

# Effects of maize cultivation on nitrogen and phosphorus loadings to drainage channels in Central Chile

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Received: 13 April 2015 / Accepted: 13 October 2015 / Published online: 22 October 2015  
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**Abstract** There are concerns about the impact of maize cultivation with high applications of nitrogen (N) and phosphorus (P) on water quality in surface waters in Mediterranean Central Chile. This study estimated the contribution of N and P from maize fields to nearby drainage channels and evaluated the effects in water quality. An N and P budget was drawn up for three fields managed with a maize-fallow system, *El Maitén* (20.7 ha), *El Naranjal* (14.9 ha) and *El Caleuche* (4.2 ha), and water quality variables (pH, EC, dissolved oxygen, total solids, turbidity,  $\text{NO}_3\text{-N}$ ,  $\text{NH}_4\text{-N}$ ,  $\text{PO}_4^{3-}$ , COD, total N, total P and sulphate) were monitored in nearby drainage channels. The N and P balances for the three fields indicated a high risk of N and P non-point source pollution, with fertiliser management, soil texture and climate factors determining the temporal variations in water quality parameters. Elevated levels of  $\text{NH}_4\text{-N}$  and  $\text{PO}_4^{3-}$  in the drainage channels were usually observed during the winter period, while  $\text{NO}_3^-$  concentrations did not show a clear tendency. The results

suggest that excessive slurry application during winter represents a very high risk of N and P runoff to drainage channels. Overall, great emphasis must be placed on good agronomic management of fields neighbouring drainage channels, including accurately calculating N and P fertiliser rates and establishing mitigation measures.

**Keywords** Fertilisation · Non-point source pollution · Pig slurry · Water quality

## Introduction

Nutrients such as nitrogen (N) and phosphorus (P) are essential for plant growth and being increasingly applied in the form of fertilisers to enhance the productivity of agricultural soils. Global consumption of N fertiliser has increased from almost negligible levels in the 1940s to about  $80 \times 10^6$  tonnes N per year in the mid-1990s (Di and Cameron 2002) and is expected to reach about  $114 \times 10^6$  tonnes N per year in 2015 (FAO 2012). Similarly, the global demand for phosphate fertiliser is expected to reach about  $44 \times 10^6$  tonnes  $\text{P}_2\text{O}_5$  per year in 2015 (FAO 2012). Unfortunately, when these nutrients are applied in excessive amounts to agricultural land they are not totally consumed by plants or crops, resulting in leaching to water bodies (Di and Cameron 2002). Elevated levels of nitrate ( $\text{NO}_3^-$ ) and orthophosphate ( $\text{PO}_4^{3-}$ ) in water bodies may lead to eutrophication, thus reducing dissolved oxygen levels and impacting ecosystem integrity (Di and Cameron 2002;

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FAO 2010). This issue is not new, but in recent decades has increased in scale to become a global problem (Trowbridge et al. 2011).

Nitrogen and P contamination of water can originate from several sources, among which agriculture plays a major role (EEA 2005). This kind of pollution has different components, including leaching (Buczko et al. 2011; Darwish et al. 2011; Salazar et al. 2014) and surface runoff (Armstrong et al. 2011; Panagopoulos et al. 2011). The leaching rates of  $\text{NO}_3^-$  are high compared with those of  $\text{PO}_4^{3-}$ , particularly in coarse-textured soils with low water retention capacity (Darwish et al. 2011; Salazar et al. 2009), causing groundwater contamination. Although  $\text{PO}_4^{3-}$  leaching has been shown to be low, even in sandy soils (Neumann et al. 2012), it has been determined that high P fertiliser and manure application rates can reduce the P sorption capacity of the soil. This increases the soil concentration of desorbable P, causing lixiviation (Salazar et al. 2011; Pizzeghello et al. 2011). In addition, surface runoff of  $\text{NO}_3^-$  and  $\text{PO}_4^{3-}$  flows directly to surface water (Armstrong et al. 2011).

The major contribution of agriculture to the total amount of pollutants lost to water has led to the establishment of guidelines and frameworks such as EU Directive 2000/60/EC and EPA (1993a) with specific focus on measures known as mitigation methods, conservation practices or best management practices (BMPs) (Cherry et al. 2008). Development and implementation of BMPs requires examination of non-point source pollution from agriculture under local conditions (Shen et al. 2015). In the central valley of Chile, there are two main pieces of evidence pointing to the large contribution of agricultural runoff and leaching to groundwater and surface water pollution. First, this area houses the largest pig population supplying the Chilean food industry and, consequently, the largest maize production area in the country. Maize, which is grown in monoculture, is systematically overfertilised, probably causing runoff and lixiviation of contaminants such  $\text{NO}_3^-$  and  $\text{PO}_4^{3-}$  (Fuentes et al. 2014; Najera et al. 2015). Second,  $\text{NO}_3^-$  concentrations are showing an upward trend in the *Rapel* River, north of the Chilean central valley (Pizarro et al. 2010). In this watershed, high levels of  $\text{NO}_3^-$  have also been observed in shallow groundwater wells (Golembeski 2004; Iriarte 2007). These two factors, involving alleged non-point pollution from maize fields and pollution evidence in the *Rapel* River watershed, indicate that maize cultivation may be

the most important cause of non-point source pollution in the central valley of Chile.

Assessment of water quality and pollution due to agricultural activities has been the subject of many studies in Mediterranean climate conditions (Casalí 2008; Arbat et al. 2013; Bermúdez-Couso et al. 2013). However, despite the evidence of widespread surface water pollution pointed out by Golembeski (2004), Iriarte (2007) and Pizarro et al. (2010), only a few studies have been carried out in Central Chile to connect this pollution with its source(s) (e.g. Ribbe et al. 2008) and to propose and evaluate mitigation measures (e.g. Tapia and Villavicencio 2007). Moreover, the few available studies only consider N pollution, while ignoring P pollution. Therefore, it is essential to have more local information about the subject in order to devise and implement appropriate BMPs in affected regions of the country. Against this background, the main objectives of the present study were primarily to estimate the contribution of N and P from maize fields to nearby drainage channels and to evaluate the effects on other drainage water quality parameters in the north-central valley of Chile.

