Dairy slurry application to grasslands and groundwater quality in a volcanic soil

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Abstract

Research in volcanic-ash soils has shown that they largely capture the dairy slurry following application to land; however, their hydrological properties would favor nutrient leaching. Our objective was to evaluate the contribution of biogeochemical and hydrological controls on the pollution of groundwater by cattle slurry applied to a permanent grassland growing on a volcanic soil. We sampled groundwater chemistry since 10 months before the fertilization (three samplings), and 16 months after, with samplings 1-2 months after the fertigation. Following fertilization, ammonium, exchangeable potassium, and magnesium soil concentrations increased in the fertilized plots compared to the control plots. In contrast, no effect of slurry on groundwater quality was detected, with the exception of dissolved organic nitrogen, a main component of dairy slurry that increased in the groundwater below the fertilized plots. Despite the fact that biogeochemical controls predominate, hydrological aspects would be important when rainfall is high, evapotranspiration is low, groundwater table level is high, and water movement in the saturated zone increases. We concluded that the application of slurry to pastures under rates comparable to a high fertilization in the short term, does not generally impact the groundwater quality in volcanic ash-derived soils.

Keywords: Andisol, groundwater pollution, hydraulic properties, saturated zone, dissolved organic nitrogen

1. Introduction

Dairy slurry is a mixture of urine, feces, rain, and washing water in a liquid phase, which is an important plant nutrient source on farms, supplying partial or total requirement for grass fertilization (Salazar *et al.*, 2003). The use of dairy slurry on grasses and crops is a common practice among farmers worldwide. However, mismanagement, such as high application rate or inappropriate application time during the year, can lead to nutrient losses to the wider environment (Smith and Chambers, 1993). In recent years, dairy production has intensified, with an increasing milk production in conjunction with an increasing use of dairy slurry in agricultural soils, in order to recycle nutrients according to grass requirements and to reduce the costs of inorganic fertilizers.

Several studies have evaluated the effect of cattle slurry or mineral fertilizer on non-volcanic soils, finding high pollution levels in shallow groundwater and the associated streams (Lowrance *et al.*, 1985; Hefting *et al.*, 2003; Dhondt *et al.*, 2006). In volcanic soils, most studies have focused on nutrient losses to the vadose zone (e.g., Di and Cameron, 2002; Alfaro *et al.*, 2008), finding comparatively low levels of nutrient losses compared to non-volcanic soils, even under a high rate of nitrogen (N) application (Salazar *et al.*, 2012). The mechanisms behind this pattern are: i) a tight N cycle (Huygens *et al.*, 2008) with low rates of N fixation and mineralization in pristine soils (Pérez *et al.*, 2003), which means that plants and microbes readily use the low soil N levels, with scarce inorganic N losses into streams (Hedin *et al.*, 1995); ii) a high phosphorus adsorption due to the aluminum and hydrous oxide composition in amorphous clays (Alfaro *et al.*, 2008); and iii) a high cationic exchange capacity associated to the crystalline clays and organic matter accumulation that predominate in riparian soils (Lowrance *et al.*, 1985; Cuevas *et al.*, 2014).

However, volcanic ash-derived soils have special hydraulic properties that may counteract the abovementioned biogeochemical controls: a low bulk density ($< 0.9 \text{ Mg m}^{-3}$, Dörner *et al.*, 2010) and a well-defined inter- and intra-aggregate pore system (Dörner *et al.*, 2010) that allows a large porosity and water holding capacity with a high saturated hydraulic conductivity (Dörner *et al.*, 2009a). This implies relatively high water infiltration rates, making runoff unlikely to occur (Alfaro *et al.*, 2008). Thus, the main pathway of nutrient losses from the soil should be the water and nutrient movement in the dissolved phase. Therefore, based on this background, the effect of application of high volumes of slurry on groundwater quality is not immediately predictable. Only one piece of research has examined this issue in a volcanic landscape in the Réunion Island in the Indian Ocean (Payet *et al.*, 2010), finding no effect of pig slurry on groundwater pollution on the scale of several years, but a significant effect at longer time scales was found.

The objective of this paper is to evaluate the contribution of biogeochemical and hydrological controls on the potential pollution of groundwater by cattle slurry applied to a permanent grassland growing on a volcanic soil. Research on this kind of soil is an important point of comparison with other environments, because volcanic soils present specific hydraulic properties and, although they only cover $< 1\%$ of the area in the world (WRB, 2006), they represent an important soil type in volcanic countries such as Chile and New Zealand.

2. Materials and Methods

2.1. Study site

Work was conducted at the Austral University Experimental Livestock and Agriculture Station, located in southern Chile ($39^{\circ} 46' 55'' \text{ S}$, $73^{\circ} 13' 24'' \text{ W}$), 4 km

north of the city of Valdivia and 15 km from the Pacific Ocean. The climate is humid temperate, with an average annual temperature of 12 °C and 2,000 mm of rainfall.

The geomorphology is an alluvial terrace, with the studied uplands covered by grassland. A forested slope (25 m wide, 35° inclination) connects with the floodplain, also covered by native forest, with a width of 20 m (Figure 1). The third order Santa Rosa stream marks the boundary of the floodplain. The grasslands are located about 17 m a.s.l., while the stream is located 13 m below the upland.

