, six soil samples (75 mm deep, 25 mm diameter) were taken from each plot and bulked for determination of soil NO_3^-, soil NH_4^+ and soil water content per plot. However, during the first 6 weeks when gas samples were collected twice a week, soil mineral N determination was limited to once a week. In the laboratory on the same or the following day, the soil samples were thoroughly mixed and about 15 g fresh soil (about 10 g dry soil equivalent) was extracted for 1 h in 50 mL 2 M KCl. The filtered solution was then frozen until analysed for nitrate N (plus nitrite N), and ammonium N. The remainder of the mixed soil was dried at 105 °C for 24 h, to determine gravimetric soil water content. Volumetric water content and water-filled pore space (WFPS) were calculated using measured bulk density and measured particle density data. Daily rainfall, ambient air and soil temperatures (5 cm depth) were logged for the entire experimental period at a site near to the experimental site in each region. A manual rain gauge was installed at each site to determine total rainfall between sampling days.

2.5. Statistical analysis

An analysis of variance (ANOVA) was performed to determine if the cumulative N_2O emission and EF_1 data obtained from different treatments were significantly different. Cumulative N_2O emission and EF_1 data, across all regions and sites, were found to be highly skewed with non-constant variance. Therefore, cumulative N_2O emission values were log transformed prior to analysis using Genstat (version 13; Payne et al., 2014).

In Experiment 1, cumulative N_2O emissions and EF_1 data for both fertiliser and FDE treatments were $\log(x+a)$ transformed prior to analysis, where a values were chosen to best stabilise the variance and remove skewness. The term a was required due to the presence of negative values. The reported cumulative means and EF_1 values were obtained following back-transformation.

Data from Experiment 2 were treated similarly, where EF_1 data were $\log(x+a)$ transformed prior to analysis. The term a differed from that used in Experiment 1. A single outlier was removed from the Otago cumulative emissions data, while a single outlier was also removed from the Canterbury EF_1 data. The reported cumulative means and EF_1 values were obtained following back-transformation.

3. Results

3.1. Climate

In 2013 (Experiment 1), Waikato, Manawatu and Otago experimental sites experienced typical annual soil (5 cm depth) temperatures (11–15 °C), with the first 3 months (September to November) of the experiments averaging between 12 and 15 °C (Fig. 1a, b and d). Canterbury was warmest, with soil temperature averaging 19 °C in the first three months and an annual average temperature of 17 °C (Fig. 1c), which was 5 °C higher than the long term average. In 2014 (Experiment 2) soil temperatures at the Waikato and Manawatu sites averaged 18 °C over the 3–4 month (September to December) period (Fig. 2a and b), while the Canterbury and Otago sites averaged 15 °C over the same period (Fig. 2c and d).

Waikato received the largest amount of rainfall during the first experiment, with 137 mm in the first month and 1031 mm for the entire year, reflecting the high long-term annual rainfall (1240 mm). The other three regions received similar amounts of rainfall during the 12 month experimental period, ranging from 627 mm (Canterbury) to 769 mm (Otago): both amounts were typical for these regions. Manawatu received 742 mm; while this was lower than the long term average of 970 mm, the first 3 months were very wet, with 276 mm being measured (Fig. 1). In 2014 (Experiment 2), the Canterbury site received the largest amount of rainfall, with 388 mm being recorded over a 126 day period. Rainfall in Waikato, Manawatu and Otago over the study period was lower, at 288, 182 and 143 mm (Fig. 2). It should be noted that measurements were made for 20–23 more days in Canterbury compared to the other regions due to differences in N_2O fluxes and soil mineral N between the FDE and control treatments being observed for a longer period. Measurements were stopped once there was no difference in N_2O fluxes and soil mineral N between the FDE and control treatments. When comparing regions over the first three months, Waikato and Canterbury had similar rainfall totals (279 and 284 mm, respectively), while the Manawatu and Otago sites received 181 and 126 mm, respectively.

3.2. Experiment 1

3.2.1. Hourly N_2O fluxes

Nitrous oxide fluxes increased immediately following application of urea fertiliser compared to the control treatments in Waikato and Manawatu, reaching levels of 0.092 and 0.399 mg N_2O–N m^{-2} h^{-1}, respectively (Fig. 3a and b). In contrast, the Canterbury and Otago sites produced very small increases in N_2O fluxes from urea application (Fig. 3c and d).

Maximum N_2O fluxes were measured from FDE treatments within 1 to 3 days of application, with the largest fluxes being measured from the Manawatu site (0.204 mg N_2O–N m^{-2} h^{-1}) 1 day following application (Fig. 3b). Fluxes returned to background levels one month following FDE application. In contrast, the Canterbury and Otago sites produced very small peak fluxes of ca 0.039–0.044 mg N_2O–N m^{-2} h^{-1} on days 2 and 3, respectively (Fig. 3c and d). Following the initial spike, N_2O fluxes remained low at all sites for the remaining 12 months; any increase in flux activity from FDE treatment was often also observed in the control treatments.

Urea treated with DCD or *n*BTPT resulted in similar patterns of N_2O emissions compared with those from standard urea (Fig. 3). Applying DCD to pasture just prior to FDE application had little effect on N_2O fluxes at all sites, although fluxes were occasionally elevated from this treatment compared to FDE with no DCD and control throughout the experiment in Waikato, Canterbury and Otago (Fig. 3a, c and d).

