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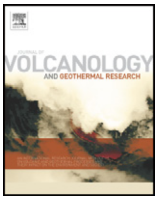

Fate and agricultural consequences of leachable elements added to the environment from the 2011 Cordón Caulle tephra fall

Carol Stewart [a,*], Heather M. Craig [b], Sally Gaw [c], Thomas Wilson [b], Gustavo Villarosa [d,e], Valeria Outes [d], Shane Cronin [f], Christopher Oze [b,g]

[a] *Joint Centre for Disaster Research, Massey University/GNS Science, PO Box 756, Wellington, New Zealand*
[b] *Geological Sciences, University of Canterbury, Private Bag 4800, Christchurch 8140, New Zealand*
[c] *Chemistry, University of Canterbury, Private Bag 4800, Christchurch 8140, New Zealand*
[d] *Instituto Andino Patagónico de Tecnologías Biológicas y Geoambientales (IPATEC), CONICET — Universidad Nacional del Comahue, Centro Regional Universitario Bariloche, Quintral 1250, 8400 Bariloche, Argentina*
[e] *CRUB, Universidad Nacional del Comahue, Quintral 1250, 8400 Bariloche, Argentina*
[f] *School of Environment, University of Auckland, Private Bag 90, Auckland, New Zealand*
[g] *Occidental College, 1600 Campus Road, Los Angeles, CA 90041, United States*

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ABSTRACT

The June 2011 eruption of Cordón Caulle volcano, Chile, dispersed tephra over ~350,000 km^2, including productive agricultural land. This resulted in the death of nearly one million livestock. Two distinct environments were affected: a proximal temperate Andean setting, and the semi-arid Argentine steppe farther from the volcano. The purpose of this study was to better understand the fate and agricultural consequences of leachable elements added to the environment by this large silicic tephra fall. Tephra, soil and surface water samples across the depositional area were collected both immediately after the eruption (tephra and water) and nine months afterwards (tephra, soil and water). Tephra samples were analysed following a new hazard assessment protocol developed by the International Volcanic Health Hazard Network (IVHHN). Water-extractable element concentrations in freshly-collected tephra were very low to low compared to other eruptions, and showed no trends with distance from the volcano. Surface water analyses suggested short-term changes to water composition due to the release of elements from tephra. No effect on the fertility of soils underlying tephra was apparent after nine months. Water-extractable fluorine (F) in freshly-collected tephra ranged from 12 to 167 mg/kg, with a median value of 67 mg/kg. Based on parallels with the 11–12 October 1995 eruption of Ruapehu volcano, New Zealand, we conclude that F toxicity was a possible contributing factor to the large-scale livestock deaths as well as to chronic fluorosis widely reported in wild deer populations across the Cordón Caulle tephra depositional area. Finally, we recommend that effective response to widespread tephra fall over agricultural areas should include: (1) rapid, statistically representative field sampling of tephra, soils, surface water supplies and forage crops; (2) analysis using appropriate and reliable laboratory methods; (3) modelling both short and long-term impacts on the ecosystem, especially for elements that may generate chronic hazard; (4) timely dissemination of results to agricultural agencies; (5) longitudinal sampling and monitoring to adapt impact models; and (6) developing reliable animal fatality diagnoses through autopsies and chemical analysis.

1. Introduction

Tephra fall may cause widespread agricultural and economic losses through chemical and physical impacts on crops and animals (Supplementary Table 1). As fertile soils are often formed from weathered volcanic deposits (Shoji et al., 1993), intensive agriculture is frequently concentrated around volcanoes. During eruptions, crops are coated, smothered or buried, and livestock deaths may be caused by starvation, dehydration and gastrointestinal blockages (Rubin et al., 1994; Cronin et al., 1998; Cook et al., 1981; Wilson et al., 2011a). In some cases animal poisoning has been caused by tephra toxicity, especially associated with fluoride and in some cases sulphur (Thorarinsson and Sigvaldason, 1971; Araya et al., 1990; Cronin et al., 2003). The possible severe productivity losses and animal health consequences mean that F toxicity is an important parameter to evaluate following a tephra fall (Cook et al., 1981; Rubin et al., 1994; Cronin et al., 2003). Conversely, there can also be beneficial outcomes for soil fertility after tephra fall (Cronin et al., 1998). The most common example of this is the addition of sulphur in beneficial amounts, leading to a reduction in the amount of fertilisers needed, such as after the 1995 Ruapehu eruption in New Zealand (Cronin et al., 1997).

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[*] Corresponding author.
E-mail address: c.stewart1@massey.ac.nz (C. Stewart).

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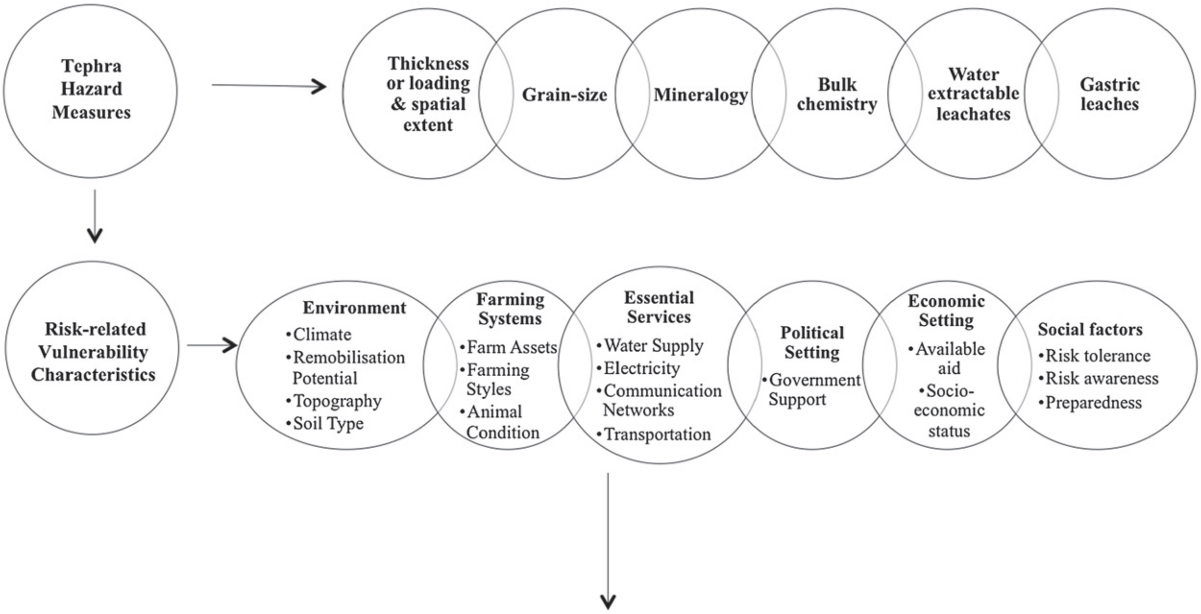
To minimise agricultural losses after an explosive eruption a timely risk assessment is needed to inform emergency response and recovery decision-making (Fig. 1). This typically takes the form of a) assessing the hazard by mapping the extent and thickness of the tephra fall (Pyle, 1989) and chemical analysis of the tephra using a range of methods (Cronin et al., 1998; Wilson et al., 2011a, 2011b) assessing agricultural systems exposed to the tephra fall and their relative vulnerability to impacts; and c) evaluating risk (Wilson and Kaye, 2007; Jenkins et al., 2014). Tephra fall risk assessment for agriculture needs to take into account both tephra deposit properties, including grain size, leachable element content, bulk composition, thickness and loading; and vulnerability characteristics such as the environmental, agricultural, political, social and economic characteristics of the affected region (Cook et al., 1981; Cronin et al., 1998; Wilson et al., 2007, 2011a; Jenkins et al., 2014) (Fig. 1). Impacts are broadly related to the thickness of the tephra deposit (Jenkins et al., 2014; Wilson et al. 2014). However, this relationship may be confounded, for example, by factors such as the leachable element content of the tephra, which is typically related to tephra surface area and thus may be higher in thinner, fine-grained distal deposits (Cronin et al., 1998; Delmelle et al. 2005; Bagnato et al., 2013). Agricultural losses can occur immediately after the tephra fall and can also manifest over weeks, months and even years (Cook et al., 1981; Cronin et al., 2003; Wilson et al., 2011b). Thus, appropriate and timely assessment of tephra fall risk to agriculture can potentially inform strategies to reduce medium to long-term impacts (Wilson, 2009).

A major focus of the tephra fall risk assessment for agriculture (Fig. 1) is a timely and reliable analysis of the tephra to determine its burden of potentially-toxic soluble elements. This is a well-established concern for agriculturalists (Cook et al., 1981; Blong, 1984) and of increasing concern to food safety authorities, such as after the 2010 Eyjafjallajökull tephra fall crisis in Europe (European Food Safety Authority, 2010). However, evidence from eruptions over the past 50 years suggests that toxic effects on livestock following tephra ingestion are relatively rare, and tend to be associated with high levels of soluble F. Evaluation of chemical impacts from tephra fall to agriculture has been hindered by a lack of standardisation of chemical analysis methods, which has limited comparison between events (Ayris et al., 2015). This has been addressed recently by the development by the International Volcanic Health Hazards Network (www.ivhhn.org) of a standardised protocol for characterising leachable element properties of tephra fall (Stewart et al., 2013).

This study focuses on the June 2011 eruption of Cordón Caulle volcano, Chile, which dispersed tephra over approximately 350,000 km^2 (extent of 0.1 mm isopach) with approximately 64,000 km^2 receiving 10 mm tephra fall. The depositional area included productive agricultural land, and the tephra fall resulted in the death of nearly one million livestock (INTA, 2012). Two distinct environments were impacted: a proximal temperate Andean setting, and the semi-arid Argentine steppe farther from the volcano. Local agricultural agencies assessed that the mass livestock deaths were likely mostly due to physical impacts of the tephra (e.g. feed destruction) rather than acute fluorine intoxication, because these levels of F are low in comparison with documented cases of acute fluorosis following other eruptions (INTA, 2012; Craig et al., 2016a). However, subsequent studies report fluorine (F) intoxication in wild deer and some livestock populations in the depositional



	Soil	Vegetation	Animal Health
Physical	Tephra permeability Cementation of tephra Lowering of soil temperature Positive mulching effect	Burial Overloading Photosynthesis prevented	Rumen blockages Feed and water sources unpalatable Starvation Tooth abrasion
Chemical	Soil acidity Low Cation Exchange Capacity Beneficial amounts of elements (i.e., S) Addition of toxic elements	Chemical burns Uptake of elements Root apex damage	Fluorosis Sulphur poisoning Excess selenium Other possible impacts from metals released from soils via acid solubility

Fig. 1. Outline of hazard and risk assessment factors needed to be considered in order to forecast and understand tephra fall impacts to agricultural systems.

area of the eruption, with tephra ingestion asserted as the source (Flueck, 2013, 2014; Flueck and Smith-Flueck, 2013a, 2013b).

The purpose of this study was to better understand the fate and agricultural consequences of leachable elements added to the environment by this large silicic tephra fall. Tephra, soil and surface water samples across the depositional area were collected both immediately after the eruption (tephra and water) and nine months afterwards (tephra, soil and water). Tephra samples were analysed following the new IVHHN hazard assessment protocol.