A 200 m long x 75 m wide soil area adjacent to the stream was studied (Figure 1). This stream is 5–6 m wide with a streamflow of 40–1,050 L s⁻¹ (summer and winter, respectively). The creek forms part of a watershed whose approximate area is 15 km². Grassland cover is about 22% of the watershed, while native forest, dispersed houses, and a very small portion of exotic tree plantations make up the remaining area. The forested slope is dominated by second-growth forests of *Nothofagus obliqua* (Mirb.) Oerst. var. *obliqua* tree, *Chusquea quila* Kunth bamboo, and *Hedera helix* L., an exotic vine. The riparian vegetation in the floodplain is characterized mainly by *Blepharocalyx cruckshanksii* (H. et A.) Nied., *Myrceugenia exsucca* (DC.) Berg, and *Drimys winteri* J. R. et G. Forster var. *chilensis* (DC.) A. Gray native trees.

The grassland was sown in April 2011 with *Lolium perenne* L. (perennial ryegrass cv. Arrow/Alto 50%/50%) after an application of 2,000 kg ha⁻¹ of CaCO₃. No fertilization was applied until October 2012, and the pastures were cut with a mower.

The soil corresponds to an Andisol, Valdivia series (Duric Hapludand or a Petroduri-Silandic Andosol, WRB, 2006). Dörner *et al.* (2015) studied the soil physical properties and water content dynamics of the first 50 cm depth. In general, the soil presents a larger predominance of silt in its horizons, and the levels of

organic matter decrease with depth (e.g., in uplands it changes from 9.9% to 0.9%, the floodplain presenting the highest values). Bulk density values ranged between 0.56 and 0.76 g cm⁻³, which allow for large volumes of macropores (e.g., > 14% at 5 cm depth), plant available water, and saturated hydraulic conductivity. The latter ranged between 3.13 to 0.89 log cm d⁻¹ (laboratory studies) and decreased with soil depth. These physical characteristics allow dynamic changes in soil water content depending on rainfall and air/soil temperatures (Dörner *et al.*, 2015). At 4 m depth, a sandstone stratum can be found in the upland, which is closer to the ground in the forested slope. The thickness of these depositions is 0.25–2.0 m. The sandstone has, in relation to its texture, a large porosity (57–68%); the macropores dominate, especially in the surface layer (29%) (Ellies and Gayoso, 1979).

2.2. Well assessment

Forty five wells were established throughout the study area to assess groundwater nutrient concentration. Wells were located at nine parallel transects (perpendicular to the stream) in both the upland (α wells), the upland-slope border (β), 15 m from the border on the slope (γ), and 30 (δ) and 45 m (ϵ) from the same border, corresponding to the floodplain (Figure 1). The ϵ wells were adjacent to the stream. Wells were cased with 7.5 cm-diameter PVC tubes, and were screened with 2 mm openings. The screened section was enveloped with a thin fabric (openings 200 μ m) to prevent blockage by incoming sediments. The borehole was then sealed with a mixture of gravel and sand. The top 25 cm were sealed with swelling bentonite mixed with soil.

To allocate the control or treatment plots, the groundwater flow vectors were determined. A topographic survey was carried out that allowed a map of the experimental area to be prepared. The groundwater level below ground was recorded with a measuring tape

several times a year and its elevation was calculated by deducting this distance from the elevation at ground level. Water contour lines were triangulated with the linear interpolation method and the water flow vectors were calculated using the software Surfer v11.0 (Golden Software, Inc., Golden, Colorado, USA).

The latter represents the gradient of the equipotential lines that define the water flow direction (assuming an isotropic behavior of the hydraulic conductivity, Dörner *et al.*, 2015), which was verified to avoid mixing of effects between the experimental and control settings (Figure 1).

Figure 1. Design for fertilization of grasslands with dairy slurry. C = control plots, F = fertilized plots. UPL = upland, SLO = slope, FPL = floodplain. Isolines correspond to August 2012 groundwater level. UTM coordinates are in meters. The groundwater loggers were placed in the F plot on the right.

2.3. Hydrology

Precipitation and potential evapotranspiration (E_t) were derived for the period 2012–2015 from the Miraflores meteorological station, 6 km from the study site in the city of Valdivia. This location has a Davis Vantage Pro 2 station (Hayward, California, USA). The equipment accumulated the records obtained over 30-min periods.

Groundwater level was studied by placing HOBO U20-001-01 pressure loggers (Onset Computer Corporation, Bourne, USA) inside the monitoring wells for most of 2015. They were installed at all points in a transect α to ε . The logger for barometric compensation was placed close to the stream. Groundwater velocity was obtained from an expression related to Darcy's law:

$$(1) \quad GV = \frac{-K_s * \Delta h}{\Delta L * TP}$$

where GV is the groundwater velocity, Δh is the difference in groundwater altitude between adjacent wells in the same line (for example, between δ and ϵ), ΔL is the slope distance between those points from the topographic survey, and TP is the soil porosity (68%, Ellies and Gayoso, 1979). The saturated hydraulic conductivity (Ks) was determined for the 45 wells using Bouwer and Rice's method (Bouwer, 1989). Consequently, each well was suddenly purged with a water pump or a retention valve, then two pressure loggers were introduced. One of the loggers stayed underwater, while the other served as a barometric compensation, taking water depth measurements every 5 sec. The Ks determination was repeated three times (May, August, November 2012, corresponding to the autumn, winter, and spring seasons, respectively).