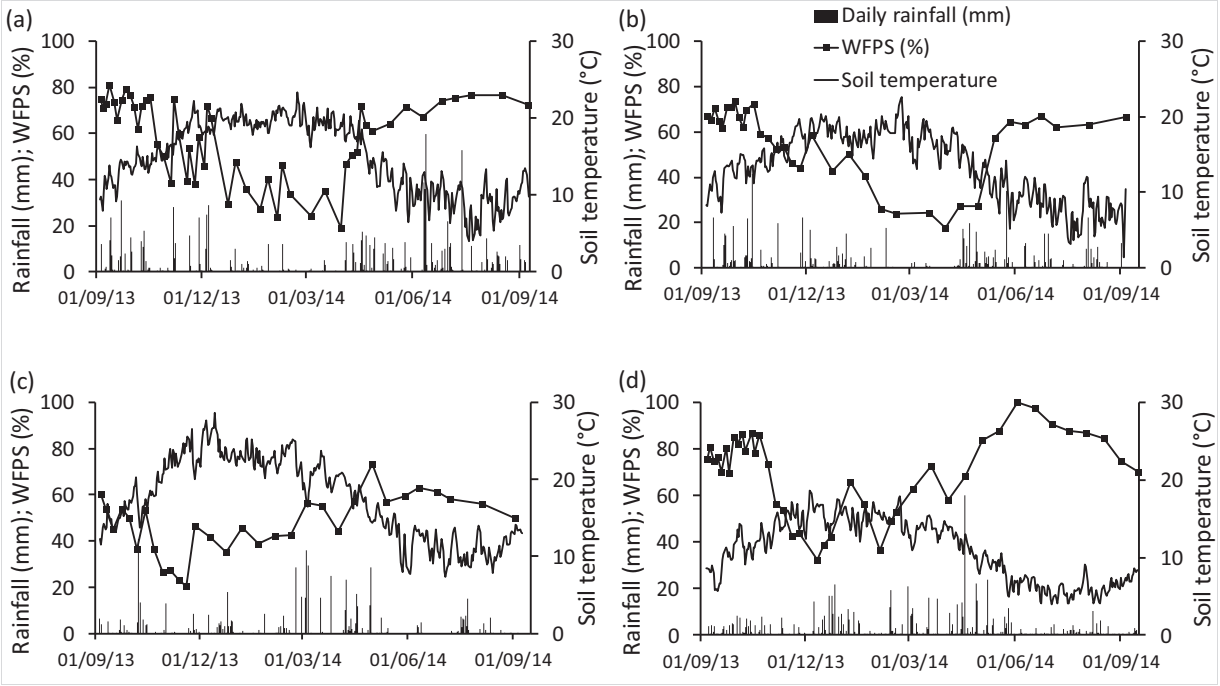

Fig. 1. Daily rainfall, average daily water filled pore space (WFPS) and soil temperature at sites used for Experiment 1 (September 2013–2014). (a) Waikato, (b) Manawatu, (c) Canterbury, (d) Otago.

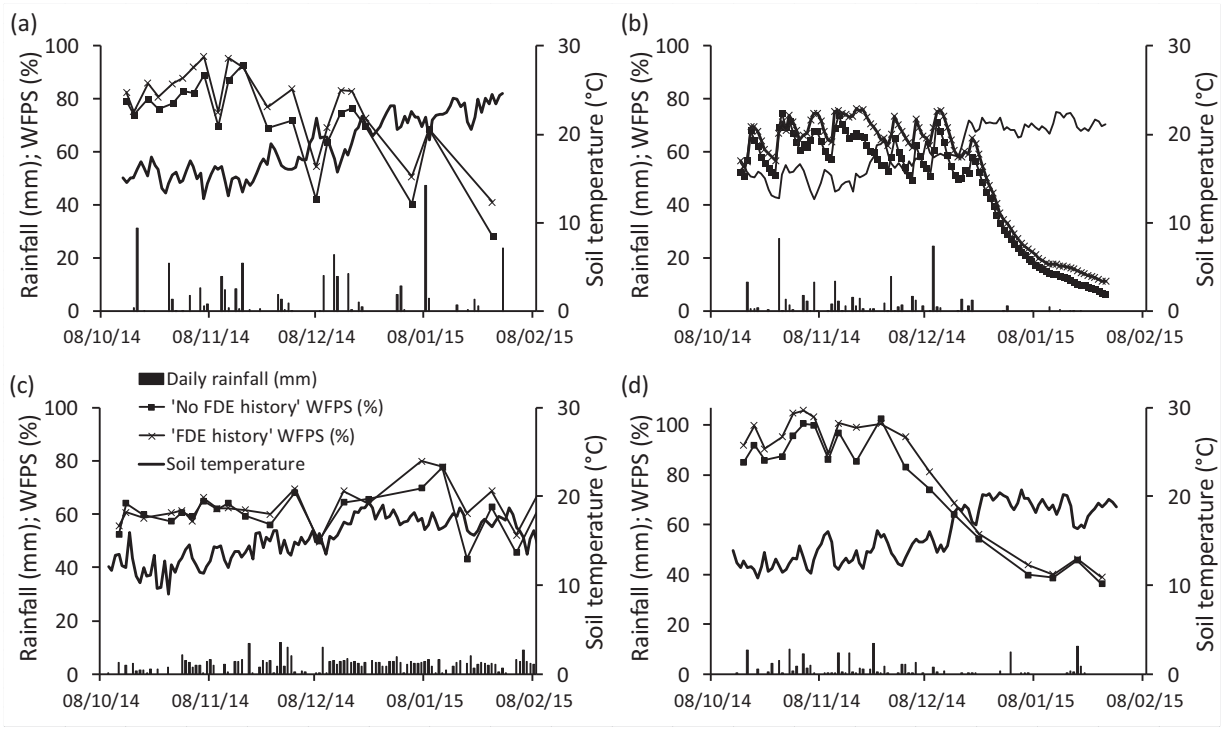

Fig. 2. Daily rainfall, average daily water filled pore space (WFPS) and soil temperature at sites used for Experiment 2 (October 2014–February 2015). (a) Waikato, (b) Manawatu, (c) Canterbury, (d) Otago.

3.2.2. Cumulative N_2O emissions

Cumulative N_2O emissions from standard urea fertiliser were significantly greater than from the control treatment ($P < 0.05$; Table 4) in Waikato, Manawatu and Canterbury, ranging from 94 to 780 g N_2O–N ha^{-1}. The cumulative N_2O loss from urea + DCD was significantly lower than from standard urea at the Manawatu site ($P < 0.05$), while cumulative N_2O losses from urea + DCD were not significantly different ($P > 0.05$) to those from standard urea treatment at the other three sites. Amending urea with *n*BTPT had no effect on cumulative N_2O losses compared to standard urea at all four sites ($P > 0.05$; Table 4).