2. 2011 Cordón Caulle eruption

The Puyehue-Cordón Caulle Volcanic Complex (PCC-VC) is located in the Southern Andes of Chile (40.5°S) (Francis, 1976) (Fig. 2). It comprises a Pleistocene caldera at the northwestern end (Cordillera Nevada), a Holocene stratovolcano (Puyehue, 2236 m), and the Cordón Caulle fissure complex, between these edifices. The most recently active section of the complex is the Cordón Caulle fissure zone, although historic eruptions have often been incorrectly attributed to Puyehue (Singer et al., 2008).

The 2011 rhyolitic eruptive sequence was centred on the Cordón Caulle fissure zone (Schipper et al., 2013). The active sequence started on 27 April 2011 when the Observatorio Volcanológico de los Andes del Sur (OVDAS) detected a swarm of volcano-tectonic earthquakes. These earthquakes increased in magnitude and frequency until 4 June 2011 when the eruption sequence began with a series of Plinian style phases (Schipper et al., 2013).

ONEMI reported that the eruption started at 14:45 LT (18:45 UTC), producing a persistent Plinian eruptive column that reached 10–12 km high (a.s.l.). Dispersal patterns of ash plumes during June and July 2011 indicate that the tephra deposited in three main directions. Tephra from different eruptive pulses was identified in some deposits where changes in grain-size were noticeable during sampling. Tephra fall in Villa La Angostura (45 km from the vent) started at around 15:00 LT and reached Bariloche (100 km from Cordón Caulle) at 16:30 LT. The tephra fall continued for several hours and a continuous collection of this pyroclastic material was carried out. Ongoing eruptions produced sporadic tephra and gas plumes up to 13 km, but they were reduced to a few kilometres by early July and continued until early January 2012 with occasional 5 km-high plumes (OVDAS, 2011).

The eruption deposited tephra east of the volcano (Fig. 2). Cordón Caulle is located ~18 km from the Chile-Argentina border, and most tephra fell in Argentina, over the Neuquén, Río Negro and Chubut provinces, due to the prevailing westerly winds. This study will focus on three of the towns that received tephra deposits: Villa la Angostura, Neuquén, 45 km ESE of the volcano received up to 170 mm of tephra; San Carlos de Bariloche located 100 km SE of the vent received 30–45 mm of coarse tephra and fine lapilli (up to 4 mm diameter); and Ingenerio Jacobacci, an agricultural service town on the steppe 240 km from the volcano, received ~50 mm of tephra (Collini et al., 2012; Pistolesi et al., 2015). The steppe was also affected by prolonged episodes of tephra remobilisation with clouds of fine airborne tephra common.

2.1. Deposit remobilisation

The most significant tephra deposit covered a wide W–E elongated area between 40°–42°S and up to 72°W. This area is characterised by a very strong precipitation gradient, ranging from 4000 mm/year in the Andes, with a wet season during the winter, to 200 mm/year in the Patagonian steppe, where the scarce rainfall is distributed almost homogeneously throughout the year. This characteristic gradient defines diverse sedimentary environments that explain the significantly different depositional and post-depositional processes that occurred since the beginning of the eruption on June 4.

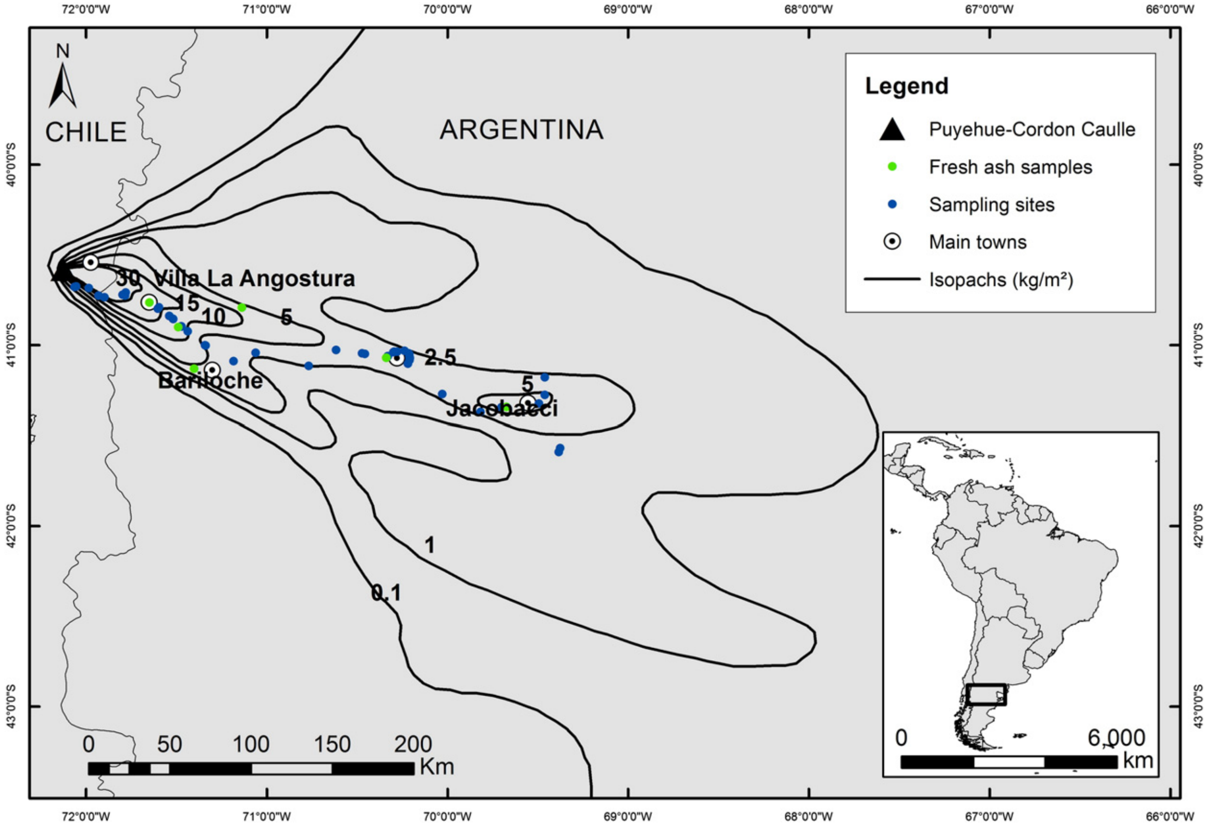


Fig. 2. Map of the 2011 tephra fall from Cordon Caulle (isopachs in mm; Collini et al., 2012), showing main towns visited, and sites where tephra and/or soil samples were taken, relative to the PCC-VC location.

In the mountainous environment (proximal areas), the tephra deposit was affected by rain and snow starting on June 8, therefore the deposits suffered compaction and fluvial remobilization of fine tephra and low-density pumice fractions, including lapilli and larger pumice fragments. This material was transported by rivers down to the lower basin, where thick floating deposits covered many rivers, lakes and even the distal portion of the Alicura Dam, >100 km away from the volcano.

In contrast, in extra-Andean arid environments, the persistent strong winds affected tephra deposition and produced important resuspension and remobilization within hours after or even during the fallout events. Ground level remobilization of coarse tephra and even fine lapilli (3–4 mm) during fallout was witnessed during sampling. Topography and vegetation played a strong control on depositional and post-depositional processes, with the presence of thickened deposits at wind protected areas evident even in the first week of the eruption. Conversely, diminished thicknesses on plateaus and open flats exposed to strong winds (such as Comallo and Jacobacci), were observed. It is clear that in the steppe the vegetation played an important role in protecting areas allowing the accumulation of tephra behind shrubs (Fig. 5), whereas erosion and formation of wind ripples were active processes in non-vegetated sectors.

3. Study area

Two distinct agricultural regions were studied. The first is the Nahuel Huapi National Park, ~40 km from the vent, where up to 300 mm of tephra was deposited. The second site is the Jacobacci steppe region, 80–220 km from the volcano, where ~50 mm of tephra was deposited (Fig. 2). Over 90% of the farming in both areas is small family owned farms, many of which are barely above subsistence level (INTA Bariloche, 2012). These two areas have contrasting environments, climates and farming styles. The Nahuel Huapi National Park is a temperate, highland climatic area, that receives between 800 and 4000 mm of precipitation per annum (Craig et al., 2016b) (Fig. 3a & b). The farming system in the area is unique due to its national park status. Farmers are allocated a quota limit of cattle, horses and goats that can be grazed over an allotted parcel of land (up to 100 ha) (Veblen and Mermoz, 1992). In contrast, the Jacobacci region (Fig. 3c & d) is situated on the semi-arid steppe and receives <200 mm precipitation per annum. In the six years prior to the tephra fall, rainfall levels were lower than this (~160 mm/year) leading to drought conditions (Departamento Provincial de Aguas, 2011). Between 200,000–300,000 sheep and ~60,000 goats are farmed around Jacobacci, the Comallo Valley and the surrounding steppe area (INTA Bariloche, 2012). Prior to the drought, the most productive grazing land was in lowland valleys (mallines), where soil moisture is the highest. Grazing also takes place on the surrounding slopes, but at a much lower stocking rate (1–2 animals per hectare, compared with 5–6 animals/ha in the valley floor areas) (J. Escobar, pers. comm. 5 March 2012).

The soil and tephra sampling undertaken for this study followed a roughly west-east transect along the main axis of the tephra fall lobe, traversing the two study areas (Fig. 2). The orographic conditions create a strong precipitation gradient from >2000 mm/yr on the western coast of Chile, to ~200 mm/yr on the eastern Argentina coast (Fig. 4) (Paruelo et al., 1998; Aravena and Luckman, 2009; Garreaud et al., 2013). The dominant soil types reflect the climates, and range from west to east through lithosols, andisols, cambisols, fluvisols, and yermisols (FAO, 1997 classifications) (Table 1 & Fig. 4).

Fig. 3. Images of the two main agricultural areas located within the study area: A) the Nahuel Huapi National Park area, B) The lapilli-dominated 2011 tephra fall deposit in this area; C) the Jacobacci/Comallo region, D) and the 2011 tephra deposit of the area.

