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Optimising Nitrogen Fertilisation in a Potato–Oat Rotation and Implications for Nitrous Oxide Emissions in Volcanic Soils

Marta Alfaro [1,*], Sara Hube [2], Francisco Salazar [2], Ignacio Beltrán [2], Luis Ramírez [2] and Surinder Saggar [3]

[1] AgResearch Ltd., 10 Bisley Road, Hamilton 3214, New Zealand
[2] Instituto de Investigaciones Agropecuarias, INIA Remehue, Ruta 5 Norte km 8, Osorno P.O. Box 24-O, Chile; sara.hube@inia.cl (S.H.); fsalazar@inia.cl (F.S.); ignacio.beltran@inia.cl (I.B.)
[3] Manaaki Whenua–Landcare Research, Riddet Road, Massey University Campus, Palmerston North 4442, New Zealand; saggars@landcareresearch.co.nz
* Correspondence: marta.alfaro@agresearch.co.nz

Abstract: High nitrogen (N) fertiliser rates are usually applied to increase agricultural yields, leading to high nitrous oxide (N_2O) emissions. This is a greenhouse gas that contributes to climate change and depletes the ozone layer. This study aimed to optimise N use efficiency and quantify N_2O emission factors (EF1) by measuring the effect of N rates on the yield of a potato-cover crop rotation, apparent N use efficiency (NUE) and N_2O emissions. The two-year experiment was carried out on volcanic soils (1.6% carbon, 1.4% N) in southern Chile (40°52′ S, 73°03′ W). Three N application rates were evaluated (80, 150 and 300 kg N ha^{-1}), 35% of which was applied at the planting stage (granular) and 65% at the tubering stage. A control treatment with no N addition was also included. Reducing N fertilisation to 80 kg N ha^{-1} increased NUE by three times, reduced N_2O-N emissions by 33% and reduced emission intensity by 27% without a detrimental impact on crop yield and marketable tuber calibre. No significant difference ($p < 0.05$) was observed in the N_2O emission factor (EF1) because of a low rainfall year. The results suggest that in rainfed agriculture systems, N fertiliser application can be significantly reduced without sacrificing potato yield, favouring the economic and environmental sustainability of potato production.

Keywords: mitigation; emissions intensity; emission factor; nitrogen use efficiency; improved management practices; foliar application; cropping

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1. Introduction

Nitrous oxide (N_2O) is a key greenhouse gas (GHG) given its important contribution to the atmospheric radiative balance and in the stratospheric ozone chemistry, with a global warming potential (WGP) of 265 relative to CO_2, in a time horizon of 100 years [1].

Agricultural soils emit 5.3 Tg N_2O-N yr^{-1}, representing 78% of total anthropogenic N_2O emissions (6.7 Tg N_2O-N yr^{-1}, [2]). This is due to the use of Nitrogen (N) fertiliser to optimize crop yields. From 2005 to 2016 the global population increased by 15%, encompassing a need to increase food production, which in turn led to an increase in the use of N fertiliser and, therefore, N_2O emissions from the agricultural sector [3].

Nitrification, under aerobic conditions, is the dominant pathway for direct N_2O production in most soils, while denitrification is dominant under anaerobic conditions [4]. Indirect N_2O emissions can also be produced by secondary deposition of volatilized ammonia [5]. The key factors controlling N_2O emissions in volcanic soils appear to be soil water content as a proxy for soil oxygen status, usually expressed as Water-Filled Pore Space (WFPS), and soil temperature [6,7], while more broadly, soil mineral N concentration has a significant role [8].

Reports suggest a linear relationship between increasing N input and increases in direct N_2O emission [9]. This relationship was adopted for the Intergovernmental Panel on Climate Change (IPCC) as a Tier 1 methodology to estimate direct N_2O emissions based on the amount of N added to agricultural soils [9]. However, there is evidence indicating a nonlinear, exponential response of direct N_2O emission to N input, which would result in N_2O emission factors (EF) values that are not constant but dependent on N input rates [10]. This could be of significance for farm-scale accounting of GHG, including that from potato production, with implications for the estimation of national GHG inventories.

Improved fertiliser N management practices, including split fertiliser N applications [11,12], the combination of soil and foliar spray applications [13], and the use of controlled release fertiliser and nitrification inhibitors were identified as N_2O emissions mitigation options in crops [14,15]. Burton et al. [16], in a rainfed potato study, also showed that split fertilizer N application can decrease cumulative N_2O emissions in a wet year, especially with rainfall during the period of planting to hilling [16]. Additionally, the use of cover or catch crops offers an opportunity to recycle post-harvest N into plant biomass [17] and reduce nitrate leaching [18] and N_2O emissions.

In Chile, the agricultural sector accounted for 10.6% of the total GHG emissions in 2020 [19], and emissions from soils accounted for 38% of sectoral emissions, including direct and indirect emissions from excreta deposition in grazed areas and N fertiliser used for agricultural production. The application of N fertiliser in Chilean agricultural soils is responsible for 18% of the total emissions from soils in the agricultural sector [19].

The potato (*Solanum tuberosum* L.) is the fifth most produced crop in the world [20], and it is the third most important crop in Chile after wheat and maize, with a production area of 31,243 ha in the 2023/24 cropping season [21]. The total potato production area has, thus, decreased by 68% from the initial 96,180 ha planted in 1960. However, total production has increased more than 50% from 0.8 in 1960 to 1.3 million t in 2019, associated with a yield increase from about 8.8 to 24 t ha^{-1}. This increase is mainly due to the use of improved cultivars and crop management such as better seed quality, fungicides, increased irrigation, and an increase in N fertiliser application, given that potato is an N-intensive crop [22], with little attention to the potential associated environmental burdens. In the past, inorganic N fertiliser was seldom used in potato production (15–50 kg N ha^{-1}). In recent years, N fertiliser application has been adjusted according to targeted yield and N soil supply via mineralization, reaching up to 400 kg N ha^{-1} for more than 70 t ha^{-1} of fresh tuber yield [23], while for 40–50 t ha^{-1}, the N rate applied often varies between 150 and 300 kg N ha^{-1}.

It is estimated that 55% of the total Chilean national production and 100% of certified potato seed production occur in Southern Chile, given sanitary restrictions established by the Chilean authorities, from the regions of La Araucanía (38°54′ S, 72°40′ W) to Los Lagos (41°45′ S, 73°0′ W) [21,24]. Potato cropping is carried out mostly under rainfed conditions, with greater intensification applied on the larger farms, including high N fertiliser rates, from 150 to 400 kg N ha^{-1} yr^{-1}, depending on edaphoclimatic conditions and cultivar yield potential [25]. Over-fertilisation results in low N use efficiency (NUE, [26]) and may also affect marketable potato calibre, resulting in large or small-sized tubers, which although adequate for processing or seed, are unfavourable for the fresh market [26,27]. This also has potential implications for the environment including N_2O emissions from potato production due to the relatively high N fertiliser input [28].

Little information is available on N losses from potato crops on volcanic soils, e.g., [7], and less on N_2O emissions, with existing estimations in Chile being solely based on empirical models [29,30]. We hypothesize that reducing N fertiliser rates and using N foliar application as part of a split N application strategy will significantly reduce N_2O emissions in a potato crop given an associated increase in NUE, without affecting yield and marketable tuber calibre distribution. Thus, the primary aim of this study was to quantify the effect of different N rates on N_2O emissions in a potato crop, and the effects of this practice on crop yield and marketable tuber calibre over a two-year rotation.