2.4. Experimental design

Slurry from the dairy farm of the Austral University Experimental Station was used instead of mineral fertilizer because i) the former is abundantly produced by the dairy farms in the region, ii) slurry application to pasture by southern Chilean farmers is a common practice, and is applied throughout the year, and iii) nutrients in a liquid phase have a higher potential to pollute soil water, especially when inadequate practices are carried out. Therefore, this extreme scenario to test the possibility of groundwater contamination was studied. Dairy slurry was accumulated in a 100 m³-storage tank, where the liquid was mechanically mixed. Then the slurry was pumped to the experimental site and stored in several 3.5 m³ PVC tanks. Dairy slurry was thoroughly mixed with a pump and two 1 L representative samples were taken for laboratory analyses, in order to adjust the rate of slurry application. The samples were analyzed for dry matter (DM), total N, ammoniacal-N, P₂O₅, K₂O, CaO, MgO, Na, following the methods of Sadzawka *et al.* (2007).

Experimental plots in the uplands were 25 m wide x 30 m long and did not receive any fertilizer until October 2012, when treated plots were fertilized with dairy slurry on seven different dates up to February 2014 (Table 1). Simultaneous plots (control/fertilized, n = 2 replicates) were monitored to allow for parallel comparisons between them (Figure 1). The fertilized portion was the most distant from the forest border (15 to 30 m), while the proximal section of the upland (0 to 15 m) was not fertilized (Figure 1).

Slurry was manually applied using a hose fitted with a splash plate, which allowed an even distribution of slurry. The liquid was pumped using the rates indicated in Table 1. Control plots were irrigated with equivalent amounts of stream water, which are known to have a very low level of nutrients (Cuevas *et al.*, 2014).

2.5. Soil chemical analyses

In October 2012, before dairy slurry application, 20 random subsamples were taken with a 21 mm diameter auger, from the soil surface (0-20 cm depth) of three 25 m-wide plots in the upland, slope, and floodplain. The 20 subsamples were combined to produce a composite sample for each plot and environment, thus the sample size was three.

Soil sampling was repeated in October 2014, after the period of dairy slurry application. Moreover, non-fertilized plots were also assessed (parallel control plots). Analyzed variables were pH, nitrate (NO₃⁻-N), ammonium (NH₄⁺-N), Olsen phosphorus (Olsen P), and exchangeable calcium (Ca²⁺), potassium (K⁺), sodium (Na⁺), magnesium (Mg²⁺), aluminum (Al³⁺), Al³⁺ saturation, and effective cationic exchange capacity (ECEC). Analyses followed the methods of Sadzawka *et al.* (2006).

Table 1. Rates ($\text{m}^3 \text{ha}^{-1}$, in parentheses) and nutrient inputs (kg ha^{-1} , fresh basis) due to dairy application in experimental plots.

Date of application	total N	$\text{NH}_4^+\text{-N}$	total P	total K	total Ca	total Mg	total Na
October 10, 2012 (88.334)	41.9	14.6	7.7	27.2	18.0	5.9	9.7
March 27, 2013 (150.647)	54.2	30.1	6.6	38.8	20.4	8.2	15.1
June 11, 2013 (184.451)	62.7	36.9	10.5	67.4	21.1	8.9	12.9
August 21, 2013 (180.000)	66.6	28.8	7.9	35.9	23.2	8.7	18.0
October 24, 2013 (330.000)	217.8	115.5	24.5	186.4	57.6	24.7	46.2
December 12-13, 2013 (330.000)	234.3	99.0	25.9	213.8	94.4	35.8	46.2
February 6-7, 2014 (330.000)	148.5	75.9	15.8	167.2	66.0	33.8	52.8
Sum	826.0	400.8	98.9	736.7	300.7	126.0	200.9

2.6. Groundwater chemistry

One to two days before water sampling, the wells were purged with either a water pump or a retention valve screwed to a thinner PVC tube introduced into the water. Groundwater was collected from the water table one to two months after each fertilization, with a clean bottle attached to a long PVC pipe. Different bottles were used for each sampled well to avoid water cross-contamination. The bottles were kept below 5°C and the samples were frozen within 10 h of being collected. The chemicals analyzed following APHA (2005) procedures were NO_3^- -N, nitrite, NH_4^+ -N, total dissolved N, dissolved organic N (DON, calculated as the difference of the total dissolved N and the inorganic N forms), phosphate (PO_4^{3-} -P), Ca^{2+} and K^+ .

Detection limits were $2 \mu\text{g L}^{-1}$ (NO_3^- -N and PO_4^{3-} -P), $3 \mu\text{g L}^{-1}$ (NH_4^+ -N), $190 \mu\text{g L}^{-1}$ (total dissolved N), and $50 \mu\text{g L}^{-1}$ (Ca^{2+} and K^+).

2.7. Nutrient balance

Variables contributing to the mass balance were derived from data obtained in this research, as well as unpublished sources. Thus, nutrient application and soil pool were evaluated in this paper. Soil retention was calculated as the difference in the soil pool after versus before fertilization. Nutrient uptake by grass was quantified by mowing the grassland 14 times during the experiment using a four wheel harvesting machine, leaving a sward height of *c.* 5 cm.

The harvester cut three or four strips of 30 m x 0.5 m distributed regularly in the 25 m-wide plots. The whole collected sample was weighed and sub-samples of *c.* 1 kg were taken and analyzed in the laboratory for N, P, K, Ca, Mg, Na and DM (AOAC, 1996). The grass yield was then calculated from the DM percentage applied to the fresh collected grass and extrapolated to one hectare ($n = 2$ replicates). Finally, the nutrient extraction by grasslands was estimated for each sampling date as the grass yield multiplied by the percentage of nutrient content in the harvested forage.