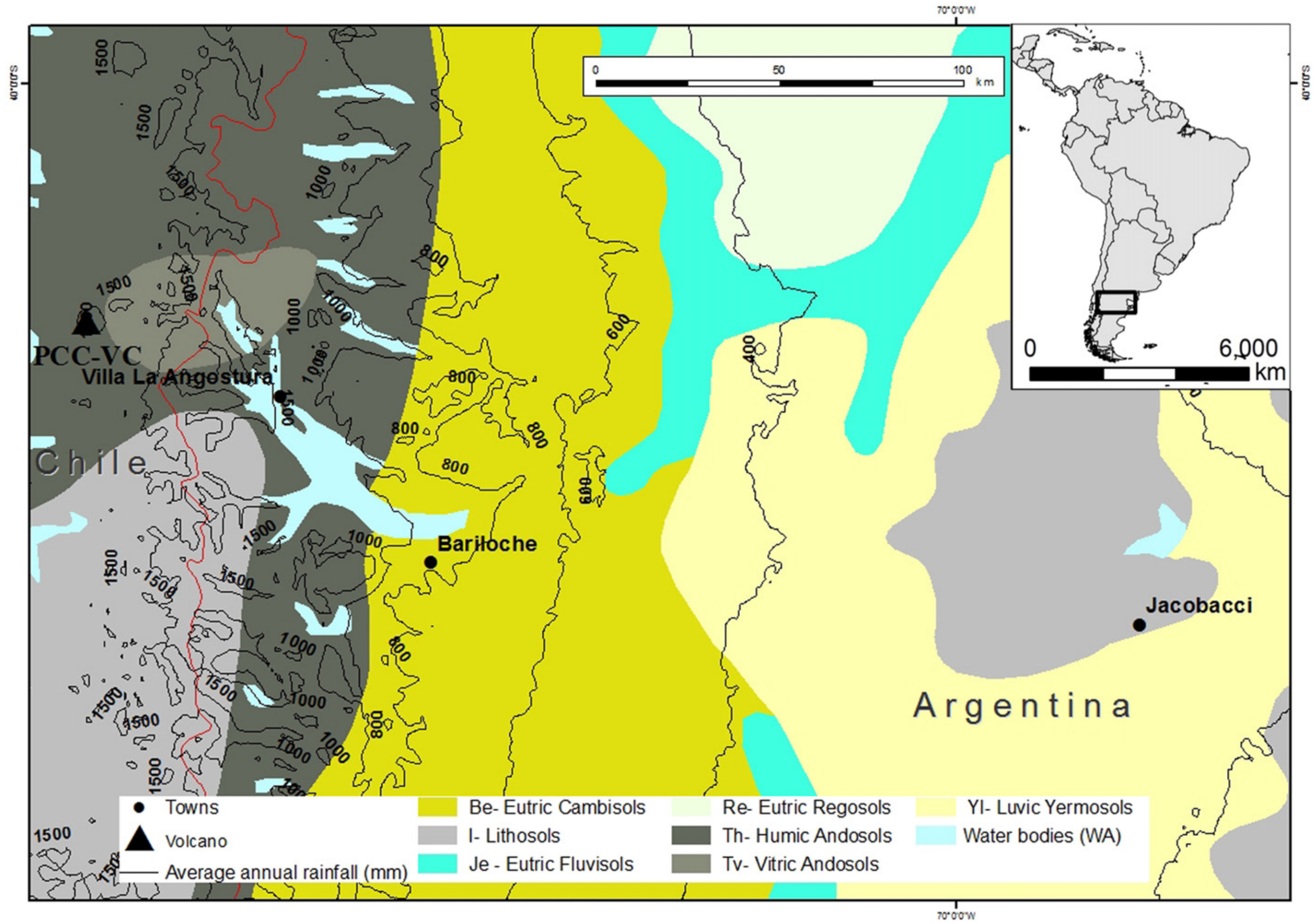


Fig. 4. Map of main soil types and rainfall isopleths for the study area.
Adapted from FAO (1997) classifications.

The productivity of the land in the tephra deposition zone decreases eastwards. The rainfall particularly restricts the type of farming. The temperate Andean zone has the capacity for high-intensity pastoral farming and horticulture, whereas, in the absence of irrigation, farms in the semi-arid steppe are mostly suited to relatively low intensity, sheep and goat farming.

The Instituto Nacional de Technología Agropecuaria (INTA) estimated that more than a million livestock died due to tephra fall impacts in the months after the 2011 Cordón Caulle eruption (INTA, 2012). In the Jacobacci steppe region, 40–60% of animals perished, while only 20–25% animals died in the temperate Nahuel Huapi National Park (Craig et al., 2016a). The high losses in the arid area may have been exacerbated by pre-existing stresses on livestock due to drought conditions (Departmento Provincial de Aguas, 2014). A further consequence of the drought and the fine grain size of the tephra was a prolonged exposure to wind-remobilised tephra, contaminating feed and slowing vegetation recovery (Folch et al., 2014; Elissondo et al., 2015). In the Nahuel Huapi National Park, despite greater thicknesses of tephra, the dispersed and free-ranging livestock could seek alternative forage including low trees and shrubs that were not buried. Further, rain could rapidly wash down vegetation and stabilise tephra from wind erosion (Wilson et al., 2012).

Table 1
Soil types found the area affected by the 2011 Cordón Caulle tephra fall events (FAO, 1997).

Soil type	Description
Lithosols	Shallow recent, weakly weathered soils with no horizons visible normally on steep slopes.
Andisols	Weathered tephra deposits, dark coloured, well drained, highly versatile, fertile soils.
Cambisols	Recent soils on alluvial, colluvial, and aeolian material, weak soil horizons, productive soils.
Fluvisols	Recent soils composed of young alluvial deposits, high natural fertility.
Yermisols	Semi-arid to arid environment soils, low organic matter, prone to cementation and salinization

4. Methods

4.1. Tephra and soil sampling

Soon after the initial 2011 eruption, a series of tephra samples were collected between 4 and 26 June 2011 along the axis of the tephra deposit (Fig. 2). Eight of these samples, with little or no rainfall leaching or other environmental modifications, were sent to the University of Canterbury (Christchurch, New Zealand) for analysis (2011 tephra samples; Supplementary Table 2). All samples were imported in accordance with the requirements of the Biosecurity Act 1993. In February–March 2012, soil and tephra samples were collected along the length of the tephra plume over a 220 km transect (Fig. 2; Supplementary Table 2). Soils were sampled from active farm land or forestry sites. At each site, four topsoil samples (150–200 mm depth), below the tephra were collected within a 1 m^2 grid and combined. If the tephra deposit had been cultivated into the upper soil horizon, the combined topsoil material was collected to represent the active growth medium. Samples of approximately 500 g were taken using a stainless steel hand trowel as

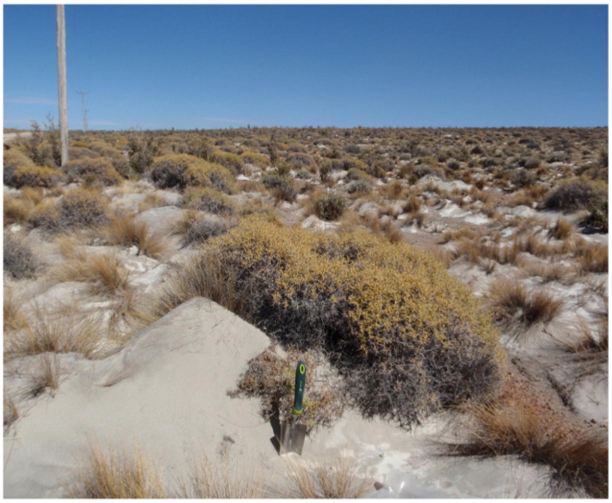


Fig. 5. Wind-remobilised tephra forming dune structures in the Jacobacci area, viewed in March 2012 (hand trowel, 25 cm long for scale).

an auger, combined and placed in clean, labelled polyethylene bags. Vegetation cover, agricultural system and any evidence of irrigation, cultivation and other modifications were noted. Samples were air dried and transported to New Zealand, where further oven drying to constant weight was completed.

Tephra samples were collected at the same locations as the soil samples using a similar grid pattern system. Samples were collected from undisturbed sites using stainless steel cutting tools, taking care to get a total cross-section of the sample but avoiding the tephra/soil interface. Samples were air-dried and transported in clean, labelled polyethylene bags. Care was taken to keep disturbance of soil and tephra samples to a minimum and preserve internal structures. Reworked tephra samples were identified by the presence of dune structures and cross-bedded internal structure, whereas undisturbed fall deposits were characterised by flat-lying bedding that draped over the topography (Fig. 5).

4.2. Soil fertility analysis

Standard soil fertility analyses (pH, Cation Exchange Capacity (CEC) and nutrient concentrations) were undertaken at R.J. Hill Laboratories Ltd. (Hamilton, New Zealand). Soil pH was measured using a slurry with a ratio of 1:2 soil:water and potentiometric pH determination (Blakemore et al., 1987). The elements K, Ca, Mg and Na were measured using ammonium acetate extraction (1.0 M, pH 7, 1:20 soil:extractant ratio, 30 min contact time) with detection by ICP-OES (Inductively Coupled Plasma — Atomic Emission Spectroscopy) (Metson, 1971). Cation Exchange Capacity (CEC) was calculated using the sum of extractable cations and the extractable acidity of the samples (Hesse, 1971).

4.3. Tephra analyses

Tephra analyses were undertaken in accordance with the protocol developed for characterising leachable elements in volcanic tephra fall (Stewart et al., 2013). Samples were all finer than 2 mm so an initial sieving step was not necessary. A Saturn DigiSizer II Laser Sizer was used to determine grain size distribution of each sample. The next step was to undertake water and gastric leaches of each bulk tephra sample.

4.3.1. Water-extractable element determinations

Tephra samples were leached with Milli-Q grade deionised water (>18 MΩ) at a ratio of 1:20 (g tephra:mL extractant) for 1 h, on an end-over-end shaker. Each solution was centrifuged at 2000 rpm for 5 min then filtered through a 0.2 μm cellulose filter. Two further repeated leaching steps were carried out on some samples, each time using fresh deionised water and applying the same methods. This was done to determine the efficiency of a single leach (Cronin et al., 2014).

4.3.2. Simulated gastric leach

Seven of the eight tephra samples collected in June 2011 were extracted using a simulated gastric leach (0.032 M HCl, adjusted to pH 1.5, at ratios of 1:100 g tephra:mL extractant), as per Stewart et al. (2013). Samples were extracted for 1 h on an end-over-end mixer, centrifuged, filtered then analysed for F using the ion selective electrode (ISE) method at Massey University (Palmerston North, New Zealand).

4.3.3. Total recoverable metals determination

Total recoverable metals were determined using a modification of the Environmental Protection Agency method 200.8 (EPA, 1994). One gram of each of the 2011 and 2012 samples was digested with 4 mL 50% HNO_3 and 10 mL 20% HCl at 95 °C for 30 min. The samples were

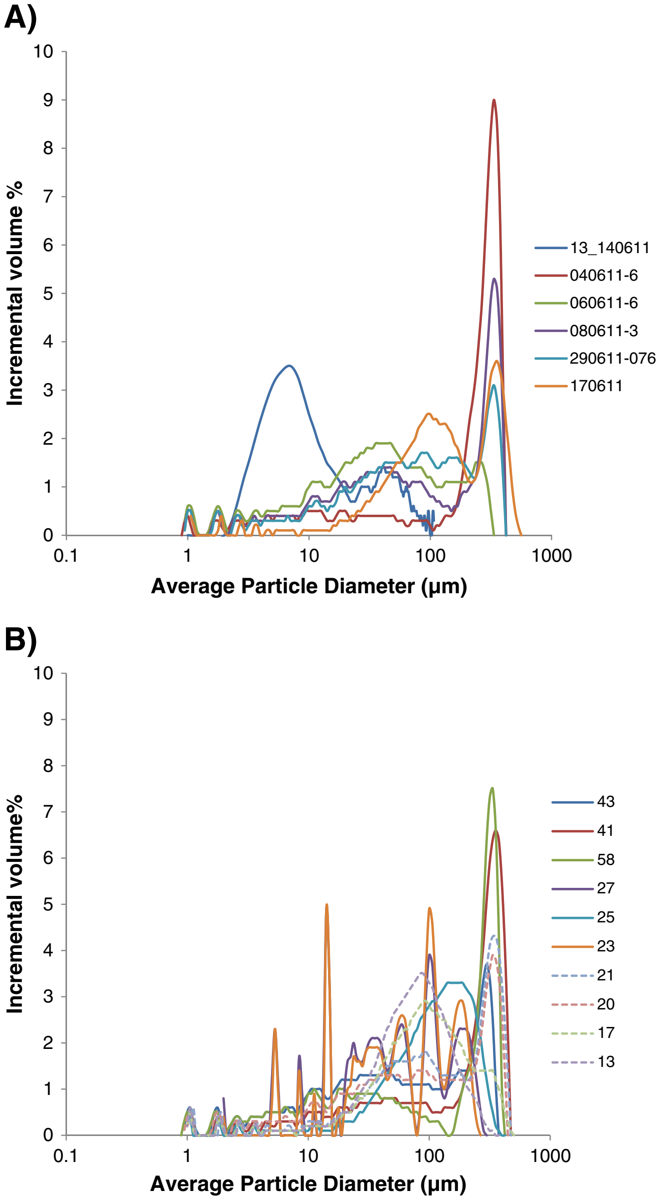


Fig. 6. Grain size distribution of 2011 (A) and 2012 (B) tephra samples used for leachate studies. See Supplementary Table 2 for detail about sample locations.