## Materials and methods

### Study sites

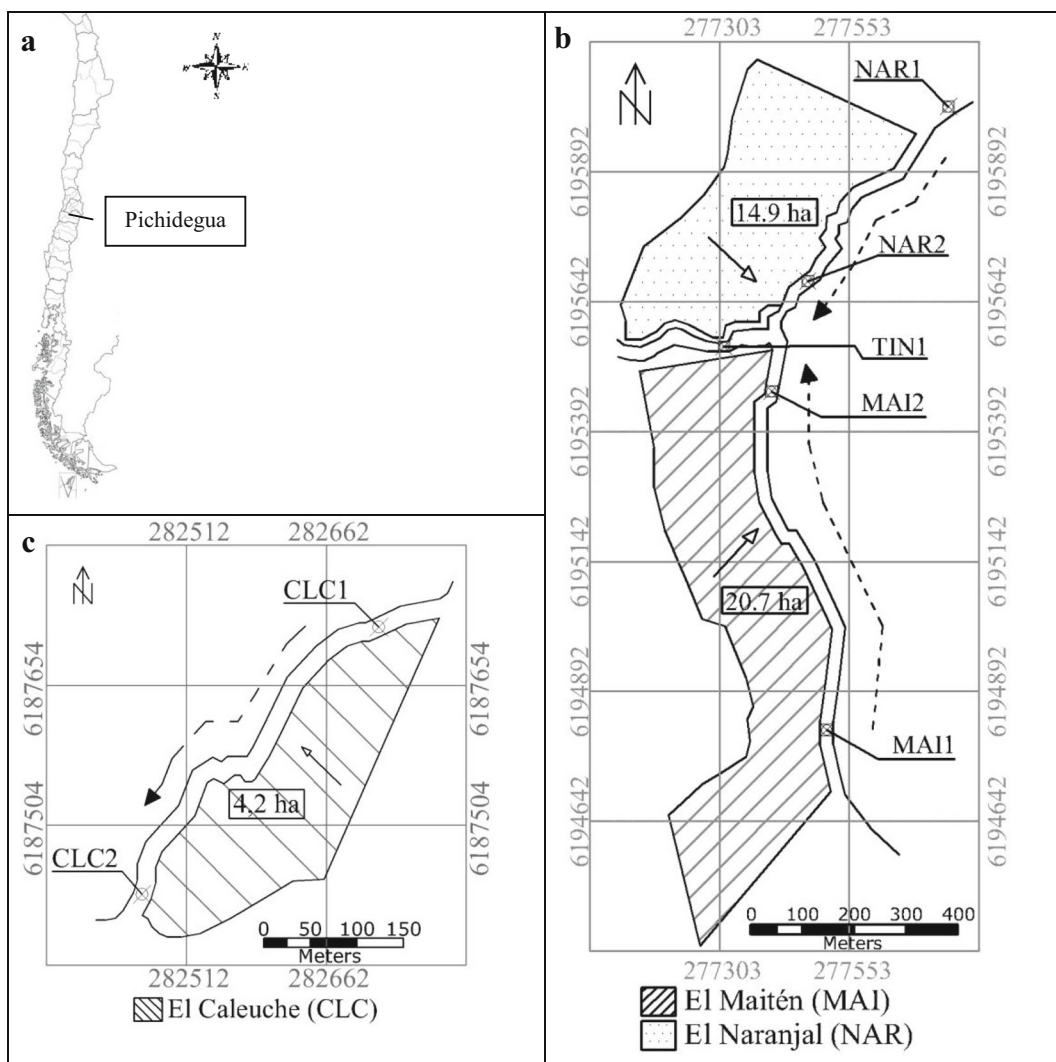
The study was conducted in three fields managed with a maize-fallow system, located in the commune of *Pichidegua* in the north-central valley of Chile (*O'Higgins* Region) (Fig. 1a). The climate at the site is semi-arid Mediterranean, with warm summers (max. and min. temperature during January, 28 and 12.2 °C) and relatively cold wet winters (max. and min. temperature during June, 15 and 5.5 °C). Mean annual rainfall is about 696 mm concentrated from May to October (Santibáñez and Uribe 1993). The first and second of the fields studied (71° 25' W, 34° 22' S), named *El Maitén* (20.7 ha) and *El Naranjal* (14.9 ha), respectively, belong to the *Tinguiririca* Soil Series, classified by CIREN (1996) as part of the coarse loamy, mixed, thermic family of Mollic Xerofluvents. This soil series is characterised by deep soil deposits with excessive drainage. These two fields are bordered along one of their edges by drainage channels, designated MAI and NAR, respectively, which converge to a common point (channel designated as TIN) between the two fields and flow

downstream to the Tinguiririca River (Fig. 1b). The third field (71° 21' W, 34° 25' S), named *El Caleuche* (4.2 ha), belongs to the *Caleuche* Soil Series, classified by CIREN (1996) as part of the fine loamy, mixed, thermic family of Typic Duraqualfs (Alfisol). This soil series is characterised by flat, thin soil deposits with imperfect drainage and a duripan (Cm horizon) ranging from 50 to 100 cm depth. This field is bordered on one of its edges by a channel, designated CLC, which flows downstream to a major watercourse (Fig. 1c). The physical characteristics of the channels are presented in Table 1.

In addition, data collected in a stream located in the National Park *Las Palmas de Cocalán* (71° 6' W, 34° 11' S), considered a pristine reference site, were used for comparison with water quality measurements obtained from the study area.

Water samples

Sampling points were established in each drainage channel to monitor the quality of incoming (inlet points: MAI1, NAR1, CLC1) and outgoing water (outlet points: MAI2, NAR2, CLC2) (Fig. 1b, c). An extra



**Fig. 1** Location of the (a) Pichidegua commune in central Chile; (b) the MAI, NAR and TIN channels, their monitoring points and the neighbouring fields El Maitén and El Naranjal and (c) the CLC

channel, its monitoring points and the neighbouring field El Caleuche. The *arrow* within the field indicates slope direction. In (b) and (c), UTM coordinates are indicated on axes

**Table 1** Description of field channels along El Maitén (MAI), El Naranjal (NAR), the confluence outlet channel (TIN), the El Caleuche inlet point (CLC1) and the El Caleuche outlet point (CLC2)

Channel	Bottom width (m)	Depth (m)	Side slope (%)	channel slope	Mean water depth (m)	Length (m)	Mean flow <sup>b</sup> (m <sup>3</sup> s <sup>-1</sup> )
MAI	7.00	1.60	95	7	0.60	700	26
NAR	8.00	1.50	85	1	0.70	450	15
TIN	8.00	0.75	35	7	0.40	280	16
CLC1	3.00	0.30	70	6	0.70	400 <sup>a</sup>	15
CLC2	7.00	1.20	140	3	0.30		5

<sup>a</sup>Distance between CLC1 and CLC2

<sup>b</sup>Calculated using Manning's equation

monitoring point was placed in the confluence channel (TIN1) (Fig. 1b). Water samples were collected every 2 weeks between June 2011 and March 2012 and every week between April 2012 and January 2013 for NO<sub>3</sub>-N analyses. On each sampling occasion, one composite sample of 235 mL, obtained from three subsamples, was sent for analysis for each monitoring point. Other water quality variables such as PO<sub>4</sub><sup>3-</sup> were gradually included during the study period, and were determined in the same composite sample used for NO<sub>3</sub>-N analysis. From July 2012 to January 2013 the analysis was restricted only to the CLC channel and included just NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> measurements. The start and end dates for each measured water quality variable are presented in Table 2. For the pristine reference site, data collected every 2 weeks between December 2013 and July 2014 were used.