2.8. Data analyses

Soil variables were compared before and after fertilization by means of ANOVAs, followed by a Tukey test. When ANOVA's assumptions were not met, the Kruskal-Wallis test was used. Groundwater chemical data was not normally distributed nor was it homoscedastic. Usual transformations did not resolve this issue, thus the non-parametric three-way ANOVA was used (that is, the Scheirer-Ray-Hare extension of the Kruskal-Wallis test). Factors considered were well (α through ϵ), treatment (control/fertilized) and time (before/after the fertilization). All interactions were analyzed too. Statistical analyses were carried out with Statistica 6.0 software (StatSoft Inc., Tulsa, Oklahoma, USA).

3. Results

3.1. Dairy slurry application

The dairy slurry was very diluted and had an average DM content of 1.1%, with a maximum of 1.7%. The most important nutrients were total N, followed by K (Table 1). Most N was either in ammoniacal or organic form (about 50%). Lower contents were found for Ca, Na, Mg and P. Regarding the rates applied,

these were very high compared to the grassland requirements (see Nutrient balance section), both for the whole period of the assays and on a yearly basis (Table 1). For instance, N was applied at a rate of 826 kg ha⁻¹ (equivalent to 620 kg ha⁻¹ yr⁻¹), while the grasslands only need 212 kg ha⁻¹ yr⁻¹.

3.2. Hydrology

It rained throughout the year (Figure 2), but rainfall was concentrated from May to September (winter). Rainfall amounts were 1,911, 1,536, 1,324 and 1,519 mm for the years 2012 to 2015, respectively. The year 2014 was probably underestimated because the meteorological station was out of service in March and November. The Las Lomas (Máfil) station at 30 km distance from the study site recorded 140 mm for those missing months.

Potential evapotranspiration (Et_0), which is exactly equivalent to the grassland evapotranspiration, was 571, 545, 459, and 673 mm for the period 2012-2015, respectively (Figure 2). 2014 may also be underestimated due to lack of data for March and November, when accumulated Et_0 was 154 mm in the Las Lomas station. Rainfall was 2-3 times larger than the Et_0 , but in some months and years (i.e., summer 2014, summer 2015) the water balance was negative (Figure 2). On the contrary, from autumn to the beginning of spring the balance was very positive.

The relationship between rainfall and groundwater dynamics was available only in the year 2015 (Figure 3). Precipitation did not influence water table levels during the summer or the beginning of autumn. From June, groundwater responded positively to rainfall, at times when rainfall surpassed Et_0 (Figure 2). From September onwards, rain could not sustain the high groundwater levels, which decreased monotonically, with an isolated peak in α . During that period, Et_0 was again surpassing rainfall.

Figure 2. Rainfall and evapotranspiration for the study period in the Miraflores (Valdivia) meteorological station. Missing points had < 80% of valid data.

Figure 3. Relationship between rainfall and the groundwater level for the year 2015, at the upland (α) and the forest border (β). The ground altitude for the upland α coincides with the upper X-axis.

The influence of rain in groundwater can also be seen when considering the lag between the middle of a rainfall event and the corresponding groundwater peak. For the eight peaks identified in Figure 3, such delays fluctuated between 11 days 2 h 15 min and 3 h 15 min, with decreasing lag times from June to October. The distance from the ground to the groundwater level was 3.2 m in that period (Figure 3).

Rain or fertigation water should move horizontally towards the stream once it has reached the saturated zone. Groundwater velocities were generally the lowest in May ($3 \pm 1.0 \text{ mm day}^{-1}$, mean $\pm$ SE), and the greatest in August ($50 \pm 28.7 \text{ mm day}^{-1}$), with intermediate values for the austral spring (November, $9 \pm 4.9 \text{ mm day}^{-1}$). At the May rate 5,000 days would have been required for the groundwater to traverse the fertilized plot (15 m wide).

In August, groundwater would have moved only 100–265 cm, considering that the water sampling after the winter fertilization was carried out after 20 and 53 days (discounting the vertical water travelling time in the soil profile). That is to say, for most of the sections of fertilized grasslands, groundwater remained within them.

3.3. Soil chemical analyses

Both for the October 2012 and 2014 control plots, most of the evaluated variables increased from upland to floodplain (Table 2). Conversely, there was more Olsen P in the upland than in the other environments. Compared with the fertilized plots sampled in October 2014, in most cases there were no significant differences ($p > 0.05$), in spite of the slight trend for fertilized plots to be higher than parallel control plots. An exception was the pH, which was lower pre-fertilization in the upland, without differences between parallel plots (control/fertilized).

NH_4^+ -N and exchangeable K^+ and Mg^{2+} concentrations were higher in the upland fertilized plots compared to the parallel controls.

3.4. Variations in groundwater quality

A significant source of variation was associated to the well position in the transect (Table 3), that is, NO_3^- -N diminution from upland to floodplain, and vice versa in the case of the other chemicals, with a non-significant variation for DON (see Cuevas *et al.*, 2014). However, the most relevant source of variation in the context of this paper must be searched when comparing concentrations before versus after the fertilization. For NO_3^- -N, there was no significant effect (Table 3, Figure 4a). For NH_4^+ -N, the effect was significant ($p = 0.047$). Notwithstanding, the rising trend in concentration was

observed in the control plots; thus, it was not an effect of dairy slurry application (Figure 4b).

On the other hand, the plot effect (control vs. treatment) was not significant for NO_3^- -N and NH_4^+ -N, indicating that both sets of plots had similar concentrations in groundwater. There was no significant interaction 'plot x time', thus both effects operated separately (Table 3).

DON had a significant time effect after the fertilization, which resulted in a slightly higher DON concentration in the fertilized plots compared to the parallel controls, as revealed by the significant interaction plot x time ($p = 0.040$) (Figure 4c). Fertilized plots doubled DON concentration (before/after slurry application), while the factor for the controls was 1.6.