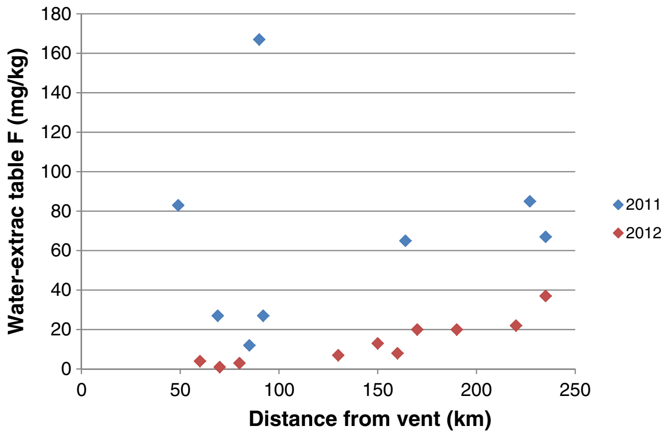


Fig. 7. Water-extractable F in Cordón Caulle tephra sampled in 2011 and 2012 (1:20 digests).

cooled, made up to 20 mL with Milli-Q grade water and filtered through a 0.2 μm nitrocellulose filter before being diluted with 2% HNO_3 for analysis.

4.3.4. Inductively coupled mass spectrometry (ICP-MS & ICP-OES) analysis

Tephra water leachates and total recoverable solutions were analysed for trace metals using ICP-MS (Agilent 7500 Series) for Al, As, Co, Cr, Cu, Pb and Zn at the University of Canterbury (Christchurch, New Zealand), and ICP-OES (Varian 720) for Ca, Fe, K, Mg, Mn, and Na at Lincoln University (Christchurch, New Zealand). Ion chromatography (Dionex ICS-2100) was used to determine Cl, F and S (reported as SO_4^{2-}) (University of Canterbury and Hill Laboratories Ltd., Hamilton, New Zealand).

Procedural blanks for all samples and the inclusion of a soil standard reference material (SRM2710, Montana Soil; National Institute of Standards and Technology) for total recoverable metal determinations were used as quality control measures. The average relative percent difference between duplicate leachate samples was <23% for all elements, with the majority below 10%. The average relative percent differences for duplicate digest samples were all <16%. Detection limits for analysis of water-extractable elements by ICP-MS were (on a dry weight basis): 0.01 mg/kg for As and 0.1 mg/kg for Co, Cu, Mn, Ni, Pb, and Zn. The detection limits for ICP-MS analysis of total digests were: 0.042 mg/kg for As, and 0.42 mg/kg for Co, Cu, Mn, Ni, Pb, and Zn. The ICP-OES detection limits (for water leachates and total digests) were: 5 mg/kg for Ca, Mg, Na, K, Al, and Fe.

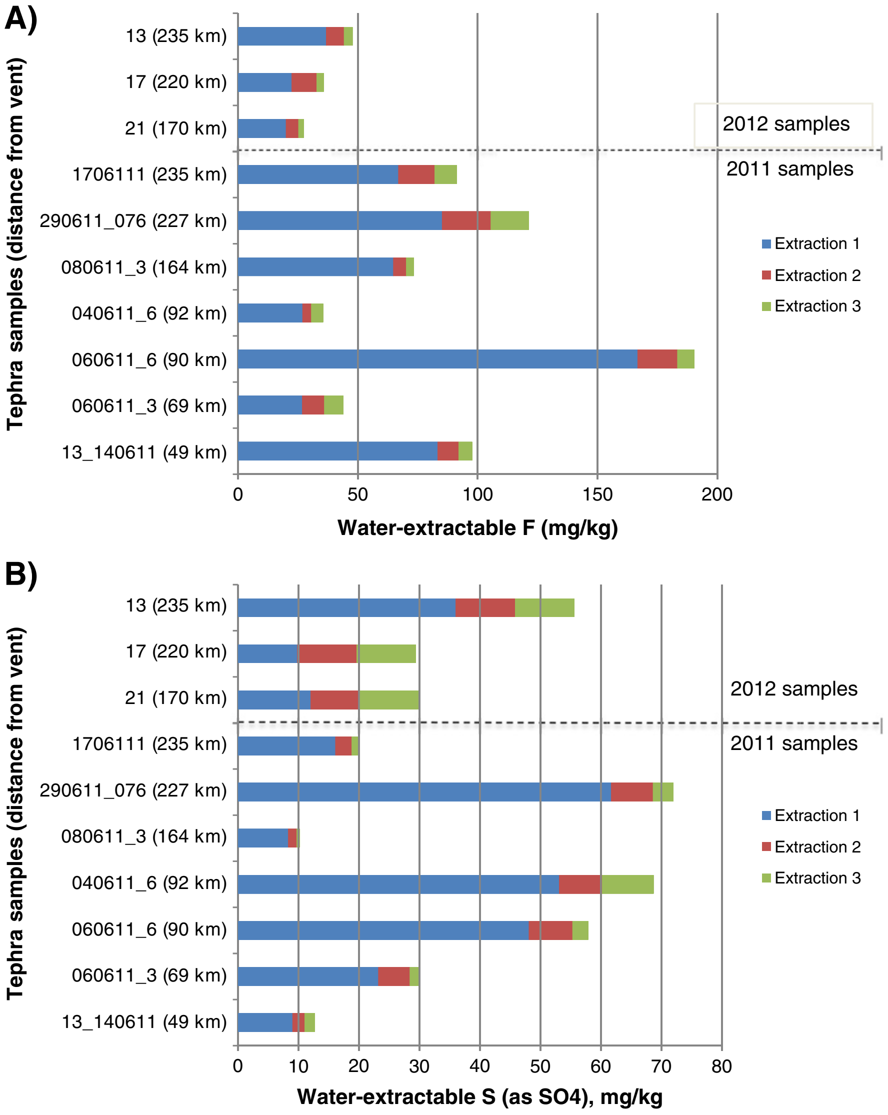


Fig. 8. A) F concentrations for sequential 1:20 water extractions of 2011 tephra samples and 2012 epiclastic samples. B) SO_4 concentrations for sequential 1:20 water extractions of 2011 tephra samples and 2012 epiclastic samples.

To test for relationships between concentrations of leachable elements in water and total digests of both 2011 and 2012 tephra samples, and distance from vent, loading and median grainsize, correlation coefficients were obtained (Supplementary Table 3). *t*-Testing was used to test for differences between the 2011 and 2012 data sets for water-extractable major element concentrations (Supplementary Table 4).

4.4. Surface water sampling and analysis

Streams in the tephra fall area of the June 2011 eruption were sampled at various intervals after the eruption. Samples were collected by G. Villarosa and V. Outes between 6 and 30 June 2011 and by C. Stewart between 1 and 14 March 2012. Determinations of pH and conductivity were made in the field using a portable meter (Oakton TESTR 35) from Eutech Instruments. Fluoride (F) was determined directly by an ion-selective electrode, with a detection limit of 0.05 mg/L. Chloride and sulphate were determined directly by ion chromatography, with detection limits of 0.5 mg/L. Dissolved metals were analysed by ICP-MS at Hill Laboratories (Hamilton, New Zealand) on filtered (to 0.45 μm) samples, with detection limits as follows: As (0.001 mg/L), Al (0.003 mg/L), Cu (0.0005 mg/L, Fe (0.02 mg/L), Mn (0.0005 mg/L) and Pb (0.0001 mg/L). Total metals were determined on unfiltered samples following a nitric acid digestion (APHA Method 3030, modified) with the detection limits as follows: As (0.0011 mg/L), Al (0.0032 mg/L), Cu (0.00053 mg/L), Fe (0.021 mg/L), Mn (0.00053 mg/L) and Pb (0.00011 mg/L). See Supplementary Tables 5 and 6 for a complete set of surface water data.

5. Results & discussion

5.1. Grain size characteristics

Grain size data for tephra samples used in the leachate studies are presented in Fig. 6a and Table 3 (2011 samples) and Fig. 6b and Table 4 (2012 samples). The 2012 tephras were not sampled at exactly the same locations as the 2011 tephras, as this was not possible, but both sets of samples span similar parts of the depositional area (Fig. 2). The grainsize distribution of the 2011 deposits with respect to distance from the vent does not follow a simple fining trend (Table 3). The eruption was complex, fed by multiple magma bodies and included multiple eruptive phases with variations in eruption flux (Alloway et al., 2015; Pistolesi et al., 2015). Also, variable meteorological conditions affected the ash column and ash cloud at different altitudes and on different days. Thus, the physical characteristics of the fall deposits were likely to have been variable and highly heterogeneous. We also note that samples were also taken at varying distances off the plume axis, and at varying lengths of time after the eruption. Further notes on sample grainsize in relation to eruption phase are provided in Supplementary Material 7. Very coarse lapilli deposits proximal to the vent were not sampled as agricultural activity was absent at these sites. More complete grain size characterisation of the 2011 Cordón Caulle tephra deposit has been reported by Daga et al. (2014) and Bonadonna et al. (2015).

A fining trend with increasing distance from the vent is also absent in the 2012 samples (Table 4), but this is not unexpected given the potential for deposit disturbance by wind and water in the intervening period. Wind-remobilised deposits (dashed lines in Fig. 6b) were found almost exclusively in the dry, windy semi-arid steppe region, including the Jacobacci area (Figs. 2 & 4) where up to 800 mm-high dunes formed (Fig. 5). The grain size distribution of the reworked deposits was not observably different to the undisturbed 2012 deposits (Fig. 6b). In comparison to other events for which remobilised tephras have been sampled, the Cordón Caulle 2012 reworked deposits are much finer than remobilised deposits sampled after the 2010 Eyjafjallajökull eruption (Arnalds et al., 2013), and slightly finer than remobilised deposits sampled in 2008 from the 1991 Hudson eruption (Wilson et al., 2011b).