Dissolved oxygen (DO) content and temperature were determined in situ using portable equipment (Hanna Instruments HI9146, USA), while grab water samples (i.e. water samples taken manually) were collected from the top and centre of each channel, stored in glass bottles, chilled on ice and sent to the Laboratory of Soil and Water Chemistry of the Faculty of Agricultural Sciences at the Universidad de Chile. Once at the laboratory, the samples were analysed within 24 h. All water samples were filtered through syringe filters (0.45 µm), NO<sub>3</sub><sup>-</sup> free, to obtain a clear filtrate in which to determine the different forms of N and P.

#### Water quality variables

The pH of water samples was measured with a potentiometer, electrical conductivity (EC) with a conductivity

meter, and total solids (TS) content by drying at 103–105 °C using a natural flow-type drying oven according Sadzawka (2006). Turbidity was evaluated by nephelometry according to EPA (1993b). The NO<sub>3</sub>-N, NH<sub>4</sub>-N and PO<sub>4</sub><sup>3-</sup> concentrations were determined using spectrophotometric methods such as chromotropic acid, ammonia salicylate and phosphorus molybdate, respectively, according to Hach (2005). Chemical oxygen demand (COD) and total N and P were analysed by digestion and subsequent colorimetric analysis with a spectrophotometer according to Hach (2005). The sulphate content (SO<sub>4</sub><sup>2-</sup>) was determined by colorimetry according to Sadzawka (2006).

#### Determination of N and P contribution

In order to determine the N and P surplus at the study sites, approximate farm nutrient budgets were drawn up regarding N and P, including soil supply, fertilisation and crop uptake. The N and P surplus were calculated as the difference between common farmer N-P rates and calculated N-P doses based on maize demand and available N-P soil status. Thus, the following equations were used: (i) to calculate the N dose, Stanford's classic approach was used that included a mass N balance for assessing crop N fertiliser needs by considering N uptake at a specific dry matter yield level and N contributions from non-fertiliser sources. Thus, the recommended N rate of fertiliser was calculated according to Eq (1).

N demand (kg N ha<sup>-1</sup>)

$$= \frac{Y \times \left(1 - \frac{H}{100}\right) \times \frac{INR}{100}}{HI} \quad (1)$$

**Table 2** Start and end date of measurement of each variable in the study sites

Variable <sup>a</sup>	Channels <sup>b</sup>		
	MAI	NAR	CLC
	date-		
pH	23 Nov. 11 to 24 Jul. 12	23 Nov. 11 to 24 Jul. 12	26 Mar. 12 to 24 Jul. 12
EC	23 Nov. 11 to 24 Jul. 12	23 Nov. 11 to 24 Jul. 12	26 Mar. 12 to 24 Jul. 12
TS	23 Nov. 11 to 12 Jul. 12	23 Nov. 11 to 12 Jul. 12	26 Mar. 12 to 12 Jul. 12
DO	23 Nov. 11 to 05 Jul. 12	23 Nov. 11 to 05 Jul. 12	26 Mar. 12 to 12 Jul. 12
T	23 Nov. 11 to 05 Jul. 12	23 Nov. 11 to 05 Jul. 12	26 Mar. 12 to 12 Jul. 12
COD	23 Nov. 11 to 24 Jul. 12	23 Nov. 11 to 24 Jul. 12	26 Mar. 12 to 24 Jul. 12
Tur	31 Jan. 12 to 24 Jul. 12	31 Jan. 12 to 24 Jul. 12	26 Mar. 12 to 24 Jul. 12
N	31 Jan. 12 to 24 Jul. 12	31 Jan. 12 to 24 Jul. 12	26 Mar. 12 to 24 Jul. 12
NO <sub>3</sub> -N	07 Jun 11 to 24 Jul. 12	23 Nov. 11 to 24 Jul. 12	26 Mar. 12 to 31 Jan. 13
NH <sub>4</sub> -N	07 Jun 11 to 24 Jul. 12	23 Nov. 11 to 24 Jul. 12	26 Mar. 12 to 31 Jan. 13
P	17 May 12 to 07Jun 12	17 May 12 to 07 Jun 12	17 May 12 to 07 Jun 12
PO <sub>4</sub> <sup>3</sup>	20 Dec. 11 to 24 Jul. 12	20 Dec. 11 to 24 Jun 12	26 Mar. 12 to 24 Jun 12
SO <sub>4</sub> <sup>2</sup>	12 Apr. 12 to 24 Jul. 12	12 Apr. 12 to 24 Jul. 12	23 Mar. 12 to 24 Jul. 12

<sup>a</sup>EC electrical conductivity, TS total solids, DO dissolved oxygen, T temperature, COD chemical oxygen demand, Tur turbidity, N total N, NO<sub>3</sub>-N nitrate-nitrogen, NH<sub>4</sub>-N ammonium-nitrogen, P total P, PO<sub>4</sub><sup>3</sup> phosphate, SO<sub>4</sub><sup>2</sup> sulphate

<sup>b</sup>Channels: El Maitén (MAI), El Naranjal (NAR), El Caleuche (CLC)

where *Y* is the grain yield (kg ha<sup>-1</sup>), *H* is grain moisture content (%), INR is the internal nitrogen requirement (%) and HI is harvest index (-). *Y* was estimated for each field according site conditions, including maize hybrid yield and soil factors such as soil depth and soil compaction. In addition, N rate per hectare is calculated as Eq (2).

$$\begin{aligned}
 & \text{N rate (kg N ha}^{-1}\text{)} \\
 &= \frac{\text{N demand (kg N ha}^{-1}\text{)} - \text{net N mineralization (kg N ha}^{-1}\text{)}}{\frac{N_{Ef}}{100}}
 \end{aligned}
 \tag{2}$$

where *N<sub>EF</sub>* is the N fertiliser efficiency (%), mostly depending on soil type and irrigation system, where Chilean studies suggest Ef values range from 50 to 65 % (Najera et al. 2015), and the net N mineralisation potential of soils that depend on soil management and N recycling (Casanova et al. 2013).

(ii) To calculate the P doses, the principle of the law of diminishing returns was used, assuming that as the nutrient status of the soil increases, the maize response to P fertilisation decreases, until the point where soil levels reach 20 mg P-Olsen per kilogram, this called critical values (CV), when there is no response to

fertiliser application. Thus, P fertiliser rates can be calculated as shown in Eq (3).

$$\begin{aligned}
 & \text{P rate (kg P}_2\text{O}_5\text{ha}^{-1}\text{)} \\
 &= \frac{(\text{P}_{cv} - \text{P}_{sa}) \times \text{Db} \times \text{SD} \times 2.29 \times 10}{\frac{P_{Ef}}{100}}
 \end{aligned}
 \tag{3}$$

where *P<sub>cv</sub>* is the critical value for P-Olsen in the soil (mg P-Olsen kg<sup>-1</sup>), *P<sub>sa</sub>* is the measured soil analysis value for P-Olsen in the soil (mg P-Olsen kg<sup>-1</sup>), *Db* is the estimated bulk density (Mg m<sup>-3</sup>), *SD* is soil depth (m) and *P<sub>EF</sub>* is P fertiliser efficiency (%), where *P<sub>EF</sub>* is usually assumed around 60 % in soils of Central Chile.