Application of FDE to pasture at the Manawatu site produced the largest cumulative N_2O emissions (1479 g N ha^{-1}), which were significantly greater than the control plots over a 12 month period ($P < 0.05$; Table 4). In contrast, all other three regions produced cumulative N_2O emissions from FDE that were not significantly different from the control ($P > 0.05$), ranging from 171–719 g N ha^{-1} (Table 4). Addition of DCD to pasture at 10 kg DCD ha^{-1} just prior to FDE application did not significantly reduce N_2O emissions compared to the untreated FDE application ($P > 0.05$). However, DCD increased cumulative N_2O emissions from FDE at the Waikato site ($P < 0.05$).

3.2.3. Emission factors

Emission factors for urea fertiliser ranged from 0.03% to 1.52% across the sites (Table 4). Three of the sites ranged between 0.03% and 0.42%, while the Manawatu site produced an unusually high EF_1 value of 1.52%. This particular site had a large spatial variation across the replicates, with the 95% confidence interval ranging from 0.53 to 3.55% (Table 4). One of the blocks displayed high cumulative N_2O emissions for several treatments: when this block was removed from the analysis, the mean EF_1 for urea became 0.98% (95% confidence interval (CI) of 0.30–2.66%). However, there was no justifiable reason for omitting this block and therefore have retained the value of 1.52%.

Amendment of urea with DCD resulted in lower EF_1 values, however they were not significantly different from those of standard urea ($P > 0.05$; Table 4). Amending urea with *n*BTPT had no significant effect on EF_1 for urea (Table 4). Farm dairy effluent EF_1 values never exceeded 1%, ranging from 0.06 to 0.78% (Table 4). Similar to the results for the urea fertiliser treatment, the largest EF_1 value was measured at the Manawatu site. Application of 10 kg DCD ha^{-1} just prior to FDE application had no significant effect on EF_1 at all four sites ($P > 0.05$; Table 4).

3.2.4. Soil analysis

The soil water content for the first month following treatment application was similar in Waikato, Manawatu and Otago, with WFPS averaging between 68 and 77% (Fig. 1a, b and d). Relatively dry conditions saw WFPS decline to low levels, particularly in Waikato, where WFPS reached 20% four months following treatment application, before increasing again due to wet conditions (Fig. 1a). Canterbury exhibited the driest soil conditions amongst all regions, averaging 52% WFPS in the first month and 47% over the entire 12 months (Fig. 1c).

Soil NH_4^+–N content increased rapidly following urea fertiliser application, with soil NO_3^-–N content increasing within 5 days of application of the urea treatments (Fig. 3). However, in Manawatu and Otago, the increase in soil NO_3^-–N content was limited. DCD and *n*BTPT appeared to have no or little influence on soil NH_4^+–N and NO_3^-–N content in the urea fertiliser treatments at all four sites (Fig. 3).

The FDE treatments applied in Waikato, Canterbury and Otago elevated soil NH_4^+–N content with addition of DCD having no effect on the soil NH_4^+–N content (Fig. 3 a, c and d). Both FDE and FDE + DCD treatments at the Manawatu site showed a small increase in soil NH_4^+–N content soon after treatment application (Fig. 3b). Soil NO_3^-–N content increased following FDE application, returning to background levels within 2 weeks of application. Approximately 6 months following FDE application, a small