5.2. Tephra surface composition

5.2.1. Water-extractable elements in June 2011 Cordón Caulle tephra samples

In general, levels of all water-extractable elements of the 2011 Cordón Caulle tephra are low to very low compared to global medians (Table 3; Ayris and Delmelle, 2012). Concentrations are broadly similar to those recorded for the 2008 eruption of the Chaitén volcano, Chile, which was also rhyolitic (Durant et al., 2012). Readily-soluble surface elements (in order of decreasing median abundance) include Cl, Na, F, Ca, SO_4 and Mg. The most abundant component by mass (Cl) is a factor of ~7 lower than the global median. The Cordón Caulle tephra also had an extremely low level of water-extractable sulphur (median of 20 mg/kg SO_4, cf. global median of 4986 mg/kg SO_4. Thus this tephra had low S fertilisation potential, compared to other eruptions such as the 1995–1996 tephra falls of Mt. Ruapehu which boosted pasture

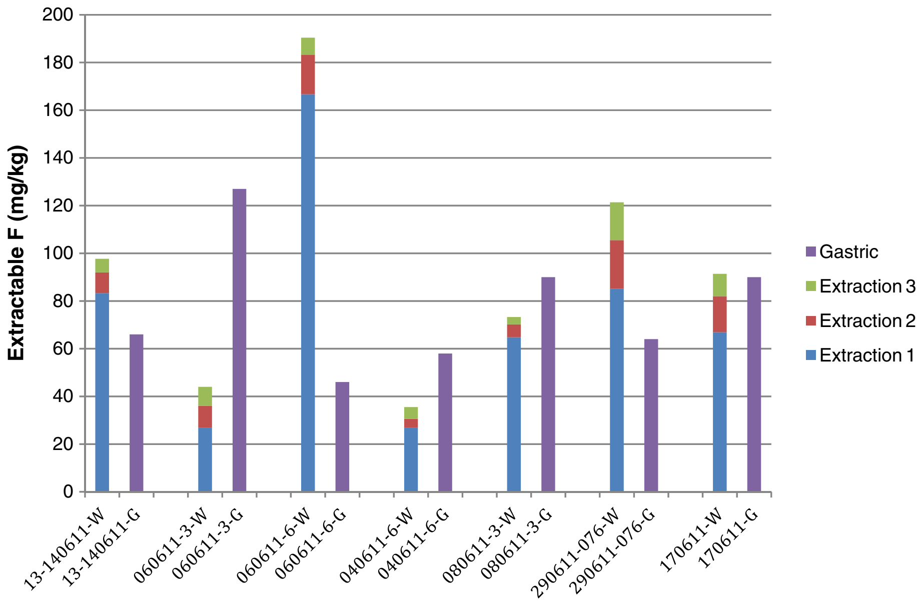


Fig. 9. Extractable F concentrations in 2011 tephra samples extracted with simulated gastric fluid (0.032 M HCl, pH 1.5) compared to sequential extractions with deionised water.

production via available S (3436–10,016 mg/kg SO_4-S; Cronin et al., 1997; Cronin et al., 1998). A possible limitation of our dataset is that tephra samples were not collected immediately after deposition, rather in the hours following various tephra fall events. This could have led to an underestimation of leachable element concentrations, for example if initial tephra fall was enriched with material from the Cordón Caulle geothermal system (Cronin et al., 2003; Sepúlveda et al., 2004). However in the absence of further information we assume that these data are representative.

Available F (as fluoride) poses the greatest toxic risk to livestock from tephra ingestion (Oskarsson, 1980; Cronin et al., 2003). Although the Cordón Caulle 2011 tephra has a low overall cargo of leachable elements, the median concentration of soluble F was 66 mg/kg (range 12–167 mg/kg, $n = 8$), half of the global median value of 129 mg/kg (Table 3). In comparison, Alloway et al. (2015) report water-extractable F data for the same event using the same methodology. For 24 tephra samples collected at a wide range of locations across the depositional area, water-extractable F ranged from 3.6 to 97 mg/kg, median concentration 23 mg/kg and mean concentration 36 mg/kg. The lower range of concentrations reported by Alloway et al. (2015) may be due to the inclusion of coarse-grained samples, which were associated with lower F concentrations.

No relationships between levels of water-extractable elements were found when compared with distance from the vent, tephra loading or grain size, other than a weak negative relationship ($r = -0.658$, $p < 0.10$) between F and median grainsize (Supplementary Table 3a). This may be due to the tephra deposit sample being composed of numerous individual tephra fall events (Bonadonna et al., 2015; Pistolesi et al., 2015).

5.2.2. Water-extractable elements in March 2012 tephra samples

Compared to the 2011 samples, water-extractable Na, Cl and F were lower overall in 2012-sampled tephra (Supplementary Table 4). Differences became more pronounced if a suspected outlier (Site 21, thought to have been subjected to fertiliser application) was omitted from the comparison. No difference was found between 2011 and 2012 data sets for Ca, Mg or SO_4. Trends with distance for water-extractable F are shown in Fig. 7 for both the 2011 and 2012 samples. F levels are highly variable (12–167 mg/kg) in the 2011 samples, collected in the hours to days following the 4 June 2011 eruption, with no systematic trend with distance. For the 2012 samples, the range of values is lower (1–37 mg/kg) with the highest levels (20–37 mg/kg) recorded in the samples collected in the semi-arid zone. Trends of increasing water-extractable content with increasing distance were found for F ($r_s = 0.933$, highly significant), Ca ($r_s = 0.812$, significant) and Na ($r_s = 0.750$, weakly significant) (Supplementary Table 3b). This suggests a difference in extent of leaching between temperate zone and semi-arid zone samples.

The 2012 tephra samples beyond 170 km from the vent were all reworked. We were particularly interested in assessing the reworked tephras to determine the residual hazard for agricultural systems. Our results suggest that leaching may be incomplete in the semi-arid zone. If leachable elements are 'conserved' in arid and semi-arid climates, this may prolong the hazard to grazing livestock.

5.2.3. Re-extractions

Previous work suggests that single water leaching experiments may underestimate the environmental availability of agriculturally-important elements such as fluoride and sulphur in some tephra (Cronin et al., 1998; Cronin et al., 2003; Cronin et al., 2014). In the case of F, this is particularly the case for tephra generated by phreatomagmatic eruptions through vent-hosted hydrothermal systems which may contain F in slowly-soluble compounds such as CaF_2 and AlF_3. If F is held in highly-soluble forms such as NaF, then sequential leaching is unlikely to show additional extraction. However, other forms of F in Al-Ca- and Si-F hydroxides, salts and complexes on particle surfaces and in aerosols mean that sequential leaches provide a more complete assessment of the potential of the tephra to release F into the environment (Stewart et al., 2013). Re-extractions may also be important for the agronomically-important element S, as very high concentrations may lead to saturation effects occurring in a single leach, particularly at the ratio of 1:20.

Three sequential leaches were carried out on the 2011 and 2012 tephra samples where sample quantities permitted (Fig. 8a & b). For F, only minor to moderate additional quantities are extracted by sequential water leaches, consistent with F being held in soluble forms such as NaF and $CaSiF_6$ (Cronin et al., 2000; Cronin et al., 2003). For S, there was a difference between the 2011 samples, where only minor additional quantities were extracted by further leaches and the reworked 2012 samples, where more substantial quantities were extracted by further leaches.

5.2.4. Gastric leach

The gastric leach estimates ingestion hazards from leachable elements in fresh tephra by leaching tephra with a simulated gastric fluid (SGF) solution that mimics conditions in the gastrointestinal tract. Results of gastric leaches performed on the 2011 tephra samples are shown in Fig. 9 for fluoride, with the sequential water leach data for the same samples shown alongside for comparison. In general, the SGF-extractable concentrations were not systematically higher than the water-extractable concentrations, and the mean of the SGF-leached samples (77 mg/kg) is lower than the mean of the sequentially water-leached samples (93 mg/kg). This implies that F is mostly present in readily soluble forms. This result is in contrast to other studies (e.g. Cronin et al., 2014; Stewart et al., 2014) where SGF-extractable F is consistently higher than water-extractable F, by factors of ~3–5.

5.2.5. Total recoverable metals (TRMs)

TRM concentrations indicate the maximum possible cumulative inputs of elements released by long-term weathering of tephra deposits (Cronin et al., 1997; Ruggieri et al., 2011). TRM concentrations in the 2011 and 2012 tephra samples are elevated by approximately two to three of orders of magnitude compared to water-extractable elements (Tables 5 & 6), thus, only ~0.1–1% of the TRMs are water-extractable.

Table 2
Soil fertility measures pre- and post- eruption compared to ideal agricultural values.

	Ideal agricultural concentrations[a]	Range in soil samples 9 months after eruption		Pre-eruption published values[b]	
		Temperate	Semi-arid	Temperate	Semi-arid
Olsen P (mg/kg)	50–100	2–8	4–17	2–6	16.8–28.2
K (me/100 g)	0.5–0.8	0.15–0.47	0.17–4.41	0.26–0.54	–
Ca (me/100 g)	6–12	2.2–8.3	1.9–37.2	5.76–8.7	–
Mg (me/100 g)	1–3	0.32–1.96	0.27–11.76	0.43–0.63	–
Na (me/100 g)	0.2–0.5	0.17–0.43	0.42–14.11	–	–
CEC (me/100 g)	25–40	5–28	3–65	10–30	25.2–35.5

[a] Horta & Torrent (2007); Blakemore et al. (1987).

[b] Aruani and Sánchez (2003); Peinemann et al. (1987); Buschiazzo et al. (2009); Mussini et al. (1984).

For comparison, a suite of TRMs are reported for tephra from the 1995 eruption of Mt. Ruapehu (Cronin et al., 1997), as this study used similar methods to those used here and TRMs are not compiled in the Ayris and Delmelle (2012) review. It may be seen that concentrations of TRMs are generally lower than for the Ruapehu 1995 tephra which was of andesitic composition. Calcium, Na, and Al concentrations in the Cordón Caulle tephra samples were all around one order of magnitude lower than those from the Ruapehu tephra fall, whereas Fe levels were similar. Potassium levels were lower than the Ruapehu samples (Cronin et al., 1997; Table 5).

When comparing the recoverable element concentrations and the deposit characteristics that are typically used in risk assessments as measures of hazard intensity, there is a significant correlation between 2011 TRM concentrations and median deposit grain size for Ca ($r_s = 0.810$), Mg ($r_s = 0.810$), Co ($r_s = 0.810$), and Cu ($r_s = 0.810$). However, the remaining elements show no correlation with distance from the vent, grain size or tephra loading (Supplementary Table 3c). Few correlations were identified when comparing the TRM concentrations for the 2012 samples with distance from vent, grainsize or loading.

5.3. Soil fertility

Soil sampling was undertaken to investigate whether leachable elements released by fresh tephra fall, and subsequent wind remobilised tephras, had a discernible effect on soil fertility. During soil sampling in 2012, little natural or mechanical mixing had occurred between the soil and tephra fall in the semi-arid area. Mechanical cultivation was also rare in the temperate zone; however, the slopes and rainfall had resulted in greater incorporation of the tephra deposit into the upper soil horizon.

The 2012 soil data were compared to pre-eruption data in nearby (but not identical) sites (Table 2). In Nahuel Huapi National Park pre-event soils had low CEC but supported forestry and small-scale pastoral farming (Table 2). The Jacobacci steppe region soils had high CEC and major nutrient contents (P, K, Na, Ca), as would be expected for alkaline soils. Low rainfall permitted only low intensity pastoral farming with some horticulture where irrigation is available.

Tephra leachates may cause an increase in acidity in soil, with some studies showing up to 9 months of pH depression following tephra fall (Cronin et al., 1997, 1998). In these cases, no difference was seen between the two sampling periods (Fig. 10). Pre- and post-eruption, soil pH was a function of the climatic zone (observed pre-eruption by Cremona et al., 2011). Temperate zone soils are typically acidic, due to higher rainfall depleting exchangeable base cations (primarily Ca^{2+}, Mg^{2+}, Na^+ and K^+), coupled with decaying plant matter contributing organic acids (McLaren and Cameron, 1996). Semi-arid soils are typically neutral to alkaline because of the higher proportion of ion-exchange sites occupied by base cations, which also confers buffering capacity (Ugolini and Dahlgren, 2002) (Fig. 10). The fresh 2011 tephra leachates were only slightly acidic (pH 6.0–7.0, Table 3), thus the acidifying influence of the tephra deposit was likely negligible.