The seasonal variations in the contribution of N and P from maize fields to drainage channel could be observed by time series analysis associated with NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup> and PO<sub>4</sub><sup>3-</sup> variables. The budget of N and P was estimated for each field considering soil N supply (according to the method proposed by Rodríguez (1993)), crop N and P extraction (using the values proposed by Setiyono et al. (2010)) and fertilisation input (farm manager, personal communication), thus determining the N and P surplus.

In addition, soil samples (0–20 cm) were taken for P-Olsen determination during October 2011 at MAI and October 2012 at CLC. Fuentes et al. (2015) reported

mean annual  $\text{NO}_3\text{-N}$  soil concentration at 1 m depth for MAI, NAR and TIN during the study period, whereas in CLC, mean annual  $\text{NO}_3\text{-N}$  soil concentration at observation wells located at 1 m depth were recorded by Salazar et al. (2015) between 2012 and 2014.

#### Water characterisation

To characterise the water samples by outlet points, different water quality standards were reviewed in order to establish a comprehensive criterion (Table 3). The guidelines established by the Chilean *Dirección General de Aguas* (DGA 2004) were used as first choice, since those are specific for the basin under study. When a standard was not available for some variables, the guidelines proposed by the Chilean Government regarding discharges of liquid contaminants to superficial water bodies were used (D.S. N° 90 2001), always following the guidelines to characterise the water as class 1, according to the Chilean *Dirección General de Aguas* (DGA 2004), the institution that establishes different water classes in relation to their quality purposes for each major watershed. For turbidity, the EPA (2004) threshold was used, since Chilean law states that when a standard is not available, that for the USA can be used as a reference (D. N°95 2008).

#### Statistical procedures

Statistical analyses were performed using R environment (R Core Team 2014). Out of a total of 184 rows of data corresponding to the information for each evaluation date (43 dates in total) and each monitoring point (8 between MAI, NAR and CLC channels), only 47 were subjected to principal component analysis (PCA). These 47 rows of data present information about all seven monitoring points, for eight different dates ranging from April to July 2012, including information of measured variables. Selection of the number of components extracted followed the Kaiser criterion, thus retaining only the factors that present eigenvalues  $\geq 1$ . The number of principal components reduces the number of parameters in the original database and is a good descriptor of the data variability (Nonato and et. al. 2007). Moreover, the relationship between these components and the monitoring points allows determination of whether the drainage channels are influenced by the neighbouring crop, the soil type and/or pollutants such as  $\text{NO}_3^-$  or  $\text{PO}_4^{3-}$ .

## Results and discussion

### Farm N and P budgets

The El Maitén field was fertilised with pig slurry, which was applied daily from June to mid-September 2011, providing 1280 kg N per hectare and 225 kg P per hectare. In addition, urea (December 2011) and a commercial compound fertiliser, which contains nitrate and ammonium forms, were applied (October 2011) according to common farming practices within the basin, in an average amount of 600 kg  $\text{ha}^{-1}$  each, making a potential contribution of 426 kg N per hectare and 25 kg P per hectare. This supplied a total of 1706 kg N per hectare and 250 kg P per hectare during the growing season of 2011 (June–December 2011: harvesting in May 2012).

The El Naranjal field was fertilised with (i) 750 kg  $\text{ha}^{-1}$  of a commercial compound fertiliser (25-10-10), which contains nitrate and ammonium forms, applied in October 2011; (ii) 750 kg  $\text{ha}^{-1}$  of urea applied in December 2011 and (iii) 15.6 t  $\text{ha}^{-1}$  of pig manure (daily dose of 260 kg  $\text{ha}^{-1}$ ) applied from June to August 2012. These supplied a total of  $590 \pm 10$  kg N per hectare and  $95 \pm 5$  kg P per hectare (according to the average composition of swine manure without bedding described by Hatfield et al. (1998)). The maize yield in the El Maitén and El Naranjal fields in the 2011–2012 season was 18 t  $\text{ha}^{-1}$ .

The El Caleuche field was fertilised with (i) 500 kg  $\text{ha}^{-1}$  of a commercial compound fertiliser (10-10-10), which contains nitrate and ammonium forms, supplying 50 kg N per hectare and 22 kg P per hectare in October 2011 and (ii) 700 kg  $\text{ha}^{-1}$  of urea supplying 322 kg N per hectare in November 2011. The maize yield obtained in the 2011–2012 season was 12 t  $\text{ha}^{-1}$ .

Estimates of the N and P surpluses indicated that about 1440 kg N per hectare and 720 kg P per hectare were susceptible to losses at El Maitén, representing the highest values among the three sites. This was followed by El Naranjal with 330 kg N per hectare and El Caleuche with 230 kg N and 105 kg per hectare (Tables 4 and 5). The potential P surplus at El Naranjal could not be determined due to missing data on available P in soil. It is important to note that most maize fields with mineral fertilisation in the area have an N and P surplus of around 360 kg N per hectare and 120 kg  $\text{P}_2\text{O}_5$  per hectare (Najera et al. 2015). Fuentes et al. (2015) reported annual mean soil  $\text{NO}_3\text{-N}$  concentration at 1 m depth around 50 mg  $\text{kg}^{-1}$  in El Maitén and El

**Table 3** Guidelines for water quality

Guideline <sup>a</sup>	Water quality variables <sup>b</sup>											
	DO ppm	T °C	pH	TS mg/L	NO <sub>3</sub> -N mg/L	NH <sub>4</sub> -N mg/L	N mg/L	PO <sub>4</sub> <sup>3-</sup> mg/L	SO <sub>4</sub> <sup>2-</sup> mg/L	COD mg/L	Tur NTU	EC μS/cm
NCh 1333	>5.0	<30	5.5–9.0	<500	<10	–	–	–	<250	–	–	<750
DS N°90	–	<20	6.0–8.5	–	–	–	<50	<10	<1000	–	–	–
DGA	>7.5	–	6.5–8.5	–	–	<0.5	–	–	<120	–	–	<600
EPA	–	–	6.5–8.5	–	<10	<30.0	–	–	<250	–	<5	–
FAO	–	–	6.5–8.4	–	<5	–	–	–	–	–	–	<700
Summary	>7.5	<20	6.5–8.5	<500	<10	<0.5	<50	<10	<120	–	<5	<600

<sup>a</sup> According to NCh 1333 (1987); D.S. N° 90 (2001); DGA (2004); EPA (2012/2004) and Ayers and Westcot (1994) (referred to as FAO)

<sup>b</sup> DO dissolved oxygen, T temperature, TS total solids, NO<sub>3</sub>-N nitrate-nitrogen, NH<sub>4</sub>-N ammonium-nitrogen, N total N, PO<sub>4</sub><sup>3-</sup> phosphate, SO<sub>4</sub><sup>2-</sup> sulphate, COD chemical oxygen demand, Tur turbidity, EC electrical conductivity

Naranjal, showing that these sites are N saturated and prone to NO<sub>3</sub>-N leaching. Similarly, Salazar et al. (2015) found in El Caleuche mean annual NO<sub>3</sub>-N soil concentration at observation wells located at 1 m depth ranging from 5 to 8 mg L<sup>-1</sup>, indicating a high risk of N contamination of the near open drainage channel. Therefore, the maize fields with pig slurry in our study, which represent an important number of farms related to pig production in the area, had an extremely high N and P surplus.