2. Materials and Methods

2.1. Study Site

The field experiment was conducted between September 2016 and September 2018 at the Instituto de Investigaciones Agropecuarias (INIA), Centro de Investigación Remehue (40°52′ S, 73°03′ W, 72 m above sea level), in southern Chile. The mean annual rainfall at the experimental site is 1253.6 mm and the mean daily minimum and maximum temperatures are 4.3 and 13.1 °C in winter (July to September), and 7.3 and 20.4 °C in summer (December to March), respectively, as average of 39 years.

The soil at the experimental site is an Andosol (AN) from the Osorno soil series [31] (Silándic Andosol [32]), with soil fertility conditions for crop production (Table 1). The preceding crop rotation at the site was maize–potato–pasture (3 years), a common rotation among farmers in the area. Four representative soil samples (0–20 cm) were collected prior to tillage, for chemical and physical soil site characterization following the methods compiled by [33] and outlined by [34], respectively. Briefly, soil pH was measured in water and $CaCl_2$ solution by potentiometry, organic matter concentration was estimated using a modified Walkley–Black method by wet digestion. Organic C was derived from organic matter concentration using the standard conversion factor for this soil type. Exchangeable cations (Ca, Mg, K, and Na) and exchangeable Al were extracted with a solution of ammonium acetate ($NH_4C_2H_3O_2$) 1 M at pH 7.0 and potassium chloride (KCl) 2 M, respectively, and analysed by atomic absorption spectrophotometry (AAS). Sulphate (SO_4^{2-}) and phosphate (PO_4^{3-}) anions were extracted in a solution of sodium bicarbonate ($NaHCO_3$) 0.5 M at pH 8.5 and calcium dihydrogen phosphate ($Ca(H_2PO_4)_2$) 1 M and analysed by the Murphy and Riley method and turbidimetry, respectively [35]. Between crop rotations, soil samples were collected (n = 3) for bulk density analysis, to correct soil water fill pore space determination in the N_2O emissions estimation.

Table 1. Soil chemical and physical characteristics before planting the potato crop (23 August 2016), and average at the end of each cropping season (September 2017 and October 2018), 0–20 cm, n = 4, ± standard error of the mean).

Parameter	Before Planting	During Vegetation	
		2016/17	2017/18
Classification [1]		Silándic Andosol	
Series [2]		Osorno	
Soil texture		Loamy	
pH H_2O (soil:water, 1:2.5)	5.7 ± 0.08	5.7 ± 0.09	5.7 ± 0.11
pH $CaCl_2$ (soil:$CaCl_2$, 1:2.5)	5.0 ± 0.07	4.9 ± 0.08	4.9 ± 0.09
Total N [3] (g kg^{-1})	14.0 ± 0.15	Not measured	Not measured
Available N (mg kg^{-1})	7.8 ± 0.86	10.4 ± 0.63	9.7 ± 2.67
Organic Carbon (g kg^{-1})	15.8 ± 0.71	13.6 ± 0.72	14.7 ± 0.68
Olsen P (mg kg^{-1})	30.3 ± 1.71	29.7 ± 0.87	28.4 ± 0.55
Available S (mg kg^{-1})	42.8 ± 3.02	30.3 ± 2.51	31.6 ± 3.56
Exchangeable Ca (cmol $_{(+)}$ kg^{-1})	5.4 ± 0.62	5.1 ± 0.92	4.2 ± 1.00
Exchangeable Mg (cmol $_{(+)}$ kg^{-1})	0.6 ± 0.07	0.5 ± 0.07	0.4 ± 0.07
Exchangeable K (cmol $_{(+)}$ kg^{-1})	0.5 ± 0.05	0.5 ± 0.06	0.6 ± 0.06
Exchangeable Na (cmol $_{(+)}$ kg^{-1})	0.1 ± 0.01	0.1 ± 0.02	0.1 ± 0.01
Al Saturation (%)	2.4 ± 0.89	4.4 ± 2.57	7.0 ± 4.80
Bulk density (g cm^{-3})	0.66 ± 0.021	0.69 ± 0.016	0.66 ± 0.022
Particle density (g cm^{-3})	1.78 ± 0.05		

[1] According to [32]. [2] According to [31]. [3] Measured only once at initial establishment of the trial.

2.2. Experimental Design

Evaluations were carried out over two rotation seasons (2016/17, 2017/18) considering a potato crop and oat (*Avena sativa* L.) as cover crop during autumn and winter (April to September each year). Four treatments were evaluated, Control (0 N kg N ha^{-1}), 80

(80 kg N ha^{-1}, urea), 150 (150 kg N ha^{-1}, urea) and 300 (300 kg N ha^{-1}, urea 46% N), distributed on a completely randomized block design (n = 3). During the 2016/17 season, potato was hand-planted on October 20 2016 on 5 × 5 m plots, using 0.7 m between rows spacing and 0.30 m within row spacing (cv. Karú INIA, size 45–55 mm). Planting was carried out following conventional tillage (0–20 cm), with a basal fertiliser application according to the initial soil analysis (Table 1). This consisted of 52 kg P ha^{-1} (Triple Superphosphate, 46% P_2O_5), 41 kg K (Potassium chloride, 62% K_2O), 20 kg S ha^{-1} (Gypsum, 18% $CaSO_4$) and 12 kg Mg ha^{-1} (Magnesium oxide, 85% MgO). Once potatoes were harvested (20 March 2017), a catch crop (Oat cv. Super Nova; seed rate 12 g m^{-2}; 5 April 2017) was established (0.17 m spacing between rows, 0–5 cm depth), without fertiliser application. During the second season, the potato crop was planted on 24 October 2017, as previously described for the first season and using the same application rates. Once the crop was harvested (7 March 2018), the catch crop (Oat cv. Super Nova; seed rate 12 g m^{-2}; 9 March 2018) was established, as per in the first season. The oat catch crop was harvested and then spray dried (Rango Full 3L ha^{-1}, a.i. glyphosate–potassium 662 g L^{-1}) prior to conventional soil preparation for the next potato crop.

Nitrogen application to treatments was split, with 35% of the N applied at planting (granular urea in all treatments) and the remaining 65% at tuber initiation (47 and 55 days after planting, 6 December and 18 December for the 2016/17 and 2017/18 seasons, respectively). Nitrogen granular fertiliser was applied and immediately incorporated into the soil (0–10 cm). In the 80 kg N ha^{-1} treatment, the second N application was applied as foliar sprayed dissolving urea in water in a proportion of one part of urea for two parts of water (100 kg_w:200 L_w). This strategy was selected as data from previous experiments showed an increase in N use efficiency when foliar spray was used as the application method (unpublished data).

On experimental plots, one-half (2.5 × 5 m) was used for destructive soil and crop sampling, and the remainder half was used for N_2O measurements (2.5 × 5 m).