For total dissolved N, the time effect (higher after fertilization) was about the same for the control and treatment (Figure 4d). Phosphate treated plots had higher concentrations than the controls, but the difference was not more marked after fertilization as indicated by the non-significant time and plot x time effects (Table 3, Figure 4e). On the other hand, the significant time effect for K^+ was expressed as a decrease in groundwater concentration for both control and fertilized plots (Figure 4f). Lastly, Ca^{2+} showed a higher concentration in the treatment, and a higher concentration after the fertilization (in the control), but in all cases the trends do not support an effect of fertilization (Figure 4g).

3.5. Nutrient balance

Nutrient input by rain was scarce in comparison to that supplied by slurry, and the largest proportion was N (Table 4). The most abundant nutrient applied was also total N, followed by K, while the lowest input was NO_3^- -N ($13.7 \text{ kg ha}^{-1} \text{ yr}^{-1}$). The soil pool at 0–20 cm depth was also low in relation to slurry application, with the exception of total N and Ca^{2+} .

Table 2. Studied sites' soil chemical composition (0-20 cm depth) before and after fertilization with cattle slurry. Values correspond to means $\pm$ standard error of three replicates. Upper, italic values correspond to control plots in 2012 (before fertilization), middle values are control plots in 2014 (non-fertilized), while lower, underlined values are the fertilized plots in 2014 (only in the upland).

Variable	Unit	Upland plots	Slope plots	Floodplain plots
pH in water (1:2.5)		5.7 $\pm$ 0.03 ^{a(d)}	5.5 $\pm$ 0.00	5.1 $\pm$ 0.10
		6.0 $\pm$ 0.04 ^b	5.7 $\pm$ 0.06	5.4 $\pm$ 0.02
		<u>6.2 $\pm$ 0.01^b</u>	<u>5.7 $\pm$ 0.04</u>	<u>5.4 $\pm$ 0.11</u>
NO ₃ ⁻ -N	mg kg ⁻¹	16.3 $\pm$ 1.23	18.7 $\pm$ 0.94	26.4 $\pm$ 7.36
		11.9 $\pm$ 3.50	18.6 $\pm$ 1.05	24.2 $\pm$ 1.05
		<u>17.9 $\pm$ 4.55</u>	<u>18.9 $\pm$ 4.90</u>	<u>15.8 $\pm$ 1.05</u>
NH ₄ ⁺ -N	mg kg ⁻¹	11.7 $\pm$ 0.47 ^a	13.5 $\pm$ 1.68	18.2 $\pm$ 3.35
		8.0 $\pm$ 1.05 ^b	9.5 $\pm$ 1.05	8.1 $\pm$ 0.35
		<u>11.6 $\pm$ 0.35^a</u>	<u>10.9 $\pm$ 1.75</u>	<u>9.5 $\pm$ 3.15</u>
Olsen P	mg kg ⁻¹	14.0 $\pm$ 0.98	4.4 $\pm$ 0.95	7.1 $\pm$ 1.80
		10.6 $\pm$ 0.10	3.6 $\pm$ 0.25	4.8 $\pm$ 1.20
		<u>12.6 $\pm$ 1.95</u>	<u>3.7 $\pm$ 1.15</u>	<u>4.4 $\pm$ 0.50</u>
Exchangeable K ⁺	cmol ⁺ kg ⁻¹	0.2 $\pm$ 0.01 ^a	0.4 $\pm$ 0.07	0.5 $\pm$ 0.13
		0.1 $\pm$ 0.01 ^a	0.4 $\pm$ 0.01	0.5 $\pm$ 0.01
		<u>0.5 $\pm$ 0.06^b</u>	<u>0.4 $\pm$ 0.15</u>	<u>0.4 $\pm$ 0.04</u>
Exchangeable Ca ²⁺	cmol ⁺ kg ⁻¹	3.5 $\pm$ 0.47	2.2 $\pm$ 0.36	4.4 $\pm$ 1.25
		2.4 $\pm$ 0.57	1.9 $\pm$ 0.00	2.2 $\pm$ 0.93
		<u>3.6 $\pm$ 0.17</u>	<u>1.8 $\pm$ 0.46</u>	<u>1.7 $\pm$ 0.23</u>
Exchangeable Mg ²⁺	cmol ⁺ kg ⁻¹	0.4 $\pm$ 0.01 ^a	1.4 $\pm$ 0.42	3.2 $\pm$ 0.87
		0.3 $\pm$ 0.01 ^b	1.2 $\pm$ 0.05	1.6 $\pm$ 0.45
		<u>0.8 $\pm$ 0.01^c</u>	<u>1.2 $\pm$ 0.15</u>	<u>1.4 $\pm$ 0.21</u>
Exchangeable Na ⁺	cmol ⁺ kg ⁻¹	0.1 $\pm$ 0.01	0.2 $\pm$ 0.05	0.5 $\pm$ 0.10
		0.1 $\pm$ 0.01	0.2 $\pm$ 0.04	0.4 $\pm$ 0.06
		<u>0.1 $\pm$ 0.00</u>	<u>0.2 $\pm$ 0.01</u>	<u>0.4 $\pm$ 0.08</u>
Sum of bases	cmol ⁺ kg ⁻¹	4.1 $\pm$ 0.48	4.3 $\pm$ 0.83	8.6 $\pm$ 2.33
		3.0 $\pm$ 0.60	3.7 $\pm$ 0.09	4.8 $\pm$ 1.44
		<u>5.0 $\pm$ 0.23</u>	<u>3.7 $\pm$ 0.76</u>	<u>3.8 $\pm$ 0.54</u>
Exchangeable Al ³⁺	cmol ⁺ kg ⁻¹	0.1 $\pm$ 0.01	0.6 $\pm$ 0.05	1.2 $\pm$ 0.26
		0.1 $\pm$ 0.02	0.6 $\pm$ 0.11	1.7 $\pm$ 0.48
		<u>0.1 $\pm$ 0.00</u>	<u>0.7 $\pm$ 0.02</u>	<u>1.8 $\pm$ 0.08</u>
ECEC ^(e)	cmol ⁺ kg ⁻¹	4.2 $\pm$ 0.47	4.9 $\pm$ 0.88	9.8 $\pm$ 2.26
		3.1 $\pm$ 0.58	4.4 $\pm$ 0.20	6.5 $\pm$ 0.96
		<u>5.1 $\pm$ 0.23</u>	<u>4.4 $\pm$ 0.74</u>	<u>5.6 $\pm$ 0.62</u>
Al ³⁺ saturation	%	2.4 $\pm$ 0.44	13.8 $\pm$ 1.42	14.0 $\pm$ 5.07
		4.1 $\pm$ 1.50	14.5 $\pm$ 1.82	28.1 $\pm$ 11.49
		<u>1.9 $\pm$ 0.13</u>	<u>16.9 $\pm$ 3.40</u>	<u>32.4 $\pm$ 2.17</u>