Seasonal variation of in-channel pollutant levels

The N and P balances for the sites (Tables 4 and 5) indicated a high risk of non-point source N and P pollution during the study period, with management, soil and climate factors giving rise to temporal variations in water quality parameters. Figures 2, 3, 4 and 5 show the time series for NO<sub>3</sub>-N, NH<sub>4</sub>-N and PO<sub>4</sub><sup>3-</sup>, including

precipitation for each site. It was found that in the MAI channel, the NH<sub>4</sub>-N and PO<sub>4</sub><sup>3-</sup> concentrations increased during winter in both 2011 and 2012 (Fig. 2), while high NO<sub>3</sub>-N concentrations were only observed during the period between June and September 2011. In the NAR channel, an increase in PO<sub>4</sub><sup>3-</sup> and NH<sub>4</sub>-N concentrations was observed between May and July 2012 (Fig. 3), although the values were not as high as those observed in the MAI channel (Fig. 2). In the TIN channel, the general tendency was similar, if not equal, to that in the NAR channel, with an increase in PO<sub>4</sub><sup>3-</sup> and NH<sub>4</sub>-N concentrations between May and July 2012 (Fig. 4). In the CLC channel, it was found that while the values for PO<sub>4</sub><sup>3-</sup> and NH<sub>4</sub>-N remained constant over time, the NO<sub>3</sub>-N concentrations increased between June and July 2012, and also between December 2012 and January 2013 (Fig. 5).

Annual cycling of the different variables has been described previously (e.g. in Chile by Ribbe et al. 2008).

**Table 4** Estimated nitrogen (N) surplus at the study sites during the period June 2011–July 2012

Study site <sup>a</sup>	Soil N supply <sup>b</sup> (kg N ha <sup>-1</sup> )	Fertilisation	Crop extraction <sup>c</sup>	N surplus
MAI	60	1706	–300	1466
NAR	60	590	–300	350
CLC	60	372	–200	232

<sup>a</sup> El Maitén (MAI), El Naranjal (NAR), El Caleuche (CLC)

<sup>b</sup> Soil N supply estimated according to Rodríguez (1993). These values are similar to those proposed by the soil nitrogen supply index system (field assessment method) in the DEFRA fertiliser manual (DEFRA 2010)

<sup>c</sup> Crop extraction of N, estimated using yield and an N uptake requirement of 16.4 kg N Mg<sup>-1</sup> of grain (Setiyono et al. 2010)

**Table 5** Estimated phosphorus (P) surplus at the study sites during the period June 2011–July 2012

Study site <sup>a</sup>	P-Olsen sowing <sup>b</sup> kg P ha <sup>-1</sup>	Fertilisation	Crop extraction <sup>c</sup>	P surplus
MAI	510	250	-40	720
NAR	- <sup>d</sup>	95	-40	- <sup>d</sup>
CLC	110	22	-27	105

<sup>a</sup>El Maitén (MAI), El Naranjal (NAR), El Caleuche (CLC)

<sup>b</sup>P-Olsen evaluated for soil samples (0–20 cm) taken during October 2011 at MAI and October 2012 at CLC

<sup>c</sup>Crop extraction of P, estimated using yield and the P internal requirement of 0.12 % determined by Mallarino et al. (2011) and a P uptake requirement of 2.3 kg P Mg<sup>-1</sup> of grain (Setiyono et al. 2010)

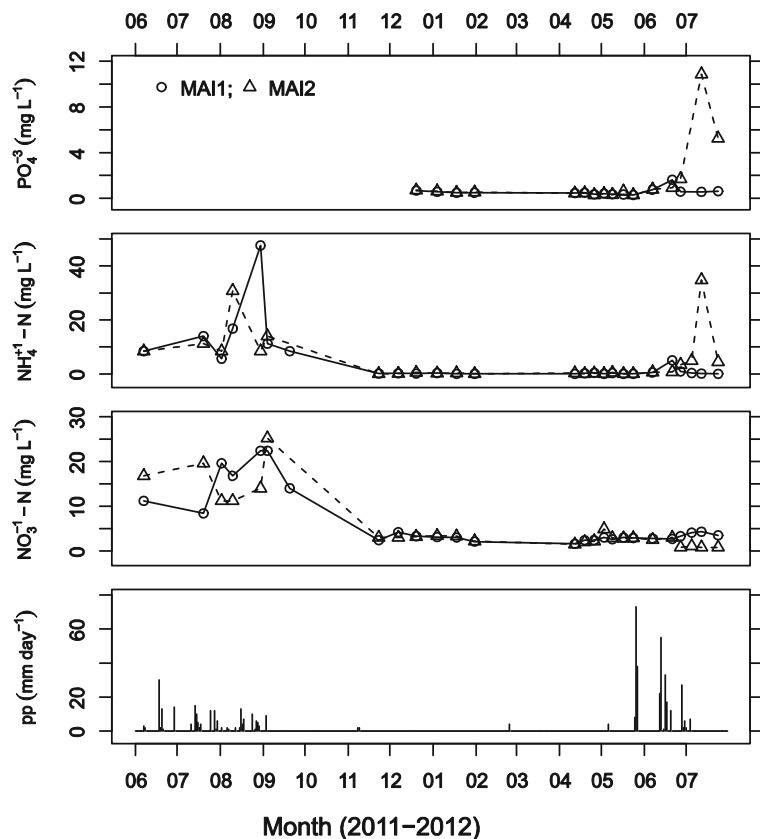
<sup>d</sup>Data not available

Bowes et al. (2011) examined the river Frome in the UK using a data set of 44 years and found that concentrations of P and NO<sub>3</sub>-N showed clear annual cycles, with the highest values in summer and winter, respectively. Despite the seasonality indicated for P concentrations,

Hanrahan et al. (2003) concluded for the Frome River that the majority of the PO<sub>4</sub><sup>3-</sup> load was transported during storm events in autumn/winter, from both non-point and point sources. In the present study, the increase in NO<sub>3</sub>-N, NH<sub>4</sub>-N and PO<sub>4</sub><sup>3-</sup> during autumn/winter was probably due to the rise in available water, which increased the capacity of the system for transporting contaminants from field to water bodies as subsurface water flow and surface runoff.