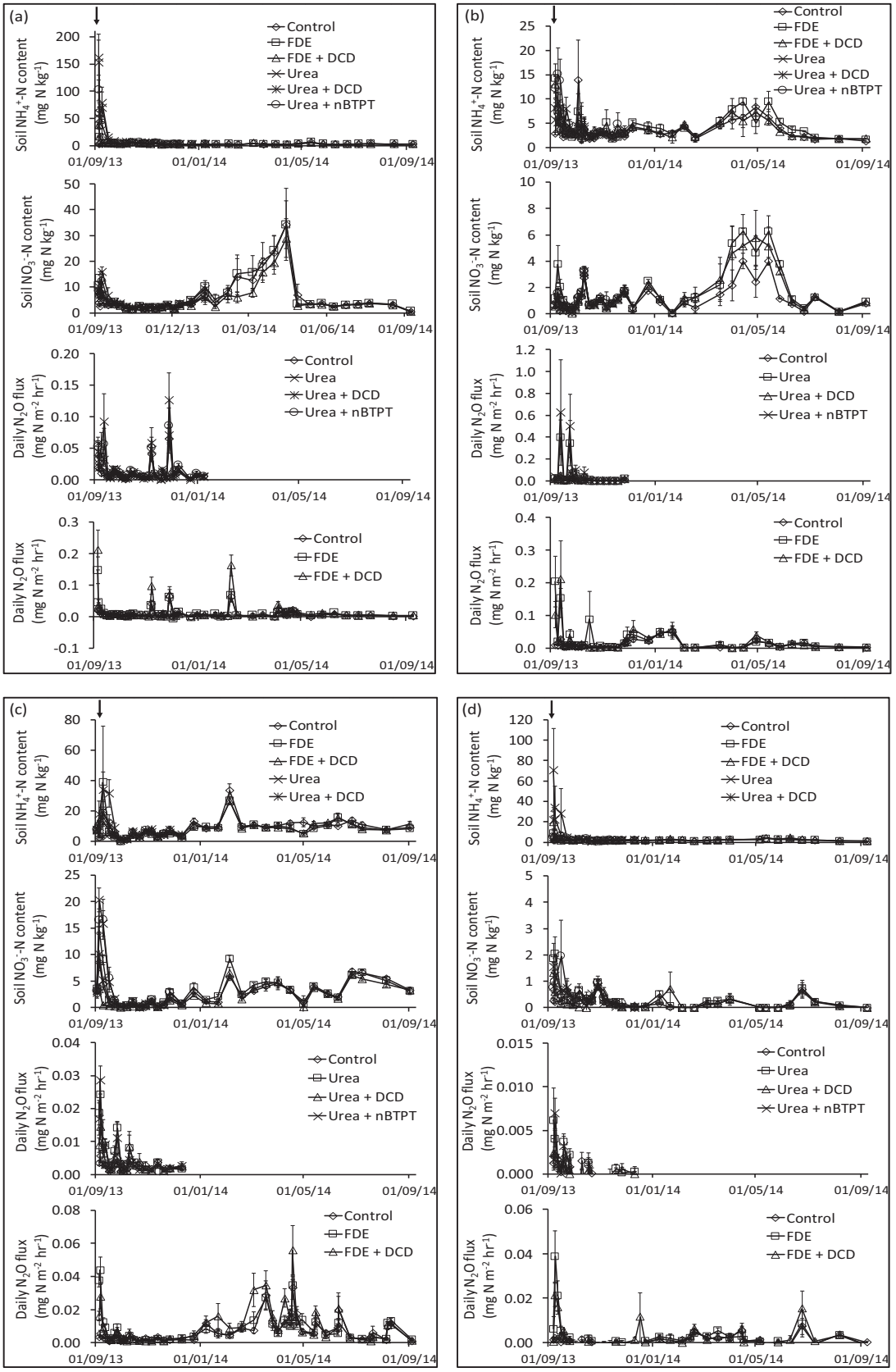

Fig. 3. Soil NH_4^+–N, soil NO_3^-–N contents and N_2O fluxes from 4 sites used for Experiment 1. (a) Waikato, (b) Manawatu, (c) Canterbury and (d) Otago. Solid arrow represents time of fertiliser and FDE application. (*Note*: different *Y* axis between experiments).

Table 4
Cumulative N_2O emissions (g N_2O–N ha^{-1}) and EF_1 for urea and FDE, with and without nitrogen inhibitors, applied to pasture at ca. 50 kg urea-N ha^{-1} in four regions on 4 or 5 September 2013 (depending on region) in Experiment 1. Emissions and EF_1 values are back-transformed and bias-corrected means of the transformation $\log_e(x+a)$, with 95% confidence intervals in brackets.

N treatment	Waikato	Manawatu	Canterbury	Otago
Synthetic N fertiliser				
Cumulative losses				
Control	269	163	56	−11
	(189–385)	(83–319)	(41–75)	(−22 to 2)
Urea	451	780	94	3
	(316–645)	(398–1530)	(69–127)	(−11 to 19)
Urea + DCD	417	264	72	−10
(0.02 kg DCD kg^{-1} N)	(292–595)	(135–518)	(53–97)	(−22 to 3)
Urea + *n*BTPT	473	928	88	−9
(250 mg *n*BTPT kg^{-1} urea)	(331–676)	(473–1820)	(65–120)	(−20 to 5)
P value				
Urea vs control	*	**	*	NS
Urea + DCD vs urea	NS	*	NS	NS
Urea + *n*BTPT vs Urea	NS	NS	NS	NS
Emission factor				
Urea	0.42	1.52	0.07	0.03
	(0.12–1.12)	(0.53–3.55)	(0.02–0.15)	(0–0.06)
Urea + DCD	0.26	0.30	0.03	0
(0.02 kg DCD kg^{-1} N)	(0.05–0.75)	(−0.06 to 1.04)	(−0.01 to 0.09)	(−0.02 to 0.03)
Urea + *n*BTPT	0.52	1.79	0.07	0
(250 mg *n*BTPT kg^{-1} urea)	(0.16–1.34)	(0.67–4.11)	(0.02–0.15)	(−0.02 to 0.03)
P value				
Urea + DCD vs urea	NS	NS	NS	NS
Urea + *n*BTPT vs urea	NS	NS	NS	NS
Farm dairy effluent				
Cumulative losses				
Control	664	931	609	84
	(543–812)	(718–1206)	(417–889)	(47–152)
FDE	719	1479	665	171
	(588–879)	(1141–1916)	(455–972)	(95–306)
FDE + DCD	1011	1515	822	211
(10 kg DCD ha^{-1})	(827–1236)	(1169–1963)	(563–1201)	(117–378)
P value				
FDE vs control	NS	*	NS	NS
FDE + DCD vs FDE	*	NS	NS	NS
Emission factor				
FDE	0.11	0.78	0.06	0.14
	(−0.1 to 0.46)	(0.13–1.62)	(−0.36 to 0.68)	(0–0.29)
FDE + DCD (10 kg DCD ha^{-1})	0.51	0.92	0.34	0.16
	(0.14–1.13)	(0.24–1.81)	(−0.17 to 1.1)	(0.01–0.31)
P value				
FDE + DCD vs FDE	NS	NS	NS	NS

NS = not significant.
* $P < 0.05$.
** $P < 0.01$.

increase in soil NH_4^+–N and NO_3^-–N content from the control and both FDE treatments had little effect on corresponding N_2O emissions (Fig. 3). During the Waikato summer months, small rainfall events appeared to be sufficient to stimulate soil nitrification activity, with soil NO_3^-–N content increasing in all treatments (Fig. 3a). During this period, DCD reduced the soil NO_3^-–N content relative to FDE treated soil (Fig. 3a). A similar significant yet minor reduction in NO_3^-–N content due to DCD was occasionally observed in Canterbury (Fig. 3c). DCD did not appear to influence soil NO_3^-–N content in Manawatu and Otago (Fig. 3b and d).

3.3. Experiment 2

3.3.1. Hourly N_2O fluxes

Maximum N_2O fluxes were measured from FDE treatments within 1 day of application at most sites, with the largest fluxes measured from the 'no FDE history' site in the Waikato and the 'FDE history' site in Otago, both peaking at 0.40 mg N_2O–N m^{-2} h^{-1}. The Waikato 'FDE history' site also produced a relatively large peak flux of 0.28 mg N_2O–N m^{-2} h^{-1} following FDE application, while the 'FDE history' site in the Manawatu and the 'no FDE history' site in Canterbury produced peak fluxes of 0.18 and 0.13 mg N_2O–N m^{-2} h^{-1} 6 days and 1 day after FDE application, respectively. Apart from the peak fluxes measured soon after FDE application, N_2O fluxes remained relatively small. Indeed, fluxes from the FDE treatment were low (<0.10 mg N_2O–N m^{-2} h^{-1}) for the entire experiment at three of the sites (Manawatu 'no FDE history', Canterbury 'FDE history' and Otago 'no FDE history').