2.3. Climatic and Soil Parameters

Soil temperature (0–20 cm depth) and gas chamber temperature was measured in conjunction with the gas sampling using digital thermometers (Digi-Sense® Traceable®, Vernon Hills, IL, USA). Daily values of air temperature (maximum, minimum, and average), relative humidity, wind speed and rainfall were recorded with an automatic weather station (CR10X-1 M Model, Campbell Scientific Inc., Logan, UT, USA) placed at 72 m of the experimental site, during all the experimental period.

2.4. Soil Analysis

To explain seasonal variations of N_2O fluxes, soil available N (NO_3^--N and NH_4^+-N) and soil gravimetric water content were measured (0–20 cm) every week after crop establishment. At each sampling date, two soil samples were collected from each plot and individually analysed for NO_3^- and NH_4^+ using extraction with 2 M KCl [33]. Soil water content was determined gravimetrically after drying the sample at 105 °C for 24 h [34]. Bulk density was measured at initial soil characterization (2016), and once per season until the end of the experiment as described by [34]. Water-filled pore space (WFPS) was calculated from the gravimetric water content results, using results of periodical bulk density sampling and the value of particle density reported in Table 1.

2.5. Potato and Cover Crop Evaluations

To determine potato yield (t DM ha^{-1}), two inner rows per plot were harvested manually, and all material collected was weighted fresh, and a sub sample was dried at 60 °C for 48 h [36]. The catch crop was mown at each plot (2.5 × 5 m^2) with a lawn mower when it reached c. 20 cm high, clippings were fully collected and weighted fresh, and a 0.5 kg sub sample was dried at 60 °C for 48 h [36]. Total N in both potato and oat crops was determined for each experimental plot and sampling date (catch crop) by the Kjeldahl digestion method [36] and it was used to calculate total N uptake per treatment. Using N uptake values, the apparent Nitrogen Use Efficiency (NUE) was estimated according to Equation (1):

$$NUE = \frac{N_{+N} - N_Z}{N_A} \times 100 \quad (1)$$

where NUE is the apparent N use efficiency (%), N_{+N} is N accumulation in potatoes and in oat biomass collected in the +N treatment (kg ha^{-1}), N_Z is the nitrogen accumulation in potatoes and in oat biomass collected in the zero N treatment (kg ha^{-1}) and N_A is the amount of total N applied (kg ha^{-1}).

Marketable tuber calibre in the potato crop was determined for each plot considering two sizes, one for seed production (28–55 mm) and one for fresh consumption (over 55 mm).

2.6. N_2O Fluxes Quantification

Fluxes of N_2O were measured daily from 20 October 2016 to 20 October 2018 using the static chambers technique described by [37] with an automated measuring system [38]. The system consists of twelve acrylic static chambers (0.50 m × 0.50 m × 0.15 m) fixed on stainless steel bases inserted permanently into the soil (0.20 and 0.10 m depth for the potato and catch crop, respectively). Two chamber bases were allocated to each plot and the measuring chambers moved between the two bases every two weeks, to minimise the effect of the chamber on crop growth and soil properties, in agreement with [37,38]. To reduce the impact of this management on the quantification of cumulative N_2O emissions, the areas of both bases received the same area-equivalent N rate at each fertiliser application. For the potato crop, acrylic extensions of 0.50 m height were used to increase the height of the chamber to a total height of 0.65 m following crop development. Extensions were added when the potato crop received the second N application. To minimise a potential climatic impact of the chamber, transparent tinted plastic coating was placed on the lids to reduce heat build-up within the chambers when closed.

The automated chambers were sealed airtight during sampling by two lids that opened and closed via pneumatic actuators. During a measurement cycle, a set of four chambers closed (one chamber per treatment) for 60 min and each chamber was sequentially sampled for 3 min followed by a known calibration standard. This process was repeated for each chamber four times over the closure period (i.e., every 15 min) before the chambers reopened and the next set of four chambers closed. A complete full cycle of twelve chambers lasted for 3 h, during which each chamber was sampled for 1 h and remained opened for 2 h to restore ambient conditions, allowing eight single fluxes to be determined per chamber each day.

A tipping bucket rain gauge (Davis Instruments Corp. CA, USA) and a temperature sensor inside of one chamber per experimental block were connected to the system, to allow for automated opening of the lids during rainfall events (more than 0.4 mm over a 5 min period) and increases of temperature (over 40 °C). After chamber closure, air samples were automatically pumped from the chamber's headspace into the sampling unit with a flow rate of 200 mL min^{-1}. At the end of a 3 min sampling period, a 3 mL gas sample was injected into the carrier stream of a gas chromatograph (SRI 8610C, Torrance, CA, USA) equipped with a ^{63}Ni electron capture detector (ECD) for N_2O analysis. To minimize the interference of moisture vapour and CO_2 on N_2O measurement, a pre-column filled with sodium-hydroxide-coated silica was installed upstream of the ECD and changed regularly. Sample gas measurements were calibrated automatically by a single point calibration using certified gas standards (Air Liquide, Dallas, TX, USA) of 0.5 ppm N_2O. The detection limit of the system was 2.0 µg N_2O-N m^{-2} h^{-1}, and 10.0 µg N_2O-N m^{-2} h^{-1} with extensions in place. Sample dilution via leakage was considered negligible.

Fluxes of N_2O were calculated from the slope of the linear increase or decrease in the three concentrations measured over the enclosure time, similarly to the procedure outlined by [37,39]. Flux rates were expressed on an elemental weight basis as both mg N_2O-N m^{-2} h^{-1} and g N_2O-N ha^{-1} day^{-1}. The flux rates were calculated and corrected for air temperature, atmospheric pressure and the ratio of chamber volume to surface area as Equation (2):

$$F = \frac{\Delta C}{\Delta T} \times \frac{M}{Vm} \times \frac{V}{A} \quad (2)$$

where F is the flux rate (mg m^{-2} h^{-1}), $\frac{\Delta C}{\Delta T}$ is the increase in headspace concentration during the enclosure time (ppm h^{-1}), M is the atomic weight of the gas (28 for N_2O-N), Vm is the pressure and temperature-corrected molecular volume (L mol^{-1}), V is the volume of the measuring chamber (m^3) and A is the area of the measuring chamber (m^2), the fraction $\frac{V}{A}$ corresponding to the high of the measuring chamber.

$$Vm = \frac{R \times T}{n \times P}$$

where R is the gas constant 0.08205 atm L mol^{-1} K^{-1}, T is the chamber temperature during the measurement (Kelvin), P is the air pressure at the experimental site (Atmosphere). Air pressure at the site was estimated from the height above sea level using a barometric equation and n is equivalent to 1 mol of the gas. To calculate seasonal cumulative fluxes, calculated daily fluxes were then summed according to the measurement period before the arithmetic mean was calculated across the three replicate chambers. Days without measures during the maintenance period of the automated sampling system were gap-filled by linear interpolation.

2.7. Emission Factor

The Emission Factor (EF1) for N_2O-N emissions, defined as the fraction of N applied as fertiliser that is lost as N_2O, was calculated for every year of continued measurement, following Equation (3):

$$EF1 = \frac{E_{+N} - E_Z}{N_A} \times 100 \quad (3)$$

where, $EF1$ is the Emission Factor (%), E_{+N} is N_2O-N emitted (kg) in any of the +N treatments, E_z is N_2O-N emitted (kg) by the zero N treatment, and N_A is the amount of total N applied as fertiliser (kg).