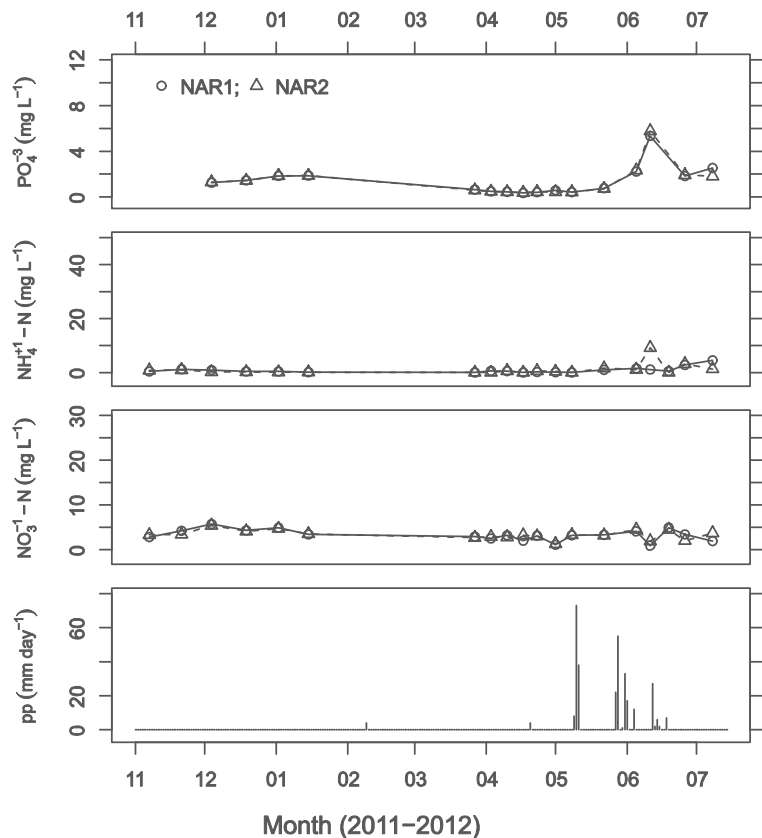
The increase in NH<sub>4</sub>-N and PO<sub>4</sub><sup>3-</sup> concentrations in the MAI channel during the wet winter period is explained by the daily applications of pig slurry between June and September, which supplied considerable amounts of both NH<sub>4</sub><sup>+</sup> (1.86 g NH<sub>4</sub><sup>+</sup> per kilogram wet material) and PO<sub>4</sub><sup>3-</sup> (0.66 g PO<sub>4</sub><sup>3-</sup> per kilogram wet material). Both these parameters showed a large coefficient of variation (CV) (Sánchez and González 2005), reflecting the within-season variability. Slurry application in the wet winter had an important effect, since the excess pig slurry applied to the field caused runoff to the drainage channel, thus contributing NH<sub>4</sub>-N and PO<sub>4</sub><sup>3-</sup>. In addition, an extra amount of PO<sub>4</sub><sup>3-</sup> could have been

**Fig. 2** Time series of NO<sub>3</sub>-N, NH<sub>4</sub>-N and PO<sub>4</sub><sup>3-</sup> concentrations at the inlet (MAI1) and outlet (MAI2) points of the MAI drainage channel between June 2011 and July 2012. Local precipitation (pp, mm day<sup>-1</sup>) is also shown





**Fig. 3** Time series of  $\text{NO}_3\text{-N}$ ,  $\text{NH}_4\text{-N}$  and  $\text{PO}_4^{3-}$  concentrations at the inlet (NAR1) and outlet (NAR2) points of the NAR drainage channel between November 2011 and July 2012. Local precipitation (pp,  $\text{mm day}^{-1}$ ) is also shown



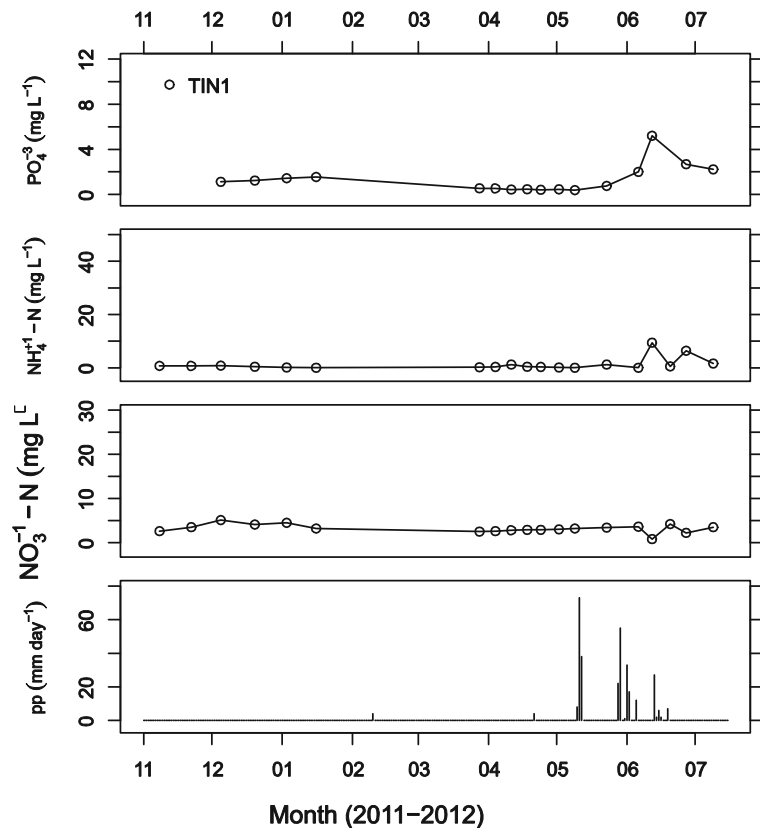
transported by leaching to the nearby water body, explaining part of the P load arriving there. This P lixiviation issue is particularly problematic in sandy soils with heavy manure applications and shallow watertables, as was the case for the MAI channel, due to rapid soil water flow and low P adsorption capacity (Nelson et al. 2005; Kang et al. 2011; Salazar et al. 2011).

In the NAR channel, the increase in the concentrations of  $\text{PO}_4^{3-}$  and  $\text{NH}_4\text{-N}$  between May and July 2012 was probably due to the similar soil, water availability and winter manure application to the neighbouring field as with the MAI channel. However, the pollutant concentrations were lower in the NAR channel because of the smaller amounts of N and P fertiliser applied to the El Naranjal field, which were less than half the levels applied to the El Maitén field (Tables 4 and 5). In this regard, it is important to consider that the study region has the largest concentration of pig production in Chile (ODEPA-CHILE 2007), so other discharges of pig slurry can probably occur on fields placed upstream of NAR1, thus causing similar effects as seen in the MAI

channel. However, this issue was not investigated in the present study. This is also true for every other channel, since it was not within the scope of this study to determine whether the flow of pollutants into the channels occurs preferentially from runoff or shallow lateral water movements.