3.3.2. Cumulative N_2O emissions

Cumulative N_2O emissions from FDE application were greatest in Waikato and Canterbury, with losses of between 1079 and 1146 g N_2O–N ha^{-1} being recorded over a 3–4 month period until fluxes and soil mineral N content returned to background levels (Table 5). Similar emissions were measured from the control

Table 5
Cumulative N_2O emissions (g N_2O–N ha^{-1}) and EF_1 for FDE, applied to pasture with no FDE history or with a history of FDE application in Experiment 2. Emissions and EF_1 values are back-transformed and bias-corrected means of the transformation $\log_e(x+a)$, with 95% confidence intervals in brackets.

N treatment	Waikato	Manawatu	Canterbury	Otago
Cumulative losses				
No FDE history				
Control	1019	430	985	64
	(795–1305)	(287–645)	(700–1386)	(44–94)
FDE	1146	433	1079	142
	(894–1468)	(289–650)	(767–1519)	(97–207)
FDE history				
Control	958	666	1238	105
	(748–1228)	(444–999)	(880–1742)	(72–154)
FDE	1082	947	1141	496
	(844–1386)	(631–1421)	(811–1605)	(339–726)
P value[a]				
FDE vs control	NS	NS	NS	*
No FDE history vs FDE history	NS	*	NS	*
Emission factor				
No FDE history	0.28	0.20	0.06	0.29
	(−0.39 to 1.22)	(−0.76 to 1.67)	(−0.33 to 0.53)	(−0.01 to 0.96)
FDE history	0.04	0.94	0.12	0.75
	(−0.56 to 0.88)	(−0.28 to 2.82)	(−0.28 to 0.61)	(0.20–2.00)
P value	NS	NS	NS	NS

NS = not significant.
[a] * $P < 0.01$.

treatments, ranging from 958 to 1238 g N ha^{-1}. Cumulative emissions from the Manawatu sites were lower, with control treatments producing between 430 and 666 g N ha^{-1} while cumulative emissions from the FDE treatments ranged from 433 to 947 kg N ha^{-1}. In the Waikato, Manawatu and Canterbury, there was no significant difference in cumulative emissions between the control and FDE treatments ($P > 0.05$; Table 5). In contrast, cumulative emissions in Otago were significantly greater ($P < 0.01$) from the FDE treatment (142 to 496 g N ha^{-1}) compared to the control treatments (64 and 105 kg N ha^{-1}) It should be noted; however, that the results from the Otago site are strongly influenced by a single relatively large flux measurement from the FDE treatment at both the 'no FDE history' and 'FDE history' sites one day following FDE application (Fig. 4d). When comparing the effect of paddock history on emissions, the Waikato and Canterbury sites showed no significant difference between the 'no FDE history' and 'FDE history' sites ($P > 0.05$). In contrast, the Manawatu and Otago sites showed cumulative N_2O emissions were significantly greater from the 'FDE history' sites compared to the 'no FDE history' site ($P < 0.05$; Table 5).

3.3.3. Emission factors

EF_1 values, calculated from the N_2O emissions over the 3–4 month period, ranged from 0.04 to 0.94%. All regions showed that there was no significant difference in EF_1 between 'no FDE history' and 'FDE history' paddocks (Table 5).

3.3.4. Soil analysis

Soils at the Waikato sites were relatively moist during the first month of the trial, with WFPS averaging 84 and 80% at the 'no FDE history' and 'FDE history' sites, respectively (Fig. 2a). Soil moisture content generally decreased over the following two months, with WFPS lowering to between 30 and 40% by the end of the experiment. Regular rainfall at the Manawatu sites maintained soil water content at between 55 and 75% WFPS during the first 2 months (Fig. 2b). This was followed by a month of dry weather, resulting in WFPS declining to a very low level of 9%, averaged across the two sites. The 'no FDE history' site consistently maintained a slightly lower WFPS compared to the 'FDE history' site (Fig. 2b). There was little difference in WFPS between the 'no FDE history' and 'FDE history' sites in Canterbury, averaging 61% across both sites in the first month (Fig. 2c). Soil water content remained relatively constant for the entire trial due to regular rainfall in this region. In Otago, soil water content was greater than in other regions, where the 'no FDE history' site maintained a slightly lower WFPS compared to the 'FDE history' site, with average water contents of 87 and 95%, respectively, during the first month of the trial (Fig. 2d). However, by late January WFPS had declined to ~40%.

The FDE treatments applied in Waikato elevated soil NH_4^+–N content to 10-12 mg N kg^{-1} dry soil one day following application, before declining to levels measured in control treatments on day 8 (Fig. 4a). In Manawatu, Canterbury and Otago, soil NH_4^+–N content remained low (<8 mg N kg^{-1} dry soil) following FDE application onto both 'no FDE history' and 'FDE history' sites (Fig. 4b–d). Initial soil NO_3^-–N content increased to ca 33 mg N kg^{-1} dry soil following application of the FDE treatment to the 'FDE history' site in Waikato (Fig. 4a). A smaller increase in soil NO_3^-–N was observed for the 'no FDE history' site in this region. In Manawatu, soil NO_3^-–N content remained below 8 mg N kg^{-1} dry soil throughout the entire trial for all treatments at both sites (Fig. 4b). Soil NO_3^-–N content increased to between 11 and 14 mg N kg^{-1} dry soil following FDE application in Canterbury and Otago; thereafter soil NO_3^-–N levels remained relatively low (Fig. 4c and d).