Tephra usually has low CEC values due to the lack of organic and clay matter (Fiantis et al., 2011; Fiantis et al., 2010; Shoji et al., 1993). According to pre-eruption data (Mussini et al., 1984; Peinemann et al., 1987; Aruani and Sánchez, 2003; Buschiazzo et al., 2009), soils in the study area exhibit a gradient in CEC, with temperate zone soils having a low-to-medium CEC content (10–30 me/100 g) and semi-arid soils showing a high CEC content (25–36 me/100 g) (Table 2). The 2012 temperate soil samples have a slightly lower CEC range than the pre-eruption published range. This is likely due to the inclusion of lower CEC forestry soils in this study (c.f., White and Hodgson, 1999). Post-eruption CEC values in the semi-arid area show a wide range of values (3–65 me/100 g; Table 2, Fig. 11) mainly reflecting whether tephra was cultivated into the soil (high CEC values), or not. The arrows in Fig. 8 indicate farms where evidence of cultivation was recorded, it is also likely that fertilisers were applied to the soil in these areas, suggested by the spike in Ca. Another feature of the semi-arid zone CEC data is the rapid drop at 220 km from the vent where extremely high on-going wind erosion has led to long-term degradation of soil fertility (Larney et al., 1998). Additionally, the soil was also recorded as sandy in texture which also leads to low CEC values (McLaren and Cameron, 1996).

Our results show that there was no observable change in soil fertility parameters from the 2011 Cordón Caulle tephra deposition nine months after the initial eruption. At all sites, we observed that little natural mixing occurred between the tephra and the underlying soil. Any beneficial effect of the tephra will likely have been mulching effects, such as occurred in eastern Washington State, USA, following the Mt. St Helens tephra fall in 1980 (Cook et al., 1981). However, we also speculate that the tephra deposit may have enhanced surface runoff, following small lahars produced around Villa La Angostura and west of Jaccobaci in 2011–12 following heavy rainfall. These observations suggest that mechanical cultivation of the tephra deposit into the upper soil horizon was probably the best option to stabilise the tephra deposit and speed soil recovery, as long as care is taken to avoid accelerated wind erosion of the soil.

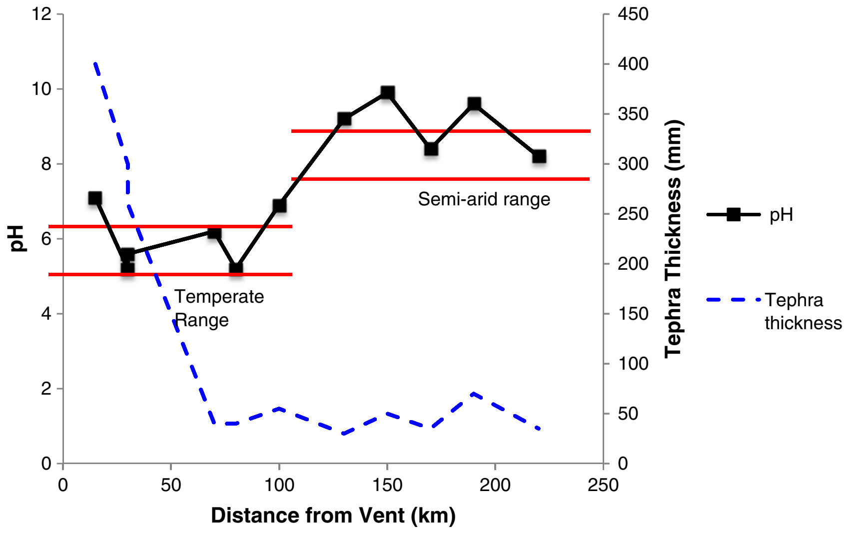


Fig. 10. Soil pH and tephra thickness values across the sampling transect with distance from vent. Normal ranges from McLaren and Cameron (1996).

Table 3
Sample properties and leachable element concentrations for Cordón Caulle 2011 tephra samples (1:20 water leaches).

Sample ID	13_140611	060,611–3	1	060,611–6	040,611–6	080,611–3	290,611–076	170,611	Cordón Caulle median	Global median[a]	Chaitén average[b]
Sample collection date	14/06/11	6/06/11	5/06/11	6/06/11	4/06/11	8/06/11	26/06/11	17/06/11			
Distance from vent (km)	49	69	85	90	92	164	227	235			
Conductivity (μS/cm)	295	248	NA	471	258	177	414	219			
pH	6.1	6.2	6.1	6.6	6	6.5	6.8	7			
Median grain size (μm)	71.8	76.2	173.7	37.1	270.5	73.6	77.2	124.8			
Major components (mg/kg)											
Al	13.0	<5	<5	34.0	<5	<5	<5	<5	<5	58.0	1.9
Ca	34	46	33	88	75	16	165	59	53	2140	76
Fe	<5	<5	<5	<5	<5	<5	<5	<5	<5	21	0.4
Mg	<5	8	6	9	15	<5	31	6	7	335	11
Na	142	79	55	189	100	96	125	70	98	378	56
K	<5	<5	<5	5	8	<5	8	<5	<5	71	19
SO_4	<10	23	<10	48	53	<10	62	16	20	1662 (as S)	34
Cl	83	174	154	378	193	130	333	142	164	1162	208
F	83	27	12	167	27	65	85	67	66	129	14
Minor components (mg/kg)											
As	<0.01	<0.01	<0.01	<0.01	0.02	<0.01	0.02	<0.01	<0.01	0.13	0.3
Co	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.19	0.002
Cu	0.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	5	0.03
Mn	0.2	0.9	0.9	2.2	0.3	0.5	0.2	0.8	0.7	20	1.5
Ni	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.5	0.01
Pb	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.11	<0.0002
Zn	0.3	0.2	0.1	0.3	2.4	0.5	0.1	0.4	0.3	3.6	0.2

[a] From Ayris and Delmelle (2012).
[b] Recalculated from Durant et al. (2012).

5.4. Surface water composition

Release of readily-soluble elements from freshly-fallen tephra may lead to concentration increases in surface waters. Changes in water composition for a particular water body depend on the thickness of tephra fall and its 'soluble cargo', the area of the catchment and volume available for dilution, and the pre-existing composition of the water body. Compositional changes in lakes and reservoirs are generally not discernible due to the large volume available for dilution. Changes in streams and rivers have been reported but are typically short-lived.

Due to public concerns about tephra fall from the Cordón Caulle eruption contaminating water supplies, health authorities in the area carried out an extensive programme of surface water sampling in relation to regulatory standards for drinking-water in the weeks and months following the eruption. However, compositional changes could not be determined as most constituents remained below regulatory thresholds and was not reported (Wilson et al., 2012). The most problematic effect of the tephra fall was increased turbidity levels (due to tephra suspended in water), which led to problems in operation of drinking water treatment systems (Wilson et al., 2012).

Table 4
Sample properties and leachable element concentrations for Cordón Caulle 2012 tephra samples (1:20 water leaches).

	43	41	58	27	25	23	21	20	17	13	Cordón Caulle median
Sample type	In situ	In situ	In situ	In situ	In situ	In situ	Epiclastic	Epiclastic	Epiclastic	Epiclastic	
Sample date	11/03/12	11/03/12	13/03/12	6/03/12	6/03/12	6/03/12	6/03/12	6/03/12	6/03/12	4/03/12	
Land use	Forestry	Pastoral	Pastoral	Malline	Malline	Malline	Malline	Malline	Malline	Steppe	
Distance to vent (km)	60	70	80	130	150	160	170	190	220	235	
pH	6.4	6.9	6.2	7.1	7.5	8.8	7.5	6.8	8.2	7.2	
Median grain size (um)	108.5	256.9	227.3	54.5	116.2	61.5	123.4	88.5	92.0	74.0	
Major components (mg/kg)											
Al	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Ca	8	5	5	32	24	59	154	36	54	42	34
Fe	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Mg	<5	<5	<5	<5	6	<5	32	10	8	7	6
Na	16	27	11	19	20	21	148	63	38	49	24
K	6	<5	<5	<5	6	<5	18	<5	8	<5	<5
SO_4	<10	<10	<10	<10	<10	<10	216	12	10	36	<10
Cl	28	<10	<10	18	34	<10	440	136	64	82	31
F	4	1	3	7	13	8	20	20	22	37	11
Minor components (mg/kg)											
As	0.01	0.01	<0.01	0.02	0.01	0.04	0.02	<0.01	0.01	<0.01	0.01
Co	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Cu	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Mn	9.7	3.2	1.1	2.1	8.7	1.9	2.3	40.2	4.9	30.1	4
Ni	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Pb	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Zn	<0.1	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.4	<0.1

Table 5
Total recoverable metal concentrations for tephra digests (modification of EPA Method 200.8) of 2011 tephra samples and Ruapehu 1995 tephra samples (Cronin et al., 1997).

Sample ID	13_140611	1	040611-6	060611-3	060611-6	080611-3	290611-076	170611	Ruapehu (range)
Sample type	Dry, fresh	Dry, fresh	Dry, fresh	Dry, fresh	Dry, fresh	Slightly humid	Dry, fresh	Dry, fresh	Dry, fresh
Sample date	14/06/11	5/06/11	4/06/11	6/06/11	6/06/11	8/06/11	29/06/11	17/06/11	11/10/95–14/10/95
Land type	Suburban	Forestry	Suburban	Lakeside	Steppe-temperate	Steppe (Malline)	Steppe (Malline)	Jacobacci	Pasture
Distance to vent (km)	45	70	75	80	90	225	225	235	15–116
Median grain size (um)	71.8	173.7	270.5	76.2	37.1	73.6	77.2	124.8	
Major components (mg/kg)									
Al	4672	2155	4671	2190	974	794	2692	1391	15,480–18,055
Ca	682	2151	4612	2105	914	763	2604	1294	9546–11,918
Fe	2518	4008	4330	15,067	3340	2243	2518	3284	4224–9704
Mg	116	717	2199	663	222	174	903	287	401–1341
Na	498	513	1006	631	810	785	847	584	2528–3352
K	91	164	276	124	147	150	268	105	506–1390
Minor components (mg/kg)									
As	0.8	1.2	2.3	0.9	0.9	0.9	1.5	0.7	6.3–<23
Co	1	10	5	2	1	1	2	1	<2.5–<4
Cu	0	94	36	16	7	6	9	8	13.1–24
Mn	18	51	120	40	23	17	100	21	15.6–1–3
Ni	0.3	0.5	0.7	1.8	0.6	0.4	2.3	0.7	0.63–<4
Pb	1	3	3	2	11	1	9	8	<25
Zn	4	29	21	7	4	3	11	4	5.5–183

Surface water samples were collected as part of this study (Supplementary Tables 5 and 6), but were limited to opportunistic sites and timing.