2.8. Emission Intensity

The N_2O emission intensity (EI) was estimated for each treatment, considering N_2O-N emissions (kg N_2O-N ha^{-1}) and DM yield (t DM ha^{-1}) as in Equation (4):

$$EI = \frac{CF}{Y} \quad (4)$$

where EI is the emission intensity (kg N_2O-N t^{-1} DM), CF is the cumulative flux emission of N_2O-N (kg N_2O-N ha^{-1}) and Y is the DM yield (t DM ha^{-1}).

2.9. Statistical Analysis

Three models were used to evaluate the effect of fertiliser treatment on crop yield, NUE, N_2O fluxes, EI, and EF. For potato, oat and potato–oat crop rotation (Models 1, 2 and 3, respectively), models included the fertiliser treatment, the cropping year and the interaction of fertiliser and year as fixed factors, while the plot was considered as random factor. A multivariate regression tree analysis was performed to identify key variables determining the N_2O-N fluxes (as dependent variable), with soil parameters (NO_3^--N, NH_4^+-N, soil temperature and WFPS) as independent variables. All data met the assumption of normality and homogeneity of variance. Comparison between treatments was carried out using the Tukey test. Results were considered significant at $p < 0.05$. All models were evaluated using R (version R-4.0.5) and Genstat 23rd Edition (version 23.1.0651) statistical software.

3. Results

3.1. Climate

The average air temperature for the experimental period was 10.7 °C, ranging from 5.7 in winter (July 2017) to 16.4 °C in summer (February 2018). This average temperature was 22% lower than the 39-year average for the same site (13.8 °C). The minimum air temperature ranged between −4.3 (winter) and 17.6 °C (summer), while the maximum air temperature varied between 3.6 (winter) and 31.7 °C (summer) during the experimental period (Figure 1a). Soil temperature varied between 4.8 and 20.7 °C, with an average of 12.1 °C during the experimental period (Figure 1a). Air and soil temperatures during the experimental period were favourable for potato growth.

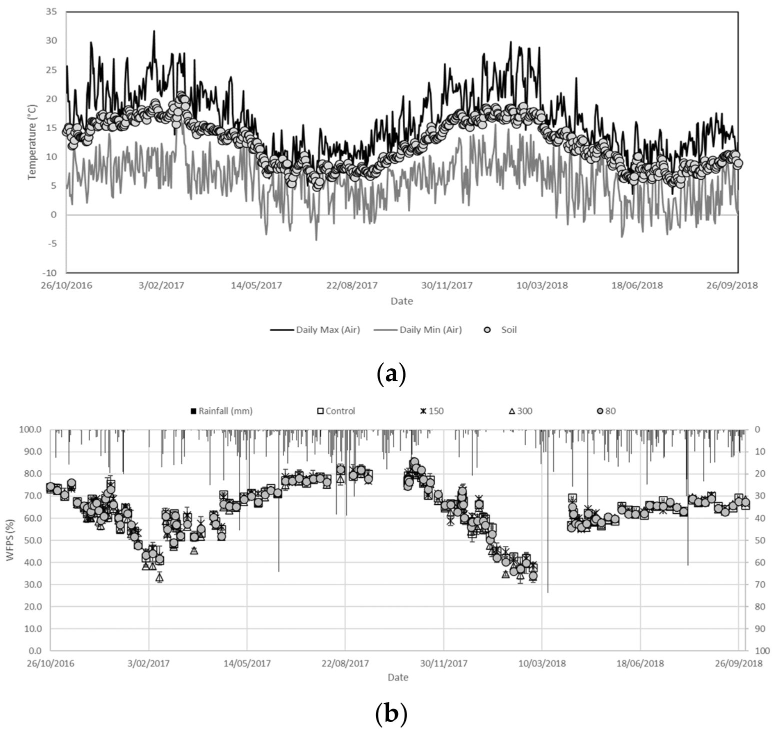


Figure 1. Temperature and rainfall over two years: (**a**) daily minimum and maximum air temperatures (°C), and soil temperatures (0–20 cm depth, °C); (**b**) daily rainfall and soil water field pore space (0–20 cm, %, n = 3, bars indicate standard error of the mean).

Rainfall for the experimental period was 1208.6 and 1117.3 mm for the 2016/17 and 2017/18 seasons, respectively, lower than the average of a 39-year period at the experimental site (1253.3 mm). In the 2017/18 season, the average rainfall was 11% lower than the annual average and 21% lower than the 39-year average during the spring–summer period (October–February). The average WFPS was 52.9% for the experimental period, varying between 89.9% (October 2017) and 28.3% (February 2018). Lower rainfall in the spring–summer of 2017/18 resulted in lower WFPS during more weeks in that same period compared with the long-term average (Figure 1b), reducing potato yield (see below).

3.2. Soil-Available N (NH_4^+ and NO_3^-)

Soil-available N was higher in the 300 (39.8 ± 0.98 mg N kg^{-1} ds) treatment, followed by the 80 (34.9 ± 1.08 mg N kg^{-1} ds), 150 (29.8 ± 0.74 mg N kg^{-1} ds), and Control treatments (24.3 ± 0.42 mg N kg^{-1} ds), respectively ($p < 0.001$, Figure 2), as an average of the experimental period.

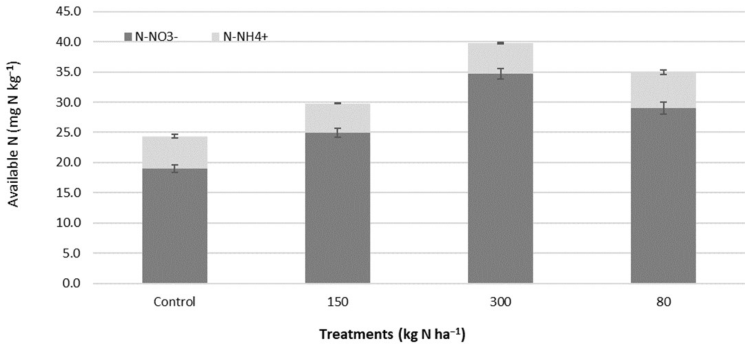
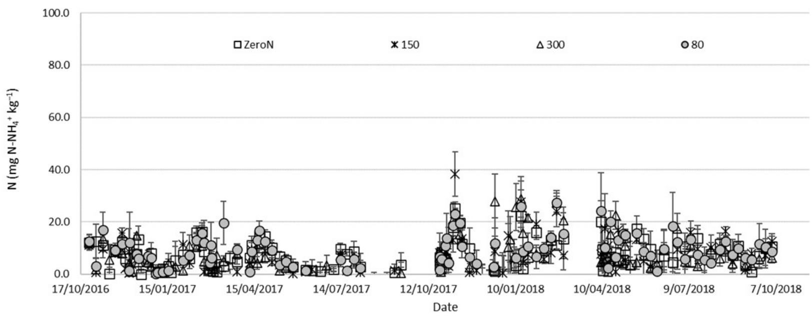


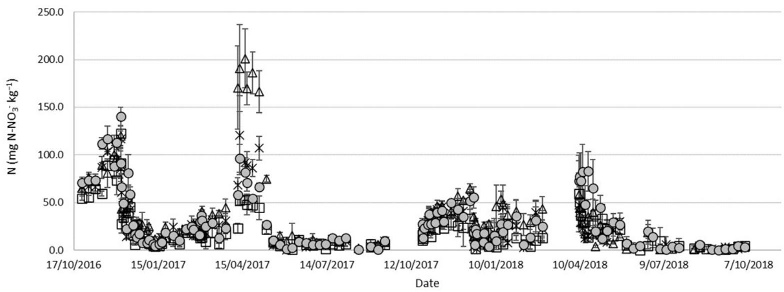
Figure 2. Average soil available N per treatment for the experimental period, as contribution of N-NH_4^+-N and NO_3^--N (mg N kg^{-1} ds) (0–20 cm, n = 3, ± standard error of the mean).