The large variation in the concentrations of inorganic forms of N in pig slurry is the possible cause of the higher  $\text{NO}_3\text{-N}$  values in the MAI channel observed between June and September 2011 compared with winter (May–July) 2012. For instance, Sánchez and González (2005) reported a CV of 58.33 % for inorganic N in pig slurry (in which  $\text{NH}_4^+$  is the prevalent N form) in a study which included 151 samples from 83 farms in Spain. Moreover, lower annual precipitation in both years (267 mm in 2011 and 311 mm to end of July 2012) may have reduced the movement of  $\text{NO}_3\text{-N}$  from soil to nearby water bodies and may also have caused a decrease in N mineralisation in coarse-textured soils (Austin et al. 2004). Based on this, the pig slurry, which was the only N source applied during winter, probably ranked as the most important (and

**Fig. 4** Time series of  $\text{NO}_3\text{-N}$ ,  $\text{NH}_4\text{-N}$  and  $\text{PO}_4^{3-}$  concentrations at the monitoring point placed in the confluence channel (TIN1) between November 2011 and July 2012. Local precipitation (pp,  $\text{mm day}^{-1}$ ) is also shown



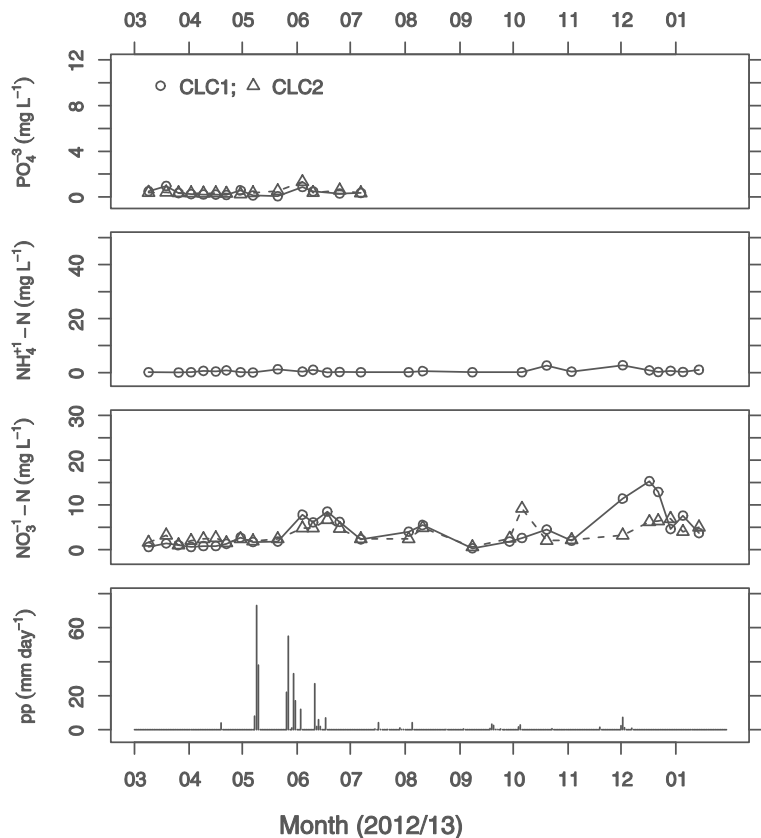
uncertain) source of  $\text{NO}_3\text{-N}$ , which is capable of passing directly from field to drainage channel during wet winters, thus explaining the variation in  $\text{NO}_3\text{-N}$  in June and July in the different years.

In the CLC channel, the  $\text{NO}_3\text{-N}$  concentrations increased between June and July 2012 and from December 2012 to January 2013, probably due to increased discharge of water from field to channel through the Cm horizon, thus avoiding leaching. This effect has been observed previously by Hofmann et al. (2004), who evaluated the  $\text{NO}_3\text{-N}$  concentrations in tile drains located in maize fields on silty clay soils (fine-silty, mixed mesic Typic Endoaquoll) in west central Indiana over a 6-year period. They found variations in  $\text{NO}_3\text{-N}$  concentrations ranging from 7 to 15  $\text{mg L}^{-1}$  and in discharge ranging from 5 to 40  $\text{m}^3 \text{ha}^{-1} \text{day}^{-1}$  and concluded that discharge was the dominant factor determining temporal variations in N export. The  $\text{PO}_4^{3-}$  concentrations in drainage water can be expected to increase during winter, in response to the greater P loads arising from the increase in P solubility produced by a shallow watertable (Sanchez Valero et al. 2007),

particularly due to the Cm horizon in the soil bordering the CLC channel. However,  $\text{PO}_4^{3-}$  did not increase in the CLC channel. This was probably the result of two mechanisms: (1)  $\text{PO}_4^{3-}$  leaching is retarded in clay soils due to their high P adsorption capacity and (2) the majority of  $\text{PO}_4^{3-}$  runoff is related to storm events (Hanrahan et al. 2003), so changes in P content occur in rapid temporal events, which were not captured by the grab water non-continuous monitoring used in this study (Cassidy and Jordan 2011). It is important to note that the  $\text{NH}_4\text{-N}$  values in the CLC channel remained constant during the study period, probably due to the high adsorption capacity of the El Caleuche clay soil. In addition,  $\text{NH}_4\text{-N}$  and  $\text{PO}_4^{3-}$  did not show variations in concentrations because manure and slurry were not applied and the field bordering the CLC channel received considerably less fertiliser overall than those bordering the MAI and NAR channels (Tables 4 and 5).

At the pristine reference site, the  $\text{NO}_3\text{-N}$ ,  $\text{NH}_4\text{-N}$  and  $\text{PO}_4^{3-}$  concentrations (mean  $\pm$  standard deviation) obtained between December 2013 and July 2014 ( $n = 10$ ) were  $0.89 \pm 0.22$ ,  $0.32 \pm 0.37$  and  $0.26 \pm 0.05 \text{ mg L}^{-1}$ ,

**Fig. 5** Time series of  $\text{NO}_3\text{-N}$ ,  $\text{NH}_4\text{-N}$  and  $\text{PO}_4^{3-}$  concentrations at the inlet (CLC1) and outlet (CLC2) points of the CLC drainage channel between March and July 2012. Local precipitation (pp,  $\text{mm day}^{-1}$ ) is also shown



respectively. These values were considerably lower than those observed in the drainage channels around the maize fields, even during winter, which suggests that excessive slurry application during winter, when the soil is moist, more rainfall occurs and watertables are at shallow depth, generates a very high risk of N and P runoff to nearby drainage channels.

**Principal component analysis**

Principal component analysis is a statistical approach that can be used to analyse inter-relationships among a large number of variables, thus condensing information regarding inter-correlated variables into statistical variables (principal components) which are able to summarise the information presented in the original variables. The starting point for the PCA here was a matrix of order  $47 \times 12$  (rows  $\times$  columns), with the variables consisting of the 12 water quality parameters measured. The correlation matrix among different water quality parameters is presented in Table 6. Pearson correlation coefficients greater than 0.5 represented 31 % of the

total correlations, with DO showing inverse correlations with EC, TS, total N,  $\text{NH}_4\text{-N}$  and  $\text{PO}_4^{3-}$  (see correlation matrix in Table 6). The EC showed positive correlations with TS, total N and  $\text{SO}_4^{2-}$ . The Bartlett’s sphericity test, performed with the correlation matrix and 66 degrees of freedom, resulted in a significant ( $p < 0.05$ ) difference, indicating sufficiency of data correlation for performing PCA.