5.4.1. Spatial trends

Table 7 presents concentrations of Cl and F, and pH and conductivity recorded in surface waters sampled between 6 and 30 June 2011 in the tephra fall area of the 4 June eruption. While a range of other constituents was determined (Supplementary Table 5), we focus this discussion on Cl and F as major components of the soluble cargo of the Cordón Caulle tephra. The two samples collected at the greatest distances from the vent, in the semi-arid area, have markedly higher conductivity and slightly higher pH than the other samples, which were collected in the temperate zone (i.e., within 100 km of the vent). The Rio Nirihau sample (102 km from vent) exhibits an intermediate pH. This compositional gradient has been attributed to decreasing rainfall away from the Andes (Martin et al., 2009). Surface waters in higher-rainfall areas are highly dilute (low conductivity) and slightly acidic, whereas, in the semi-arid zone they are highly saline (high conductivity) and slightly alkaline.

Compared to the background, fluoride and chloride concentrations were elevated in the distal samples. However, this may also be associated with the pre-existing compositional gradient. The temperate zone samples showed no trends in F or chloride concentrations with increasing distance from the vent. Interpretation of the data was confounded by sampling being carried out at different time intervals after the eruption. In addition, catchment sizes and flow volumes vary widely, but cannot easily be accounted for. Nonetheless, a strong positive association exists between F and Cl in this data set ($r = 0.941$, $p < 0.001$) suggesting that elevated concentrations in the temperate zone samples are due to leaching from the tephra fall.

5.4.2. Temporal trends

Table 8 contains a time series of Cl and F concentrations in water samples collected from four streams at distances of 36–70 km from the vent. For the whole data set, a strong positive correlation exists between Cl and F concentrations ($r = 0.902$, $p < 0.001$) implying a common source. Both elements showed strong 'spikes' in concentration following the 4 June 2011 eruption, but were consistently lower when sampled in 2012. As background concentrations of Cl and F for these

Table 6
Total recoverable metal concentrations for tephra digests (modification of EPA Method 200.8) of 2012 tephra samples.

Sample ID	43	41	58	27	25	23	21	20	17	13
Sample type	In situ	In situ	In situ	In situ	In situ	In situ	Epiclastic	Epiclastic	Epiclastic	Epiclastic
Sample date	11/03/12	11/03/12	13/03/12	6/03/12	6/03/12	6/03/12	6/03/12	6/03/12	6/03/12	4/03/12
Land use	Forestry	Pastoral	Pastoral	Malline	Malline	Malline	Malline	Malline	Malline	Steppe
Distance to vent (km)	60	70	80	130	150	160	170	190	220	235
Median grain size (um)	108.5	256.9	227.3	54.5	116.2	61.5	123.4	88.5	92.0	74.0
Major components (mg/kg)										
Al	1719	1729	1484	2920	2989	1187	1536	1245	2000	1148
Ca	1727	1729	1484	2404	2989	1003	1536	1245	2000	1148
Fe	2446	2546	2718	3764	3045	1793	2396	1819	2825	1396
Mg	645	550	736	970	86	284	448	292	535	250
Na	567	572	439	735	689	774	605	691	536	463
K	208	168	155	256	175	307	259	242	250	143
Minor components (mg/kg)										
As	1.0	1.0	1.7	1.0	1.1	1.0	1.0	0.9	1.0	0.7
Co	1.4	1.6	1.6	1.6	0.8	1.4	0.9	2.4	1.2	0.6
Cu	13	14	12	8	6	8	4	9	7	5
Mn	36	36	41	75	48	34	32	28	44	20
Ni	1.7	2.1	1.9	0.5	0.2	0.3	0.2	0.9	1.4	0.2
Pb	1.2	0.8	1.6	0.8	0.9	0.8	0.8	0.7	0.8	0.4
Zn	7	8	7	7	5	7	6	8	6	3

Table 7
Trends in pH, conductivity, fluoride and chloride in surface waters sampled in June 2011 with increasing distance from the vent in the Cordón Caulle depositional area.

	Sampling date	Distance from vent (km)	pH	Cond (μS/cm)	Cl (mg/L)	F (mg/L)
Rio Pireco	22/06/11	35	6.83	58	11.3	0.49
A° Totoral	22/06/11	36	6.7	74	16.6	0.91
Lago Espejo Chico	23/06/11	37	6.7	22	1.4	0.25
A° Espejo Chico	23/06/11	37	7.3	39	1.2	0.2
Rio Ruca Malen	14/06/11	38	7.1	20	1.1	0.13
Rio Pichitraful	23/06/11	44	7.4	51	2.3	0.12
A° Las Piedritas	8/06/11	50	6.7	110	26	1.57
	14/06/11		7	50	8	0.66
A° unnamed	6/06/11	57			4.2	0.32
A° la Estacada	6/06/11	62			3.3	0.35
	8/06/11		6.4	127	21	1.37
	14/06/11		7.1	41	7.4	0.64
A° Ragintuco	6/06/11	64			2.8	0.33
A° Huemul	6/06/11	70			2.4	0.25
	14/06/11		7.4	53	7.6	0.7
A° Cullin Manzano	14/06/11	88	7.55	71	9.4	1.08
Rio Nirihuãu	30/06/11	102	7.76	66	1.1	0.07
A° Comallo	8/06/11	164	8	633	28	1.35
Rio Quetrequile	29/06/11	262	8.1	657	24	1.2

streams are not known, no comment can be made on whether inputs of leachable elements from the tephra fall were continuing. However it seems probable that elevated concentrations of these elements at the most-proximal site sampled in 2012 (Arroyo Totoral, 36 km from the vent) are due to continued leaching from the heavy tephra falls recorded in this area (>300 mm tephra fall, Table 8).

5.4.2.1. Risks to livestock drinking water in the temperate zone. Livestock in the temperate zone obtain their drinking-water exclusively from surface waters. An increase in suspended solids (turbidity) is known to be the most common risk of tephra fall into surface waters (Wilson et al., 2010; Stewart et al., 2013). The Cordón Caulle tephra did not generate impacts that exceeded livestock drinking-water guidelines developed by the Food and Agriculture Organisation (FAO) of the United Nations (Ayers and Westcot, 1994) (Table 9). Considering also that these guidelines incorporate wide safety margins (Ayers and Westcot, 1994) and that disturbances to water composition are likely to be a short-term phenomenon, chemical impacts were not expected for the majority of elements, with the exception of F.

5.4.2.2. Risks to livestock drinking water in the semi-arid zone. Moderate levels of F were recorded in both surface water samples collected in the semi-arid zone (1.2–1.35 mg/L F), but these are probably normal levels for the area due to the background salinity (Edmunds and Smedley, 2013). Municipality staff in the town of Ingeniero Jacobacci explained that dissolved constituents such as F in raw water sources (primarily groundwater) are, in general, high and towards the upper range of acceptability for human drinking water. Thus compared to the more temperate zone, livestock in this area are normally subjected to an elevated F environment, especially if forage is irrigated with the same water.

A further source of exposure to F is via contamination of stock drinking water troughs by tephra fall. Table 10 shows an indicative calculation for a 60-gallon oblong water trough in the Jacobacci region, contaminated with 50 mm tephra fall containing 65–85 mg/kg water-extractable F. Predicted concentrations range from 11.1 to 14.5 mg/L F, assuming that tanks are filled with rainwater rather than groundwater. In practice, tanks in this region are likely to be filled with groundwater which is likely to contain >1 mg/kg F. While these calculations are indicative, they clearly point to the potential for tephra contamination of shallow uncovered water supplies leading to F concentrations well in excess of FAO guidelines.

5.5. Relationship of these findings to observed impacts on livestock

5.5.1. High livestock losses

Fluoride is known to be the principal element of toxicological importance in tephra leachates (Witham et al., 2005). Acute (short-term) impacts of F exposure require high doses and concentrations (Livesey and Payne, 2011). The very high fatality rates of livestock reported following the tephra fall were considered by local agencies to be caused by physical impacts of tephra (e.g. feed destruction) rather than F toxicity. We note that water-extractable F levels in fresh Cordón Caulle tephra (12–167 mg/kg, median 67 mg/kg) were much lower than those reported for well-documented cases of acute animal fluorosis following other eruptions. Following the 1970 eruption of Hekla volcano, Iceland, tephra containing ~1000 mg/kg adsorbed soluble F (Óskarsson, 1980) was responsible for deaths of 'thousands' of grazing livestock, especially sheep (Thorarinsson and Sigvaldason, 1971). Georgsson and Petursson

Table 8
Chloride and fluoride concentrations (mg/L) in four streams from June 2011 to March 2012 in the Cordón Caulle depositional area.

	Stream sampled (distance from vent)				Stream sampled (distance from vent)			
	A° Totoral	A° Las Piedritas	A° La Estacada	A° Huemul	A° Totoral	A° Las Piedritas	A° La Estacada	A° Huemul
	36	50	62	70	36	50	62	70
Date sampled	Chloride (mg/L)				Fluoride (mg/L)			
6-Jun-11			3.3	2.4			0.35	0.25
8-Jun-11		26	21			1.57	1.37	
14-Jun-11		8	7.4	7.6		0.66	0.64	0.7
22-Jun-11	16.6				0.91			
1-Mar-12			7.2	6.6			0.11	0.11
11-Mar-12			5.9	5.6			0.08	0.09
14-Mar-12	9.2	5.6			0.33	0.08		

Table 9
Comparison of surface water composition in Cordón Caulle tephra fall depositional area (temperate zone only) with FAO livestock drinking water guidelines.

	Maximum value recorded[a] ($n = 17$)	FAO guidelines
Salinity (μS/cm)[b]	127	1500
Fluoride (mg/L)	1.57	2
Aluminium (mg/L)[c]	1.01	5
Arsenic (mg/L)	0.01	0.2
Copper (mg/L)	0.003	0.5
Iron (mg/L)	0.76	–
Manganese (mg/L)	0.03	0.05
Lead (mg/L)	0.0007	0.1

[a] For complete data set refer to Supplementary Tables 5 & 6.
[b] Water with salinity <1500 μs/cm is rated as 'excellent' for livestock uses.
[c] Total metal concentrations are reported here for comparability to guidelines.

(1972) reported that 3% of sheep and 8–9% of lambs in the tephra-covered areas died. Thorarinsson and Sigvaldason (1971) report that tephra-contaminated grass was as high as 4000 mg/kg F dry weight in some samples.

In a parallel case to that described here, the 11–12 October 1995 eruption of Ruapehu volcano in New Zealand had even lower available fluoride (11–28 mg/kg F for single leach; 55 mg/kg for sequential leach of one sample; Cronin et al., 2003). Despite this, approximately 2.5% of pregnant or lactating sheep died in the downwind Rangataiki Plains area which received approximately 2 mm tephra fall. Fluorine toxicity was suggested to be the probable cause of death (Shanks, 1997) based on both elevated F concentrations in rumen contents and kidney histology. There were several factors that apparently increased the susceptibility of the animals to F toxicity. The Ruapehu eruption occurred at the end of winter, when feed supply was short and animals were facing high energy demands; it was notable that the animals most affected had the highest energy demands (i.e., heavily pregnant or feeding lambs). A fasted state may have led to rapid F absorption. Cronin et al. (2003) also proposed that a single water leach may have underestimated the F hazard from Ruapehu tephra ingestion. Repeated water leaches yielded substantially larger amounts of F and the authors proposed that F was present in slowly-soluble phases such as CaF_2, AlF_3 and $Ca_5(PO_4)_3F$, which were thought to have originated from the hydrothermal system at the base of the Crater Lake. A further possible contributing factor is that decades of phosphate fertiliser applications to New Zealand farmland are known to have caused accumulation of contaminants (including F) in surface soils in farmed areas relative to non-farmed areas (Cronin et al., 2000; Taylor et al., 2010). Thus it is possible that livestock in these areas have already accumulated substantial body burdens of F prior to any additional loading from tephra ingestion.