4. Discussion

4.1. Nitrous oxide emissions

Urea fertiliser application produced a large variation in N_2O emissions and associated EF_1 values, ranging from 0.03% to 1.52% in Experiment 1. Applying urea in spring, as carried out in our study, is representative of typical practice in New Zealand, as the majority of urea applied to pasture occurs in this season (Jeff Morton, pers. comm.). We applied urea at 50 kg N ha^{-1}; this is within the typical range used for dairy pasture in New Zealand (30–50 kg N ha^{-1}; Roberts and Morton, 2012). The use of small, frequent N applications to lessen fertiliser-induced spikes has been highlighted as a potential mitigation strategy (Venterea et al., 2012; Rees

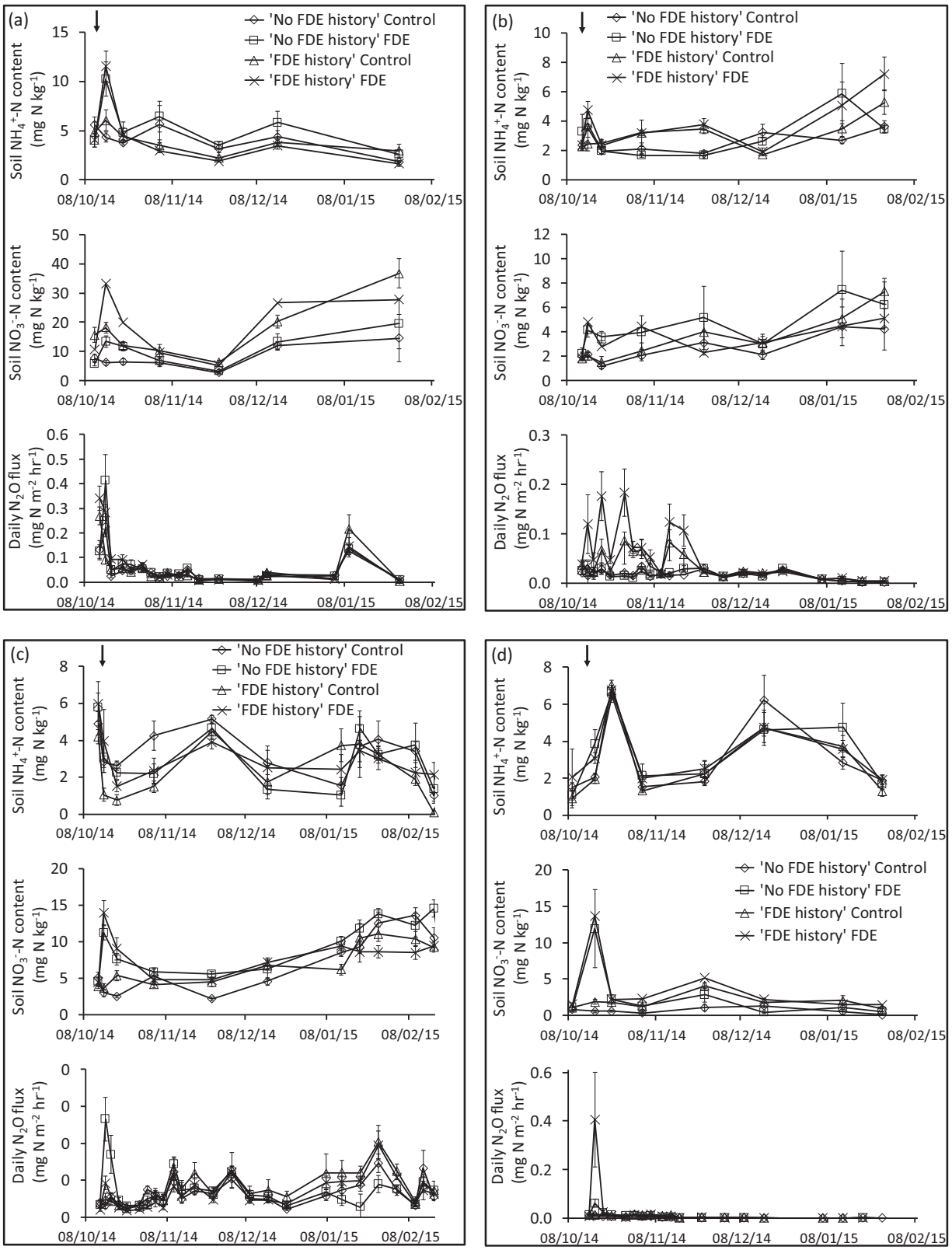

Fig. 4. Soil NH_4^+–N, soil NO_3^-–N contents and N_2O fluxes from 4 sites used for Experiment 2. (a) Waikato, (b) Manawatu, (c) Canterbury and (d) Otago. Solid arrow represents time of FDE application. (*Note*: different *Y* axis between experiments).

et al., 2013), as it has been observed that EF_1 increases with increasing N fertiliser application rate (Shcherbak et al., 2014). However, one of our sites (Manawatu) produced an unusually high EF_1 value of 1.52%. As noted earlier, one of the blocks at this site displayed high cumulative N_2O emission for several treatments. We were not able to determine the cause of the high emission from this single block. Smith et al. (2012) also reported a large range of EF_1 values (0.08–1.76%) for urea applied at between 40 and

120 kg N ha^{-1} per application to eight UK grassland sites. Our analysis of the data from Smith et al. (2012) (data not shown) would suggest no rate effect. Instead, Smith et al. (2012) attributed the large variation in EF_1 to differences in soil wetness, temperature and soil available N. From the results of our current field trials, we were unable to identify specific drivers of urea EF_1, undoubtedly due to the limited dataset of 4 values.