Soil NO_3^- made up 83% of the total available N, on average, with a greater contribution observed in the 300 kg N ha^{-1} treatment (87 ± 0.17%), in comparison to the 78 ± 1.52% contribution registered in the Control ($p < 0.05$; Figure 2). Average soil NH_4^+-N was the lowest in the treatment with the highest application rate (5.0 ± 0.12 mg NH_4^+-N kg^{-1} ds, $p < 0.05$, Figure 2), while soil N-NO_3^- was the highest in the same treatment (34.7 ± 0.88 mg NO_3^--N kg^{-1} ds, $p < 0.01$, Figure 2).

Soil NH_4^+ concentration did not vary significantly during the growing seasons (Figure 3a), with an average value of 5.3 ± 0.22 mg N-NH_4^+ kg^{-1} ds across the seasons and the different N treatments ($p > 0.05$ in both cases). Nitrate soil concentrations increased in autumn, after the initial rainfalls (April 2017 and 2018), reaching up to 257 mg NO_3^--N kg^{-1} ds in the 300 kg N ha^{-1} treatment in the 2016/17 season (Figure 3b). Greater values were also found after crop establishment during the first season. Despite this variation, the average concentration ranged between 19.0 ± 0.61 mg NO_3^--N kg^{-1} ds in the Control and 29.0 ± 0.99 mg NO_3^--N kg^{-1} ds in the 80 kg N ha^{-1} treatment ($p > 0.05$).



(**a**)



(**b**)

Figure 3. Dynamic of soil-available N per treatment over two years (0–20 cm): (**a**) NH_4^+-N (mg NH_4^+-N kg^{-1} ds); (**b**) NO_3^--N (mg NO_3^--N kg^{-1} ds). Bars indicate standard error of the mean (n = 3).

3.3. Crop Yield, N Uptake and NUE

3.3.1. Yield

Potato tuber yield was higher in the N treatments ($p < 0.05$, Table 2), and twice as much in the 2016/17 season compared with the 2017/18 season ($p < 0.01$, Table 2). Oat yield was also 12% greater in the 2016/17 season than in the 2017/18 season ($p < 0.05$, Table 2), but there was no difference among the different N treatments ($p > 0.05$), averaging 2 ± 0.06 t DM ha^{-1} in both growing seasons.

Table 2. Effects of N rates on crop yield (t DM ha^{-1}), N plant uptake (kg N ha^{-1}), NUE (%), N_2O emissions (kg N-N_2O ha^{-1}), emission intensity (EI, kg N-N_2O t^{-1} DM) and Emission Factor (EF, %) per growing season and overall (±standard error of the mean).

Season		Parameter	N Rate Applied (kg N ha^{-1} yr^{-1})				Treatment Effect
			0	80	150	300	
2016/17							
	Crop	Potato yield (t DM ha^{-1})	8.8 ± 0.65 ^{b}	12.7 ± 0.88 ^{a}	11.3 ± 1.06 ^{a}	11.9 ± 0.78 ^{a}	*
		Oat yield (t DM ha^{-1})	2.0 ± 0.20	2.3 ± 0.17	2.4 ± 0.22	2.3 ± 0.17	NS
		N uptake (kg N ha^{-1})	150 ± 22.1 ^{b}	226 ± 26.8 ^{a}	220 ± 11.6 ^{a}	242 ± 31.0 ^{a}	*
		NUE (%)	NA	95.5 ± 27.0 ^{a}	46.2 ± 17.9 ^{b}	30.5 ± 7.4 ^{b}	*
		Seed yield (t ha^{-1}) [1]	16.9 ± 2.88	16.5 ± 0.35	16.5 ± 1.99	16.2 ± 1.80	NS
		Fresh consumption (t ha^{-1}) [1]	26.2 ± 4.66	41.6 ± 2.49	37.3 ± 3.98	39.5 ± 4.05	NS
	Emissions of N_2O	Potato (kg N_2O-N ha^{-1})	1.4 ± 0.03 ^{c}	2.1 ± 0.04 ^{b}	2.2 ± 0.08 ^{b}	3.2 ± 0.26 ^{a}	*
		Oat (kg N_2O-N ha^{-1})	0.4 ± 0.03	0.5 ± 0.05	0.6 ± 0.02	0.7 ± 0.01	NS
		EI (kg N_2O-N t DM^{-1})	0.19 ± 0.02 ^{b}	0.18 ± 0.02 ^{b}	0.22 ± 0.03 ^{b}	0.29 ± 0.01 ^{a}	*
		EF (%)	NA	0.87 ± 0.15	0.62 ± 0.08	0.72 ± 0.09	NS
2017/18							
	Crop	Potato yield (t DM ha^{-1})	5.1 ± 0.54	4.9 ± 0.29	6.1 ± 0.13	6.3 ± 0.33	NS
		Oat yield (t DM ha^{-1})	1.9 ± 0.03	2.0 ± 0.12	2.0 ± 0.22	1.9 ± 0.12	NS
		N uptake (kg N ha^{-1})	109.9 ± 12.9	140.5 ± 1.7	136.8 ± 16.3	173.4 ± 15.3	NS
		NUE (%)	NA	93.5 ± 21.3	49.0 ± 18.2	30.1 ± 8.2	NS
		Seed yield (t ha^{-1}) [1]	8.9 ± 0.59	9.2 ± 0.25	10.2 ± 0.79	11.7 ± 0.81	NS
		Fresh consumption (t ha^{-1}) [1]	13.7 ± 1.16	16.5 ± 0.79	18.4 ± 0.19	16.9 ± 0.10	NS
	Emissions of N_2O	Potato (kg N_2O-N ha^{-1})	0.2 ± 0.01	0.3 ± 0.02	0.3 ± 0.06	0.4 ± 0.04	NS
		Oat (kg N_2O-N ha^{-1})	0.5 ± 0.01	0.6 ± 0.01	0.7 ± 0.01	0.7 ± 0.01	NS
		EI (kg N_2O-N t DM^{-1})	0.12 ± 0.01 ^{b}	0.13 ± 0.003 ^{b}	0.13 ± 0.01 ^{b}	0.16 ± 0.02 ^{a}	*
		EF (%)	NA	0.09 ± 0.03	0.16 ± 0.05	0.16 ± 0.03	NS