In addition to the sheep deaths, the Department of Conservation reported that approximately 5% of the wild sika deer population (mainly pregnant hinds and fawns) died in late 1995 in the Kaimanawa Ranges (Keys, 1996). According to Cronin et al. (1998) this area received in the region of 5–10 mm depth tephra fall from the 11–12 October 1995 eruption. Fluorosis was considered to be a contributing factor along with aggravated nutritional stress and physical impacts of tephra ingestion. The fact that animals with high energy demands were most-affected supports the interpretation that F toxicity was a contributing factor.

In the case of the Ruapehu tephra fall, the first animal deaths occurred nine days afterwards, suggesting that these deaths were not sudden-onset acute fluorosis resulting from a lethal dose. Cronin et al. (2003) proposed that given the poor condition and lowered resistance of the grazing animals, a sub-lethal dose of F may have been sufficient to cause their deaths, in combination with other stressors. In the case of the Cordón Caulle tephra fall, animals were also stressed and in poor condition, with feed shortages due to both drought and winter conditions (Craig et al., 2016a). The observed levels of available F in Cordón Caulle tephra (higher than for Ruapehu 11–12 October 1995 tephra) suggest that the role of F toxicity as a contributing factor to the observed livestock deaths cannot be ruled out.

A further issue is that with the low number of tephra samples analysed in this study, it is difficult to be certain that we have captured the F content of ash throughout the entire eruptive episode. The F concentration of tephra may vary considerably during an eruption, such as observed by Cronin et al. (1998) during the 1996 Ruapehu eruption — in this case early-erupted tephra had five to ten times the concentrations of F than tephra erupted several hours later. In the Ruapehu case, winds changing during the eruption spatially separated high-F tephra from tephra bearing lower concentrations. It cannot be ruled out in the Cordón Caulle case that F concentration varied, for example, with the proportion of country-rock or vent-hosted hydrothermal system materials taken up in the eruption. However samples 040611-6 and 060611-3, which represented the first explosive pulse of the eruption (Supplementary Material 7), had F concentrations towards the lower end of the range thus increasing confidence that the samples collected provide adequate representation of the whole event.

5.5.2. Initial tephra chemical characterisation — lessons learned

An initial analysis of leachable elements from the fresh Cordón Caulle tephra was performed using a standard method for analysing borosilicate glass (ASTM Method C 169-92 Chemical Analysis of Soda-Lime and Borosilicate Glass Volume 15.02), which yielded a result of 0.7 mg/kg F (Hufner and Osuna, 2011). This method varies from recent methods developed for assessing leachable elements (Stewart et al., 2013) in several important aspects: the ratio of tephra to extractant is unspecified; the extraction was carried out at 50 °C rather than room temperature; and a colorimetric method was used for detection of F. The analysis appears to have strongly underestimated the level of water-extractable F in the 2011 tephra fall, as the levels recorded in this study at comparable distances were 27 mg/kg (at 80 km) and 167 mg/kg (at 90 km, Table 3). This situation provides a useful lesson highlighting the need for accessible, reliable and appropriate guidance on tephra analysis to enable a rapid assessment of tephra toxicity hazard.

We further note that further work may be required to develop more reliable methods of tephra toxicity hazard assessment for grazing livestock. Flueck (2016) describes the complex physicochemical conditions that characterise ruminant digestive tracts. Mastication of feed occurs in an alkaline environment (pH 8.2–8.5) followed by near-neutral conditions in the rumen, followed by strongly acidic conditions (pH 1–2) in the abomasum. Therefore, neither a water leach nor a gastric leach may adequately predict the toxicity of adsorbed F on tephra.

Table 10
Calculations of fluoride concentration in livestock water trough contaminated with 50 mm tephra fall in Jacobacci region.

	C_{tephra}[a] (mg/kg)	Tephra depth (m)	Density[b] (kg/m^3)	A/V[c] (m^2/L)	C_{water}[d,e] (mg/L)
F (low end of range)	65	0.05	700	0.0049	11.1
F (high end of range)	85	0.05	700	0.0049	14.5

[a] From Table 2.
[b] J. Wardman, pers. comm.
[c] For tank of length 2 m, width 0.66 m, depth 0.38 m (Hynds 60 gal oblong protector trough).
[d] Assumption that tanks are filled with rainwater (very low F content).
[e] $C_{water} = C_{tephra}$ (mg/kg) $*$ tephra depth (m) $*$ density (kg/m^3) $*$ A/V (m^2/L) (Stewart et al., 2013).

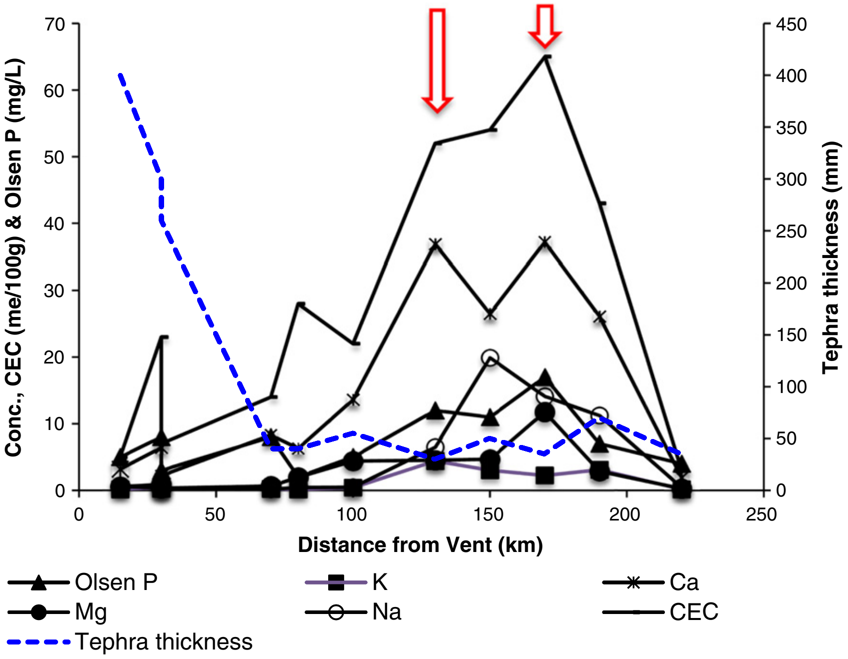


Fig. 11. Soil fertility parameters and thickness with distance from vent. Arrows indicate sample sites where there was evidence of cultivation and/or irrigation.

5.5.3. *Reported dental and skeletal fluorosis in wild deer and livestock populations in years following eruption*

Chronic exposure relates to continuous or repeated intake of F over months to years. Dental fluorosis is the earliest visible sign of chronic fluorosis in mammals (Livesey and Payne, 2011). Severe dental fluorosis can cause difficulty in eating. At higher levels of exposure, skeletal fluorosis can cause painful lesions on bones and joints, lameness, osteosclerosis and an increased risk of fractures (Suttle, 2010). Direct mortality is rare, but the useful lifespan of the animal is commonly reduced.

In addition to acute fluorosis, chronic fluorosis was also reported following the 1970 Hekla eruption (Georgsson and Petursson, 1972). Dental fluorosis was reported in 25% of 550 sheep that were examined, four to nine months after the eruption. Fluoride accumulation in bones of lambs in areas receiving >1 mm tephra was over twice as high as in lambs in unaffected areas. Following the 1988–89 eruption of Lonquimay volcano, clinical signs of osteofluorosis were observed in cattle four months later, with the main symptoms being weight loss, kyphosis and lameness along with intense pain when long bones were palpated. Fluoride-contaminated forage (240–315 mg/g dry weight, compared with maximum allowable level of ~40 mg/kg) was thought to be the main cause. Further work (Araya et al., 1993) concluded that levels of F in forage may remain high enough for two years after the eruption to maintain fluorosis symptoms in exposed livestock.

Several studies have reported severe chronic fluorosis in populations of wild red deer (Flueck and Smith-Flueck, 2013a, 2013b; Flueck, 2014) and livestock (Flueck, 2013) in the Cordón Caulle tephra depositional area. Evidence to support this diagnosis includes high rates of F accumulation in bone, and clinical symptoms of dental fluorosis (damaged enamel, rapid wear, pitting, mottling and variable stages of development). The deer populations studied (Flueck and Smith-Flueck, 2013a; Flueck, 2014) had been monitored annually since 1991, and as clinical fluorosis symptoms were absent before the June 2011 eruption of Cordón Caulle, fluorosis was attributed to the eruption. These authors suggest that, based on rapid post-eruption accumulation of F in bones of wild deer, these animals may be at risk of osteofluorosis.

Our tephra composition results are consistent with this scenario; however to determine exposure more satisfactorily, a time series of analyses of forage samples would have been needed. A further difficulty is that there are very few events where chronic fluorosis has been well documented and related to tephra composition, thus there are few comparative case studies available.

A relevant finding from our study was that leachable elements were partially conserved in tephras sampled in the semi-arid zone; this may act to prolong exposure of grazing livestock in these areas. A further issue is that in the steppe area, our calculations indicate (Table 10) that tephra contamination (and recontamination) of shallow drinking water sources may lead to concentrations of F well in excess of FAO guidelines. It is also relevant to note that there is a high background concentration of F in groundwater in this area (approximately 1.2–1.4 mg/L). This may help explain chronic fluorosis in the semi-arid zone.

6. Conclusions

Overall, water-extractable element concentrations in freshly-collected Cordón Caulle tephra were very low to low compared to other eruptions, and showed no trends with distance from the volcano. Surface water analyses suggested short-term changes to water composition due to the release of elements from tephra. No effect on the fertility of soils underlying tephra was apparent after nine months.

Water-extractable fluorine (F) in freshly-collected tephra ranged from 12 to 167 mg/kg, with a median value of 67 mg/kg. While these F concentrations are low compared to eruptions worldwide (global median 129 mg/kg, Ayris and Delmelle, 2012) they are nonetheless higher than those recorded for the 11–12 October 1995 eruption of Ruapehu volcano, New Zealand, where F toxicity contributed to livestock deaths. Taking into account the circumstances of the Cordón Caulle tephra fall, where other stressors were present, we thus conclude that the role of F toxicity as a contributing factor to the large-scale livestock deaths cannot be ruled out. We reach a similar conclusion with respect to reports of chronic fluorosis in wild deer and livestock populations across the Cordón Caulle tephra depositional area. Additional findings from our study strengthening this conclusion are: (1) that analysis of tephra sampled nine months after the eruption showed that water-extractable elements are partially conserved in semi-arid zone samples, thus prolonging exposure of grazing animals; and (2) that contamination and recontamination of shallow water sources by wind-remobilised tephra may lead to F concentrations well in excess of livestock drinking-water guidelines, suggesting an additional exposure pathway.

In summary, early warning of F intoxication hazards would enable rapid response during future major eruption crises to protect livestock. An effective response to widespread tephra fall over agricultural areas should include the following steps:

- Rapid, statistically representative field sampling of tephra, soils, surface water supplies and forage crops;
- Analysis using appropriate and reliable laboratory methods;
- Modelling both short and long-term impacts on the ecosystem, particularly for elements that may generate chronic hazard;
- Timely dissemination of results to agricultural agencies;
- Provision for longitudinal sampling and monitoring to adapt impact models; and
- Developing reliable animal fatality diagnoses through autopsies and chemical analysis.

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Appendix A. Supplementary data

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