(d) ^{a, b, c} Different superscripts indicate significant differences at $p < 0.05$ (Tukey test) for comparisons between treatment and control, within each environment. (e) ECEC = effective cationic exchange capacity

The only nutrient that accumulated appreciably in the soil after fertilization was K^+ , which explains why it was subtracted from the mass balance. Grassland uptake was an important sink, varying from 21 (Ca) to 71% (NH_4^+-N) of the nutrients artificially supplied (for Mg and Na the proportions were 15 and 23%, respectively, data not shown). As the N form that was absorbed by grasses was not quantified, the NH_4^+-N and NO_3^--N absorptions are taken as maximum potential values in Table 4, explaining why total N is not the sum of the inorganic forms. Conversely, this means

that grasslands received between 0.06 (NO_3^--N) and 7 (Mg) times the fertilization that they required.

By adding and subtracting the variables in Table 4 (not including the original soil pool), it was concluded that 66% of total N would have leached from the upper soil (0–20 cm) compared to that applied as slurry and rain ($417 \text{ kg ha}^{-1} \text{ yr}^{-1}$). Most nutrients largely decreased their loads after passing through the soil profile, with NO_3^--N being predicted to be filtered in amounts higher than those available in soil. Only DON had a budget with scant variations in the soil.

Table 3. Non-parametric three-way ANOVA for the groundwater nutrient concentrations before and after fertilization with cattle slurry. Italic values represent significant effects at $p < 0.05$.

Effect	Nitrate-N		Ammonium-N		Dissolved organic nitrogen		Total dissolved nitrogen		Phosphate-P		Potassium (K^+)		Calcium (Ca^{2+})	
	H ^(a)	<i>p</i> ^(b)	H	<i>p</i>	H	<i>p</i>	H	<i>p</i>	H	<i>p</i>	H	<i>p</i>	H	<i>p</i>
Well (position in the transect)	144.1	<0.001	91.6	<0.001	7.3	0.121	27.3	<0.001	18.9	<0.001	80.9	<0.001	100.6	<0.001
Plot (control vs. treatment)	0.0	0.840	1.4	0.232	0.2	0.655	1.2	0.273	8.8	0.003	0.2	0.80	5.2	0.022
Time (before/after fertilization)	1.0	0.309	3.9	0.047	37.7	<0.001	35.3	<0.001	3.3	0.068	18.4	<0.001	4.1	0.042
Well x plot	1.7	0.784	9.1	0.058	1.8	0.772	12.1	0.017	7.9	0.096	8.4	0.078	5.0	0.286
Well x time	1.6	0.815	10.0	0.040	3.7	0.448	3.4	0.493	3.3	0.512	12.9	0.012	13.8	0.008
Plot x Time	0.0	0.993	0.0	0.964	4.2	0.040	2.9	0.089	0.3	0.560	0.0	0.924	1.2	0.279
Well x plot x time	1.5	0.826	1.7	0.794	2.3	0.681	0.9	0.925	1.0	0.916	0.4	0.986	1.9	0.756

(a) H = Kruskal-Wallis statistics; (b) p = probability; degrees of freedom are 4 for wells, 1 for plots, and 1 for time.

Figure 4. Groundwater concentration in control and fertilized plots (all wells pooled), before and after the fertilization with dairy slurry (mean ± standard error). The statistics are detailed in Table 3.

Table 4. Nutrient balance for the experimental application of dairy slurry to grasslands. The plus or minus signs indicate whether the values must be summed or discounted. No sign indicates a neutral effect on the balance. Mean $\pm$ standard error.