Table 2. *Cont.*

Season	Parameter	N Rate Applied (kg N ha^{-1} yr^{-1})				Treatment Effect
		0	80	150	300	
Overall rotation						
	Yield (t DM ha^{-1})	8.9 ± 0.87^{b}	10.9 ± 1.73^{a}	10.9 ± 1.22^{a}	11.2 ± 1.28^{a}	*
	N uptake (kg N ha^{-1})	147 ± 21.0^{b}	223 ± 16.6^{a}	219 ± 18.3^{a}	238 ± 15.2^{a}	*
	NUE (%)	NA	94 ± 24.2^{a}	48 ± 12.8^{b}	30 ± 5.5^{c}	*
	Seed yield (t ha^{-1}) [1]	12.9 ± 2.20	12.9 ± 1.50	13.4 ± 1.68	13.9 ± 1.34	NS
	Fresh consumption (t ha^{-1}) [1]	20.0 ± 3.51	29.0 ± 5.29	27.9 ± 4.34	28.2 ± 5.03	NS
	N_2O (kg N_2O-N ha^{-1})	1.4 ± 0.01^{c}	1.8 ± 0.07^{bc}	2.0 ± 0.09^{b}	2.7 ± 0.17^{a}	***
	EI (kg N_2O-N t DM^{-1})	0.15 ± 0.01^{b}	0.16 ± 0.01^{b}	0.17 ± 0.02^{b}	0.22 ± 0.01^{a}	***
	EF (%)	NA	0.48 ± 0.09	0.39 ± 0.06	0.44 ± 0.06	NS

Different letters in rows indicate significant differences between treatments (* = $p < 0.05$; *** = $p < 0.001$). NS = not significant ($p > 0.05$). NA: not applicable. [1] fmb = fresh matter basis.

The total annual DM yield (potato + oat crops) was 1.8 times greater in 2016/17 than in 2017/18 ($p < 0.001$; Table 2). This yield was also 24% greater in the N treatments (11 ± 0.8 t DM ha^{-1}) compared with the Control (9 ± 0.9 t DM ha^{-1}), for the average over both growing seasons ($p < 0.05$).

3.3.2. Marketable Calibre Distribution

There was no interaction between N application and season for the distribution of tuber calibre ($p > 0.05$), nor for the effect of the N addition ($p > 0.05$), but the proportion of the consumption calibre was higher in the 2016/17 season with a 68 ± 2.9% for the total production compared to a 62 ± 1.0% in the 2017/18 season ($p < 0.001$). The overall 2016/17 potato yield reached 36 ± 2.6 t ha^{-1} while in 2017/18 it only reached 16 ± 0.6 t ha^{-1}, on a fresh matter basis with regard to the consumption calibre (Table 2).

3.3.3. Nitrogen Uptake

There was no interaction between cropping season and N application for N concentration in aboveground biomass (Table S1) and N uptake for the potato or the oat crops ($p > 0.05$), but N uptake was greater in the N treatments compared to the Control ($p < 0.05$).

Annual potato N uptake in N treatments was 115 ± 10.3 kg N ha^{-1}, in comparison to the Control with no N addition (74 ± 11.1 kg N ha^{-1}; $p < 0.05$). Also, this uptake was 1.9 times higher in 2016/17 (137 ± 10.8 kg N ha^{-1}) than in 2017/18 (73 ± 5.9 kg N ha^{-1}; $p < 0.05$; Table 2).

Annual oat N uptake in the N treatments was 75 ± 2.3 kg N ha^{-1}, 34% higher than in the Control treatment (56 ± 2.9 kg N ha^{-1}; $p < 0.05$) with no significant seasonal effect ($p > 0.05$; Table 2).

The total annual N uptake by potato tubers and oats was higher with the N treatments (226 ± 8.3 kg N ha^{-1}) than with the Control (147 ± 21.0 kg N ha^{-1}; $p < 0.05$), and there was no observed seasonal effect ($p > 0.05$; Table 2).

3.3.4. Nitrogen Use Efficiency, NUE

The apparent NUE was three times higher in the 80 kg N ha^{-1} treatments than in the 300 kg N ha^{-1} treatment as an average of both years ($p < 0.05$; Table 2). There was no interaction between cropping season and N application for the NUE in the potato crop

($p > 0.05$). Overall, NUE across the cropping rotations increased with decreasing N rates applied, reaching up to 30 ± 5.5, 48 ± 12.8 and 94 ± 24.2% for the 300, 150 and 80 kg N ha^{-1} treatments, respectively, as an average of both growing seasons ($p = 0.08$).

3.4. Nitrous Oxide Emissions

The average N_2O flux was 3.7 times greater in the 2016/17 season (1.08 mg N_2O-N m^2 d^{-1}) than in the 2017/18 season (0.29 mg N_2O-N m^2 d^{-1}; $p < 0.05$), being more closely related to soil temperature and moisture (WFPS), with a minor role of soil N-NH_4^+ on N_2O fluxes (Figure 4).

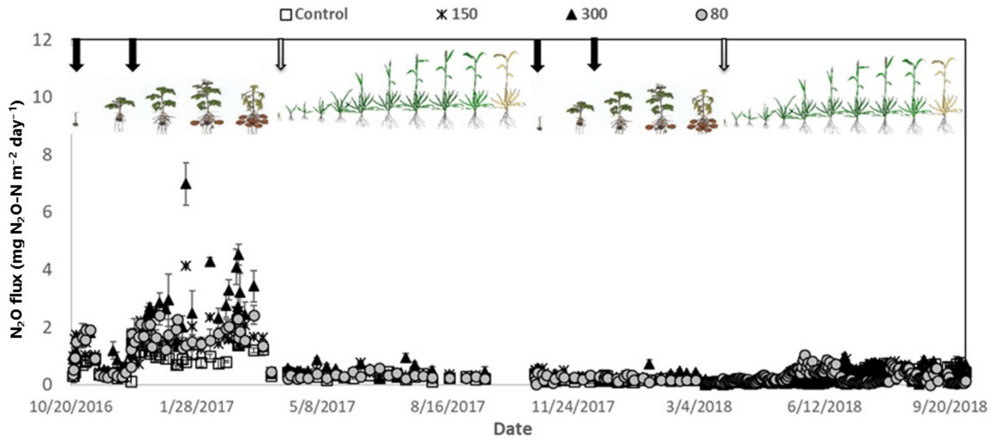


Figure 4. Flux of N_2O (mg N-N_2O m^2 d^{-1}) per treatment over two cropping seasons. Bars indicate SEM (n = 3). Black arrows indicate N fertiliser application to the potato crop (35% and 65% for the first and second arrow in each season, respectively), grey arrows indicate the date of the oat cover crop seeding. No N fertiliser was applied to the cover crop.

The flux of N_2O varied between −0.012 and 1.025 mg N_2O-N m^2 d^{-1} during the experimental period and was affected by the fertiliser treatment. The highest average fluxes were observed in the 300 kg N rate, being 1.8 times higher than those observed in the Control (0.63 and 0.34 mg N_2O-N m^2 d^{-1} for the 300 and 0 kg N ha^{-1} treatments, respectively, on average for the experimental period; $p < 0.01$). The average fluxes for the 150 and 80 kg N ha^{-1} treatments were 0.51 and 0.45 mg N_2O-N m^2 d^{-1}, respectively, on average for the same period (Figure 4). The peak of emissions was observed on the 19 January 2017 (0.8, 1.4, 4.1 and 7.0 mg N_2O-N m^2 d^{-1} for the Control, 80, 150 and 300 kg N ha^{-1} treatments, respectively, $p < 0.05$), following a 41.4 mm rainfall event registered 7–10 days prior, which resulted in a 10-point increase in WFPS, from 37% to 47%, with no differences between treatments ($p > 0.05$). At this time, soil temperature varied between 9 and 15 °C, meaning that soil temperature and moisture (expressed as WFPS) were the key factors affecting N_2O fluxes (Figure 5).