A large proportion of the cumulative N_2O loss from the fertiliser treatments occurred within the first two weeks following application, where rainfall events appeared to induce some of the peaks in N_2O fluxes (Figs. 1 and 3). Urea hydrolysis is rapid, occurring within several hours of urea fertiliser in contact with soils (Saggar et al., 2013), leading to an elevation in soil NH_4^+ content. This rapid hydrolysis of urea can result in the loss of ammonia (NH_3) gas (Saggar et al., 2013), an indirect source of N_2O, with New Zealand adopting a 10% emission factor ($Frac_{GASF}$, fraction of total N fertiliser emitted as nitrogen oxides and NH_3) (Ministry for the Environment, 2015). As a result of NH_3 loss, the net amount of N remaining in the soil as a potential source of N_2O is reduced, which may partly explain why urea has a lower EF_1 value compared to other forms of mineral N fertilisers such as calcium ammonium nitrate (Smith et al., 2012). Soil WFPS varied between 50 and 77% during the first 4 weeks at all sites, providing suitable soil conditions for both nitrification and denitrification to proceed. Limited increases in soil NO_3^- content was probably due to a combination of denitrification within anaerobic microsites and rapid uptake of available N by pasture during the spring months, although we cannot estimate N uptake because pasture production was not measured. Leaching of soil NO_3^- was unlikely, as soil moisture contents continued to decline over the three months of measurements from the urea treatments (Fig. 1).

Farm dairy effluent contains a supply of readily available N, labile C and a high water content that can lead to anaerobic zones within an otherwise aerobic soil immediately after application (Barton and Schipper, 2001; Bhandral et al., 2007). Unlike urea fertiliser, NH_3 emissions from FDE following land application are low, with losses measured in New Zealand studies ranging from 0.05% to 3.1% of total N (Laubach et al., 2015). These small losses will have a minor impact on the net amount of N remaining in the soil as a potential source of N_2O. Under such conditions, N_2O production can be rapid and substantial via both nitrification and denitrification. In Experiment 1, we observed initially higher N_2O fluxes from FDE than from urea fertiliser following application (Fig. 3), where the latter may have been limited by organic C supply (Pelster et al., 2012). Barton and Schipper (2001) also observed greater N_2O emissions over a 3 day period from FDE application than from N fertiliser applied with water, suggesting enhanced denitrification activity from the FDE due to either increasing the C supply and/or decreasing soil aeration following an increase in soil respiration. Nitrous oxide emissions from FDE remained greater than from adjacent control treatments for up to 3–4 months in both Experiments 1 and 2, suggesting mineralisation of the organic N within the FDE contributed to prolonged N_2O production. In contrast, N_2O production from urea is typically complete within ca 1–2 months (Luo et al., 2007; Smith et al., 2012; as well as Experiment 1 in the current study) and from urine deposition typically within 2–3 months (van der Weerden et al., 2011; de Klein et al., 2014).

In Experiment 2, the cumulative N_2O emissions from the FDE treatments at the Otago sites were significantly higher than from the control treatments at both the 'no FDE history' and 'FDE history' sites (Table 5). In contrast, there was no significant difference in cumulative N_2O emissions from the FDE treatments and control treatments at the Waikato, Manawatu and Canterbury sites. This was possibly due to the large spatial variation in emissions from both the FDE and control treatments in these regions, while Otago exhibited lower spatial variation within treatments. However, it is important to note that the calculated cumulative emissions from both FDE treatments were reliant on a single relatively large N_2O peak measured from this treatment at both sites in Otago. This result should therefore be interpreted with caution.

The influence of paddock FDE history on cumulative N_2O emissions from subsequent FDE application remains unclear. Two of the regional sites (Manawatu and Otago) produced greater emissions from control and FDE treatments applied to pastures, which had previously received annual FDE applications, compared to pastures that had never previously been treated with FDE. The Manawatu and Otago 'FDE history' sites have received at least one FDE application each year for the past 25 and 10 years, respectively. It can be perceived that a history of FDE application will increase soil organic N and C inputs relative to soils not receiving FDE: this was apparent in our study, particularly at the Waikato, Manawatu and Otago sites where total N and C content was greater (Table 1). An increase in soil C over time may add to the pool of readily available C for denitrifying organisms, which was probably making a significant contribution to N_2O emissions during the first month following FDE application, as WFPS was generally between 60 and 80% (Fig. 2). Examining WFPS more closely, this may be the cause of the higher emission from the 'FDE history' paddocks in Manawatu and Otago, as these sites exhibited a higher WFPS compared to paddocks with no FDE history (Fig. 2).

The low FDE EF_1 value of 0.06% from the Canterbury site in both experiments was likely due to the relatively dry soil conditions: soil water content was 52% and 60% WFPS over the first month in Experiments 1 and 2, respectively (Fig. 1c and 2c). In contrast, as noted above, most other sites had average WFPS over the first month above 65%, ensuring soils were kept near or above field capacity, producing conditions more suitable for N_2O production. However, an analysis of the WFPS data and other specific soil and climatic variables across both experiments showed no significant relationship with FDE EF_1 (results not shown).

Farm dairy effluent was applied at N loads ranging from 32 to 56 kg N ha^{-1} in this study; this could be regarded to be at the lower end of the range of N loads applied (30 and 150 kg N ha^{-1}). However, a recent review of New Zealand studies, where FDE was applied at 13 to 100 kg N ha^{-1}, has suggested that EF_1 would not be influenced by N load (Laubach et al., 2015). While studies with loadings greater than 100 kg N ha^{-1} have not be conducted, given the lack of an N load effect up to 100 kg N ha^{-1}, it is unlikely EF_1 will be influenced significantly by N load of up to 150 kg N ha^{-1}: further research is required for confirmation.

4.2. Influence of inhibitors on urea fertiliser and FDE EF_1

Treating urea with DCD at 0.02 kg DCD kg^{-1} urea-N significantly reduced N_2O from urea by 90% ($P < 0.01$; Table 4) in the Manawatu. It was at this site where the cumulative N_2O emission for urea fertiliser was greatest, with an EF_1 value of 1.73%. DCD had no effect on N_2O emissions and EF_1 for urea fertiliser at the other three sites, possibly because emissions were already very low (EF_1 ranging from 0.03% to 0.42%) making it difficult to detect differences between treatments. DCD has a half-life of 9 days at 25 °C and is therefore considered to be more effective if applied to soils when temperatures are less than 10 °C (Kelliher et al., 2014). In our study, all 4 sites had soil temperatures at or just below 10 °C at the time of application (Fig. 3), suggesting DCD degradation would have been minimal. Akiyama et al. (2010) conducted a meta-analysis on the effectiveness of N process inhibitors on reducing N losses from fertilisers, and found that DCD applied with urea to grassland reduced N_2O emissions by, on average, 50%. An updated meta-analysis with three times the number of suitable studies produced a similar level of effectiveness (48%; Gilsanz et al., 2016). However