Variable	Unit	total N	NH ₄ ⁺ -N	NO ₃ ⁻ -N	DON	P	K	Ca
Rain input ^(a)	kg ha ⁻¹ yr ⁻¹	+10.0 $\pm$ 2.02	+0.5 $\pm$ 0.14	+0.1 $\pm$ 0.00	+9.4 $\pm$ 1.82	+<0.03 $\pm$ 0.000 (available)	+<0.8 $\pm$ 0.00 (available)	+<0.8 $\pm$ 0.00 (available)
Nutrient application ^(b)	kg ha ⁻¹ yr ⁻¹	+619.5	+300.6	+13.7	+305.2 ^(c)	+74.2 (total) +44.8 (available)	+552.5 (total) +486.2 (available)	+225.5 (total) +155.4 (available)
Soil pool (0-20 cm) (pre-fertilization) ^(d)	kg ha ⁻¹	5,915 $\pm$ 469.2	15.2 $\pm$ 0.61	21.2 $\pm$ 1.61	nd ^(f)	18.2 $\pm$ 1.27 (available)	101.7 $\pm$ 2.93 (available)	911.8 $\pm$ 121.83 (available)
Soil net retention ^(e)	kg ha ⁻¹ yr ⁻¹	nd	-0.5 $\pm$ 0.46	-0.2 $\pm$ 2.50	nd	+1.1 $\pm$ 0.20 (available)	-85.6 $\pm$ 12.81 (available)	+36.7 $\pm$ 45.53 (available)
Fertilized grassland uptake	kg ha ⁻¹ yr ⁻¹	-212.5 $\pm$ 18.10	-212.5 $\pm$ 18.10 (max) ^(h)	-212.5 $\pm$ 18.10 (max)	na ^(g)	-21.4 $\pm$ 0.93 (total)	-204.8 $\pm$ 15.68 (total)	-48.3 $\pm$ 2.80 (total)
Sum	kg ha ⁻¹ yr ⁻¹	417.0	88.1	-198.9	314.6	24.5	196.6	144.6

(a) Cuevas *et al.* (unpublished data for this same study site, 2014).

(b) P, K, Ca bioavailability were derived from Salazar *et al.* (2007).

(c) Calculated from total N less inorganic N and assuming that all N was dissolved, due to the very low dry matter content (1.1%).

(d) Calculated from Table 2 and considering a bulk density of 0.65 g cm⁻³ for this study site (Dörner *et al.*, 2015). Total N was estimated from organic carbon content and a C/N = 16.7 (Paulino, L. *et al.*, unpublished data, 2014).

(e) Calculated as soil nutrient concentration post-fertilization minus pre-fertilization (Table 2), and weighing by a bulk density of 0.65 g cm⁻³ and a soil depth of 20 cm.

(f) nd: non determined, (g) na: non applicable, (h) max: maximum values possible.

4. Discussion

4.1. Dairy slurry application

DM was low in comparison to the 3.9% reported by Salazar *et al.* (2007) in a study of 50 farms through the Los Lagos Region in southern Chile. In the same way, the different forms of N had a lower concentration in the present research. As slurry was applied at rates of 1,195 m³ ha⁻¹ yr⁻¹ (Table 1) with a mean DM of 1.1%, these rates are comparable to those applied by farmers

in the region (300 m³ ha⁻¹ yr⁻¹ with a DM of 3.9%, Salazar *et al.*, 2003). Therefore, our applications were realistic for the local situation.

4.2. Hydrology

From autumn to the beginning of spring the water balance was very positive, therefore nutrient losses by leaching can be expected. Conversely, since precipitation was surpassed by E_{t0} in summer and water moves slowly when soil is dry (Dörner *et al.*, 2009b), it is

unlikely that rainfall or fertigation reached groundwater 9 m belowground (Figure 3), under such dry conditions. Moreover, in this season the plants were taking up soil nutrients. Another line of evidence deals with the volumetric water content (θ). Dörner *et al.* (2015) developed pF curves relating θ and the matrix potential for the same soil studied. In spite of the fact that there is no consensus on whether field capacity corresponds to pF = 1.8 or pF = 2.5, taking 1.8 as a conservative estimation, field capacity would be about $\theta = 50\%$ (Dörner *et al.*, 2015). They showed that in the uplands this value is exceeded especially in winter. Hence, water cannot be retained by the soil and moves gravitationally through the fast drainage pores, percolating to deeper soil zones, coherent with the analyses of rainfall, E_t , and phreatic level.

Thus, only in winter (and exceptionally in rainy periods such as in December 2012, Figure 2) could rainfall and slurry nutrients move quickly from the soil surface to the groundwater, given that the plants were not using soil nutrients.

Regarding the groundwater movement, our analysis of velocity discarded the idea that groundwater was flowing faster than the temporal separation in the sampling program, making it unlikely that we missed a possible nutrient signal. As stated by McHugh *et al.* (2016), the monitoring frequency vs. monitoring duration is an important trade-off in groundwater studies.

4.3. Soil chemical analyses

Cuevas *et al.* (2014) have provided explanations for the trends observed for nutrients and other soil properties found in the same transect studied from upland to floodplain. Here only differences between before and after fertilization, as well as in the response of fertilized and non-fertilized parallel plots are analyzed. Significant differences were only detected in the upland grassland, which was the site for fertilizer

application. For example, the pH was lower pre-fertilization than post-fertilization. According to Whalen *et al.* (2000), high rates of manure application in acid soils, as in this case, have resulted in an increase in soil pH, due to the acid neutralizing capacity (carbonates, bicarbonates, organic acids) found in the manure used by those authors (pH = 6.8). The slurry mineralization and subsequent ammonium release should also increase pH.

Regarding $\text{NH}_4^+\text{-N}$ behavior, this was an expected result based on the prevailing contribution of ammoniacal N in dairy slurry with respect to total N (34–59% according to our data, and also supported by Salazar *et al.*, 2012). As no differences were detected when comparing the fertilized treatment (year 2014) with the 2012 control, this implies that this baseline plot partially exhausted the $\text{NH}_4^+\text{-N}$ pool when no fertilization was applied, resulting in low levels in the parallel controls. Conversely, levels recovered after fertilization in the fertilized plots approaching the baseline. K^+ and Mg^{2+} patterns were also expected from the amounts applied as slurry (Table 1).