Total emissions following N fertiliser application to the potato crop were affected by fertiliser and rotation year ($p < 0.01$). Emissions were high in the 300 kg N ha^{-1} treatment (1.78 kg N_2O-N ha^{-1}) and low in the Control (0.78 kg N_2O-N ha^{-1}) in 2016/17. However, this effect was not observed in 2017/18 (Table 2). The 2016/17 N_2O emissions were seven times greater than those in 2017/18 (2.18 and 0.80 kg N_2O-N ha^{-1} for 2016/17 and 2017/18, respectively, $p < 0.01$). In the cover crop, N_2O emissions in the control and 80 kg N ha^{-1} treatments were half that of treatments receiving the higher N rates ($p < 0.05$). Overall, in the potato–oat rotation, N_2O fluxes were high and varied with N addition and the cropping year ($p < 0.01$), i.e., lower fluxes were measured in the Control treatment, and during the second cropping year (Table 2). Thus, overall, a rotation with 51% lower N_2O emissions was observed in the Control treatment (1.4 kg N_2O-N ha^{-1}) compared to the highest N rate application (2.7 kg N_2O-N ha^{-1}; Table 2).

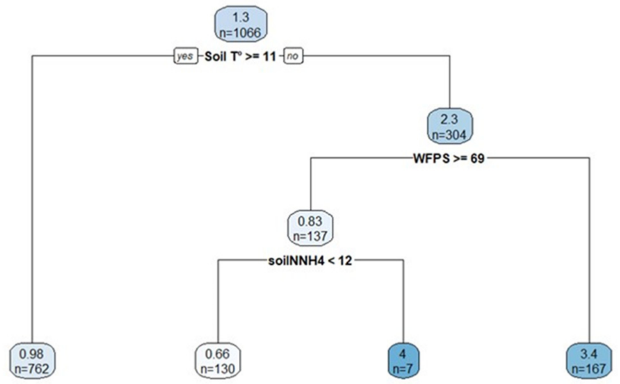


Figure 5. Key factors affecting N-N_2O fluxes in a volcanic soil under potato-crop rotation (r = 31.5%), including impact of soil temperature (Soil T°), soil moisture expressed as soil water field pore space (WFPS) and soil ammonium concentration (Soil NH_4^+-N). n = number of values within the range.

3.5. Emission Intensity, EI

The EI was 1.8 times higher in the highest N application treatment ($p < 0.01$) compared to the Control for the potato crop during the 2016/17 year ($p < 0.01$). Overall, EI increased with the highest N rate ($p < 0.01$).

3.6. Emission Factor (EF1)

The EF1 was 0.44 $\pm$ 0.07% on average, and it was not affected by the N rate used ($p > 0.05$). The EF1 was significantly lower (reduction of 81%) for the 2017/18 growing season compared to the 2016/17 season ($p < 0.01$; Table 2). The highest relationship was found between the EF and potato DM yield ($p < 0.001$, r = 79.4, Figure 6), but no correlation was found with NUE.

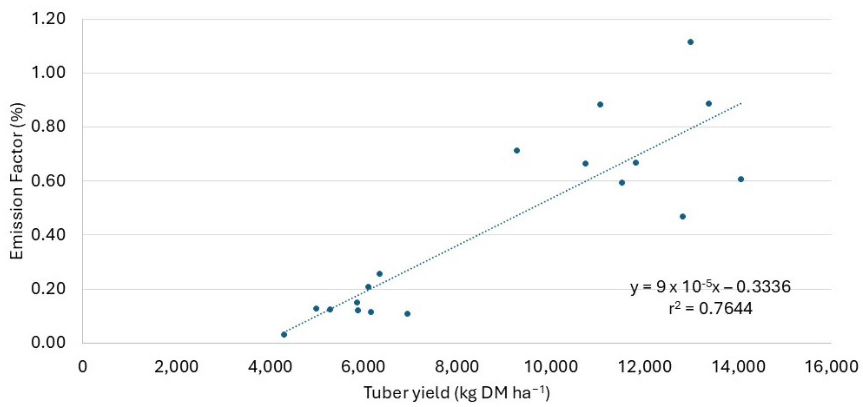


Figure 6. Relationship between tuber yield (kg DM ha^{-1}) and Emission Factor 1 (EF1, %).

4. Discussion

The findings from this study, conducted in the volcanic soil of Southern Chile under rainfed conditions, provide quantitative data on N_2O emissions under a potato–oat rotation.

Our data challenges the perceived thinking that potato production requires large inputs of N fertiliser to optimize tuber yield and marketable calibre given its inefficiency in capturing applied N in a limited root zone [40]. The results also suggested a high potential for N losses during the growing season as N_2O emissions [41]. Additionally, high fertiliser inputs can lead to soil mineral nitrate accumulation at harvest, which may later result in leaching to groundwater [42].

4.1. Overall Influence of Climate and Soil Factors

In this study, potato yield was high in the N fertilized treatments, in comparison to international production (35–45 t ha^{-1}, [43]), with an average of 39 t ha^{-1} (Control) and a maximum yield of 65 t ha^{-1} with the highest N treatment (fresh weight). The difference between the total potato and marketable tuber yield was not significant, in agreement with [29,43] (Table 2).

However, during 2016/17, we obtained a higher total yield and marketable tuber yield with N fertiliser application. This is attributed to the greater amounts of available soil N (particularly NO_3^--N) following N fertiliser application (Figure 2), and the adequate rainfall distribution, resulting in adequate soil WFPS for plant growth over the season (50%, on average between December 2016 and March 2017, Figure 1b), in contrast with lower available soil N concentrations (Figure 3a,b), lower rainfall and lower WFPS in 2017/18 (38% on average between December 2017 and March 2018, Figure 1b).

We also observed a lower NH_4^+-N contribution to total available soil N, which could be associated with NH_4^+-N immobilization through abiotic fixation into labile fractions of the soil organic matter and clay minerals [44,45]. This would also explain the relatively constant soil NH_4^+-N concentrations found during all experimental periods, despite the addition of urea fertiliser (Figure 3a). Nitrification could also have occurred (see ahead).

As observed in our data (Figure 3a), soil NO_3^--N varied significantly only in 2016/17 and differences in NO_3^--N peaks measured in 2016/17 rather than in 2017/18 could reflect the carry-over effect of prior management (including legumes in the pastures and a N fertiliser residual effect), in combination with conventional tillage, which is known to favour soil microbial activity and increase soil N mineralization [46]. After that initial intervention period, NO_3^--N would undergo a Dissimilatory Nitrate Reduction to Ammonium process [47]. As a result, NO_3^- was not found to be related to N_2O losses (Figure 5), which supports previous findings for this volcanic ash soil [6].