Akiyama et al. (2010) stated there were many studies that showed no effect. McTaggart et al. (1997) conducted a two year study where urea was applied at 120 kg N ha^{-1} on three occasions each year. DCD significantly reduced N_2O emissions when applied as a solution to the grass plots at 12.5 kg ha^{-1}. Recently, Misselbrook et al. (2014) conducted a series of field experiments across the UK where DCD was applied as a solution at 15 kg ha^{-1} immediately following fertiliser application and observed a 69% reduction in N_2O emission from urea. In both studies (McTaggart et al., 1997; Misselbrook et al., 2014) the DCD was applied to the entire soil surface. This implies the chemical may have also acted on a larger proportion of the indigenous soil N compared to the current study, resulting in a potentially larger difference in N_2O emissions from fertiliser plots treated with DCD compared to fertiliser plots with no DCD. This possibility cannot be verified due to the absence of a DCD treatment excluding fertiliser in these studies. In the current study, DCD was applied with urea fertiliser at a lower rate equivalent to 1 kg DCD ha^{-1} (0.02 kg DCD kg^{-1} urea-N × 50 kg N ha^{-1}). Adding DCD directly to urea ensures the inhibitor is in contact with the N source to optimise the efficiency of inhibition. However, the DCD loading rate appears to have been too low to provide sufficient inhibition: a significant reduction in EF_1 was restricted to one site where N_2O emissions were otherwise relatively large. These results suggest a higher DCD loading rate is required.

Amending urea with the urease inhibitor *n*BTPT had no effect on N_2O emissions. Akiyama et al. (2010) conducted a meta-analysis of 113 field experimental datasets and concluded that while urease inhibitors reduced N_2O emissions by, on average, 10%, this was not a significant reduction. These workers suggested the lack of any significant reduction in N_2O emissions may be due to the hydrolysis of urea not being directly related to N_2O emissions as the inhibitor only temporarily delays hydrolysis of urea. If there is no increase in plant N uptake due to the use of urease inhibitors, then a similar amount of NH_4^+ will eventually undergo nitrification and subsequent denitrification. Smith et al. (2012) suggest that the reduced NH_3 emissions from the use of urease inhibitors would increase the amount of N remaining in the soil, which could result in increased N_2O emissions. However, these workers compared N_2O emissions from urea with or without *n*BTPT applied to both grassland and arable sites, and found that *n*BTPT addition did not reduce or increase N_2O from urea fertiliser.

Application of DCD to pasture just prior to FDE addition did not reduce N_2O emissions and EF_1 in our study, suggesting this was not an effective mitigation strategy. Indeed, cumulative N_2O emissions were significantly greater from the FDE + DCD treatment compared to FDE alone at the Waikato site ($P < 0.05$; Table 4). There is no known explanation for this observation. However, the EF_1 values from Waikato produced no significant difference between FDE and FDE + DCD ($P > 0.05$; Table 4). It is possible the low N_2O emissions from these treatments made it difficult to determine if DCD is beneficial in reducing emissions further (Li et al., 2015). Mkhabela et al. (2006) also observed no significant reduction in N_2O when DCD was applied at 66 kg DCD ha^{-1} with hog slurry to soil in a laboratory study. In contrast, Li et al. (2014) observed a significant reduction in N_2O emissions of between 51 and 90% compared to untreated FDE when DCD was mixed with the FDE just prior to application. Ensuring good mixing of the inhibitor with the NH_4^+–N content probably improved the effectiveness of the nitrification inhibitor, as well as being more practical and cost-effective. Others have shown significant reductions in N_2O emissions from slurries when applied to soils with DCD (e.g. Hatch et al., 2005; Merino et al., 2002) although reductions are often greater under laboratory conditions than field conditions (Chadwick et al., 2011).

While the inhibitors had no or little effect on reducing N_2O emissions and EF_1 from urea fertiliser and FDE application in the current study, further opportunities for mitigating N_2O emissions exist. Our study suggests the timing of FDE application to soils with respect to the initial soil moisture content may provide a means for reducing emissions. In addition, DCD application with urea fertiliser could be re-evaluated using higher DCD loadings.

4.3. Effect of paddock history on FDE EF_1

Paddock FDE history did not affect EF_1. In Experiment 2, all four regions showed that there was no significant difference in EF_1 between soils that have not received previous FDE applications and soils that have received FDE for more than 10 years. We were unsure if more than 10 years of effluent application would alter the soil microbial population and/or activity, thereby influencing N_2O emission factors. We did, however, observe that cumulative emissions were greater from the 'FDE history' site than the 'no FDE history' site in Otago. But as both the control and FDE treatments were equally affected, there was no resulting difference in EF_1 between the two sites. We ensured field sites within each region were located on the same farm. A further objective was to ensure the 'FDE history' sites had a similar number of years of receiving FDE, however our ability to achieve this objective was influenced by the region's general history of effluent management and the availability of suitable farms. Consequently, effluent history varied from 10 years in Otago to approximately 25 years in Manawatu. It is also likely that the amount of FDE applied each year differed between each region. Our study suggests a single country specific EF_1 value can be calculated for effluent application to dairy pastures in New Zealand, regardless of the number of years paddocks have received effluent.

5. Conclusions

Urea fertiliser produced EF_1 values ranging from 0.03% to 1.52%. Application of FDE resulted in EF_1 ranging from 0.06% to 0.94% across both experiments. Findings from our two experiments do not provide sufficient evidence to support our first hypothesis, that the nitrification inhibitor DCD can effectively reduce EF_1 for urea fertiliser and FDE. Our second hypothesis, amending urea with the urease inhibitor *n*BTPT would reduce the associated EF_1 was not supported by our results either. And lastly, our results did not support our third hypothesis that repeated application of FDE would change EF_1.

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