4.4. Variations in groundwater quality

Generally, the most significant source of variation in groundwater chemistry was the well position in the transect from uplands to riparian forests, a phenomenon already analyzed by Cuevas *et al.* (2014) for a baseline without fertilization. By contrast, there were no effects of fertilization with dairy slurry on groundwater inorganic N, total dissolved N, $\text{PO}_4^{3-}\text{-P}$, K^+ , and Ca^{2+} , even after the application of doses several times the grasslands requirements.

The only exception in groundwater was DON, which increased in the fertilized plots more than the control ones. As slurry N is composed of c. 50% organic N (the difference of total N and inorganic forms in Table 1), and the DM content is very low, this means that the

organic N is found mainly as DON. Thus, our results suggest that the source of the concentration signal found in the fertilized plots is the slurry DON. In fact, agricultural and wetland watersheds have been related to increased dissolved organic carbon (DOC) (Graeber *et al.*, 2012) and DON concentrations (Heinz *et al.*, 2015) in stream water in comparison to forest environments. The mechanism behind this pattern for agricultural landscapes seems to be related to soil tillage practices but, as far as we know, no study has suggested a relationship with dairy slurry applied to pastures. For instance, Royer *et al.* (2007) have not observed higher DOC concentrations in streams due to the application of organic fertilizers (i.e., manure) to agricultural fields, and Graeber *et al.* (2012) did not support this possibility based on fluorescence data. The present results open the possibility that if slurry DON reaches surface waters and is processed by aquatic microorganisms, inorganic N could be produced, and depending on the resulting concentrations an eutrophication problem might occur. This hypothesis is worth studying in future research.

4.5. Nutrient balance

The inputs by slurry application were the main source of nutrients in the system. Nutrient uptake by grass was comparatively high, in line with an expected main output when fertilizer is applied. We consider that the N balance is incomplete, because several sources and sinks were not quantified by this study. For example, at first sight NO_3^- -N, being a minor component of slurry N (3%), would not readily affect groundwater quality. However, important amounts can also be formed by nitrification ($320 \text{ kg ha}^{-1} \text{ yr}^{-1}$, Cárdenas *et al.*, 2013), increasing the concentration available for leaching. Higher rates of NO_3^- -N consumption should also be taken into account, such as abiotic immobilization to soluble organic N pools

and dissimilatory reduction of nitrate to ammonium as important nitrate sinks in these soils in southern Chile (Huygens *et al.*, 2008). Regarding NH_4^+ -N, a large mineralization rate has also been reported in the region ($336 \text{ kg ha}^{-1} \text{ yr}^{-1}$, Martínez-Lagos *et al.*, 2015), which determines a higher availability in relation to that applied as slurry; but in turn slurry ammonium is lost as volatilized ammonia when it is applied (Muñoz *et al.*, 2016), reaching up to 16–82 % of the applied NH_4^+ -N (Salazar *et al.*, 2014). Other sources and sinks for N have low rates: non-symbiotic fixation (Pérez *et al.*, 2003), denitrification (Paulino *et al.*, unpublished data), and runoff (Alfaro *et al.*, 2008).

For the other elements, the balance is expected to be more accurate, because there are less sources and sinks involved, namely the lack of variation of groundwater P as a response to fertilization agrees with an expected high P adsorption to volcanic soils, well documented by Morgan (1997) and Alfaro *et al.* (2008). However, our results do not show a net retention in the upper soil (0–20 cm, Tables 2, 4), thus the retention processes should occur in a major depth of the soil profile. Alfaro *et al.* (2008) have also shown that P runoff instead of leaching is the main pathway for P movement in volcanic soils, but this only explains $25 \text{ g ha}^{-1} \text{ yr}^{-1}$ (total P).

The retention in the upper soil is a possible sink for K^+ , as for other basic cations (Tables 2 and 4). Cuevas *et al.* (2014) have documented a cationic exchange capacity measured at the soil pH that slightly increases from the upland to the floodplain, which may explain this retention (see also Lowrance *et al.*, 1985).

The soil filter effect is compounded by its great depth compared to similar research: a vadose zone of 2 to 9 m below ground was detected, compared to 1–2 m in Northern Hemisphere studies (Hefting *et al.*, 2003; Dhondt *et al.*, 2006). Thus, there are several meters for nutrient filter by the soil, a zone that has not been included in the mass balance due to absence of data.

In summary, biogeochemical processes appear to be contributing to the retention, transformation or elimination of nutrients from the soil before they encounter the groundwater.

5. Conclusions

Scant effect on groundwater quality could be proven under high rates of slurry application typical for the southern regions in Chile. The exception was DON, which responded to fertilization. As the response was slight, this compound would not be overstimulating growth and reproduction in aquatic, heterotrophic communities. However, an effect cannot be discarded if higher rates of slurry application were applied in a large portion of agricultural watersheds with less soil and riparian vegetation development.

Several processes related to the pastures and the volcanic soil physical, chemical and biological properties are responsible for controlling diffuse pollution coming from agriculture in the studied system.

In spite of the fact that biogeochemical controls seem to be predominating, hydrological aspects could also be important in winter when rainfall is high, evapotranspiration is low, phreatic level is high, and water movement in the vadose and saturated zone increases.

This marks a contrast to non-volcanic settings, with a more intense agricultural activity, and shallower groundwater as found in the Northern Hemisphere, whose effect in water resources is very intense compared to southern Chile (Srinivas *et al.*, 2015).

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