Despite the increase in crop yield with the addition of N fertiliser and normal rainfall distribution in 2016/17 (Table 2), no overall effect of N rate on DM yield and marketable tuber calibre was observed. The lack of yield response to N rate application is ascribed to the contribution of natural N soil mineralization and fertility (Table 1) masking the initial fertiliser impact on crop growth. Previous field studies in similar soils have shown that N mineralization in soils receiving 400 kg N ha^{-1} yr^{-1} can reach 382 kg N ha^{-1} yr^{-1} with daily rates of over 1.06 kg N ha^{-1} d^{-1} and contribute to summer–autumn growth period (45% of annual mineralization, [48]), in agreement with the first summer rainfall effects on soil N spikes observed in the current experiment (Figure 3b). For the current experiment, N mineralization based on N uptake in the control treatment was estimated at 150 and 110 kg N ha^{-1} for 2016/17 and 2017/18, respectively.

This potential masking effect of soil N mineralization on applied fertiliser N contributions was previously observed in this soil (e.g., [6]). Moreover, lower rainfall availability in the spring–autumn 2017/18 season resulted in lower crop growth (both for potato and catch crop), and plant N uptake, in agreement with [49,50], increasing the need for irrigation in traditional rainfed areas.

The carry-over effect of N applied to the potato crop on N uptake by the oat crop observed in this study corroborates the benefits of catch crops in mopping up the available N in the rotation. The uptake by the catch crop would reduce the risk of N being leached over the winter [18], offering a simple strategy for reducing N leaching losses.

4.2. Effects on Yield and NUE

The N fertiliser recovery by the potato tuber was c. 57% on average, lower than the 36–69% reported for both foliage and tuber but within the range for potato production with different N rates and sources (55–94%, [41]). The apparent NUE increased with tuber yield (3.6 times greater in the 2016/17 season) and it was greater in the treatments with the lowest N rate that also included foliar N application (94%).

Complementing a N fertiliser application strategy that considers both a reduced granular application at planting with foliar N application at later stages of development offers an opportunity to increase NUE [17,50], as our results suggest, although N foliar application was only considered in the 80 kg N ha^{-1} treatment in our experiment so that the effect of the reducing N rate and the foliar N application could not be separated.

The lack of negative impacts of reduced N fertiliser application on tuber yield and marketable calibre demonstrates that from an agronomic perspective, potato growers can significantly reduce the amount of N fertiliser application resulting in a reduced environmental impact of the potato crop and a significant reduction in production costs. This would be particularly relevant in years of reduced rainfall as observed in 2017/18. Under the soil and climate conditions of our experiment in a highly organic volcanic ash soil, N application rates by farmers on average rainfall seasons could be reduced to 80 kg N ha^{-1} considering the soil N supply via N mineralization, without affecting crop yield and marketable tuber calibre distribution. In growing seasons with rainfall below the average, the N rate could be reduced to a minimum (28 kg N ha^{-1}) to enhance plant growth at the initial stages of development only.

4.3. Effects on N_2O Emissions, EI and EF1

Cumulative N_2O emissions quantified in our trials were within the range usually reported for potatoes (0.6-control to 2.1 kg N-N_2O ha^{-1} in the fertilized treatments) by other authors (e.g., [22]), but are higher than the N_2O values measured in cereal cropping systems (0-control to 1 kg N ha^{-1} in the fertilized treatments receiving 120 kg N-N_2O ha^{-1} yr^{-1} [51]), and pastures (0.2-control to 0.4 kg N-N_2O ha^{-1} yr^{-1} in the fertilized treatments receiving 120 kg N ha^{-1} yr^{-1}, [6,52]) in the same area and soil type.

The high emissions after N application were likely induced by precipitation events. These results suggest that the local weather conditions (especially the amount of precipitation and the resulting WFPS) in the months following fertiliser application is a key factor in determining the magnitude of N_2O emissions per unit of N fertiliser applied, which is in agreement with the results observed in previous studies [13,22]. The rewetting of dry soil induced short-term pulses of high N_2O emissions (Figure 4), and winter emissions were not affected by the quantity of residual N fertiliser applied during the cropping period; therefore, WFPS was the main key factor affecting N_2O emission.

Application of higher N rates increased N_2O emissions during the cropping period when soil moisture was available, in agreement with the results of previous experiments on pastures [7]. Reduced N application reduced N_2O emissions in the 2016/17 season but had no significant effect in the catch crop or the second year, most likely given the differences in cumulative rainfall. This agrees with the results of [16,28], who found an effect of split N application in wet years and who observed that most N_2O emissions occurred between planting and the split N application in the initial rotation year.

The EI values calculated increased with increasing N rates applied and were affected by the decrease in emissions during the 2017/18 growing season. The values measured in the current experiment (150–290 g N_2O-N t^{-1} DM) were greater than those reported for an oat crop in the same area (50–76 g N_2O-N t^{-1} DM) fertilized with 120 kg N ha^{-1}, even for treatments with similar or lower N application rates (80, 150 kg N ha^{-1}; [52]). The EI values were also greater than other international data for potato production following urea application at a rate of 200 kg N ha^{-1} (36–84 g N_2O-N t^{-1} DM; [53]) probably given differences in yield potentials and the consideration of total and net N_2O emissions in ours and [54]'s results, respectively.

The measured EF1 values (range 0.09–0.87%) were lower than the IPCC (2006) proposed default value (1%; [9]), and the recently updated values (1.3–1.9%; [55]) for wet climates. The EF1 values calculated for the experiment were within the range provided by the IPCC for N inputs in dry climates (0–1.1%; [9]), which would reflect the rainfed conditions used for the current experiment and the effect of a dry season. The average EF1 values obtained in this study (0.39–0.48%) are within the range of values measured for other crop rotations in similar soil and climatic conditions of Chile (e.g., 0.16–0.54%, [53]).

Our results suggest that using country-specific EFs, developed in combination with normal and dry weather years, integrating interannual weather variability, would provide a more accurate representation of national N_2O emissions associated with the use of N fertiliser applied to soils and for estimating and reporting in a national emissions inventory.

Our results also showed that N fertiliser rates used for potato production in Chile can be reduced and aligned with the traditional 4R fertiliser best management practice (Right source, at the Right rate, Right time, and Right place). This approach offers an opportunity to maintain tuber yield and marketable tuber calibre, reducing the direct cost for N fertiliser and minimizing N_2O emissions and NO_3 leaching, and provides a basis for the decision-making process in N fertiliser application to a potato crop by farmers and advisors.

5. Conclusions

We found no significant differences in the total and marketable tuber yields when rates of between 80 and 300 kg of N ha^{-1} were applied. The lack of yield response to the N rate application could be related to the contribution of soil N mineralization and fertility, although crop yield was most likely limited by water supply rather than N. The findings of this study, which included a N fertiliser application strategy that involves both a granular application at planting with a foliar N application during the later stages of development, offer an opportunity to increase NUE, as well as mitigate N_2O emissions. This strategy will result in a significant reduction of direct N fertiliser costs for farmers.

The consideration of environmental conditions, particularly rainfall availability during a cropping season is key to N fertiliser rate decisions at the farm level, as well as for the generation and adoption of country-specific emissions factors to better reflect interannual weather variability.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/agronomy14102202/s1, Table S1: Effects of N rates on N concentration (%) in each crop and growing season (±SEM).

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Data Availability Statement: Data will be made available upon reasonable request.

Conflicts of Interest: Marta Alfaro was employed by the company AgResearch Ltd. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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