The data were scaled and centred in order to avoid the disparity of data units. The Kaiser’s criterion suggests that only components with variance above 1 must be conserved. In our analysis, only the first three components fulfilled this requirement (Fig. 6). The cumulative proportion of variance explained for each one of the first three principal components was 42.5, 62.6 and 74.3, respectively (Table 7).

The first component had majors loadings for DO with a negative vector and total N,  $\text{NH}_4\text{-N}$ ,  $\text{PO}_4^{3-}$ , EC, TS and COD and was thus probably related with the MAI channel, where higher loadings of these compounds were observed in the channel during winter (Fig. 7). The  $\text{NH}_4\text{-N}$ ,  $\text{PO}_4^{3-}$  and total N loadings are

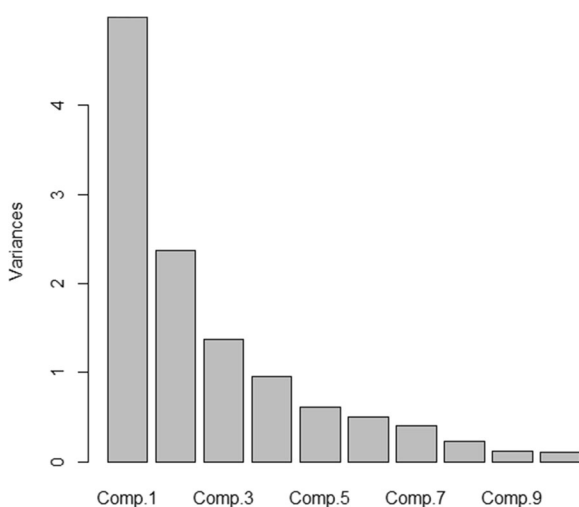
**Table 6** Correlation matrix of water quality parameters measured in the drainage channels in this field study

Variables <sup>a</sup>	DO	T	pH	EC	TS	COD	Tur	N	NO <sub>3</sub> -N	NH <sub>4</sub> -N	PO <sub>4</sub> <sup>-3</sup>	SO <sub>4</sub> <sup>-2</sup>
DO	1.00	0.78	0.39	0.00	0.00	0.00	0.07	0.00	0.42	0.00	0.00	0.04
T	0.04	1.00	0.00	0.11	0.29	0.46	0.44	0.14	0.01	0.43	0.65	0.03
pH	0.13	0.46	1.00	0.51	0.17	0.51	0.60	0.63	0.01	0.99	0.44	0.03
EC	-0.61	-0.24	-0.10	1.00	0.00	0.03	0.34	0.00	0.00	0.03	0.01	0.00
TS	-0.75	-0.16	-0.20	0.77	1.00	0.03	0.36	0.00	0.09	0.00	0.00	0.00
COD	-0.44	-0.11	-0.10	0.31	0.32	1.00	0.00	0.00	0.54	0.00	0.00	0.13
Tur	-0.26	-0.11	0.08	0.14	0.14	0.85	1.00	0.00	0.73	0.01	0.00	0.44
N	-0.59	-0.22	-0.07	0.57	0.58	0.75	0.55	1.00	0.20	0.00	0.00	0.03
NO <sub>3</sub> -N	0.12	-0.39	-0.40	0.43	0.25	0.09	0.05	0.19	1.00	0.19	0.30	0.00
NH <sub>4</sub> -N	-0.58	-0.12	0.00	0.31	0.46	0.59	0.40	0.77	-0.20	1.00	0.00	0.61
PO <sub>4</sub> <sup>-3</sup>	-0.67	-0.07	0.11	0.37	0.47	0.67	0.51	0.86	-0.16	0.78	1.00	0.42
SO <sub>4</sub> <sup>-2</sup>	-0.30	-0.31	-0.31	0.73	0.42	0.23	0.11	0.33	0.47	0.08	0.12	1.00

DO dissolved oxygen, T temperature, EC electrical conductivity, TS total solids, COD chemical oxygen demand, Tur turbidity, N total N, NO<sub>3</sub>-N nitrate-nitrogen, NH<sub>4</sub>-N ammonium-nitrogen, PO<sub>4</sub><sup>3</sup> phosphate, SO<sub>4</sub><sup>2</sup> sulphate

<sup>a</sup> Correlation coefficients >0.5 are indicated in italic

associated with slurry application increasing the EC, TS and COD and decreasing DO parameters (Sánchez and González 2005). This suggests that, in channels with a direct influence of slurry application on neighbouring fields, any of the water quality parameters associated with the slurry composition can be evaluated in order to determine whether the channel is been influenced by the neighbouring field, as well as every other physical or chemical parameter involved with slurry application, such as EC, TS and COD. Furthermore, the



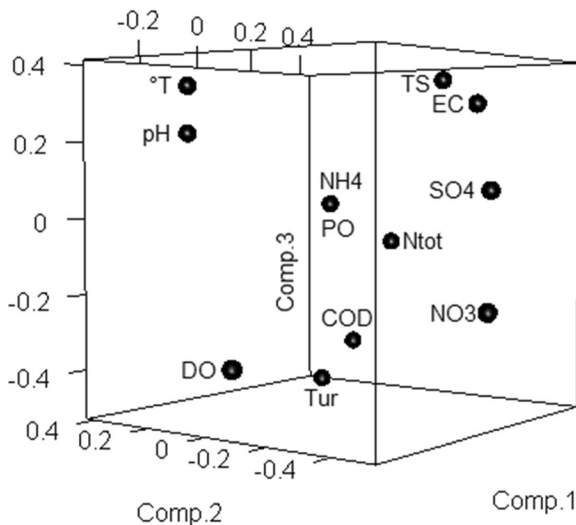
**Fig. 6** Principal component analysis screen plot. The first three components were selected according to Kaiser's criterion

observations and analysis suggest that the most representative of the parameters studied in this regard was total N, which was not involved in any other principal component (Table 7).

**Table 7** Non-rotated loadings for water quality parameters measured in drainage channels in the field study, where comp. 1–3 are the first three components in principal component analysis

Variables	Comp. 1	Comp. 2	Comp. 3
DO	-0.344		-0.362
T	-0.121	0.336	0.354
pH		0.389	0.227
EC	0.321	-0.288	0.306
TS	0.332	-0.163	0.374
COD	0.342	0.169	-0.385
Tur	0.258	0.212	-0.490
N	0.407		
NO <sub>3</sub> -N		-0.491	-0.237
NH <sub>4</sub> -N	0.334	0.249	
PO <sub>4</sub> <sup>-3</sup>	0.364	0.274	
SO <sub>4</sub> <sup>-2</sup>	0.217	-0.407	
Standard deviation	2.233	1.540	1.171
Proportion of variance	0.425	0.202	0.117
Cumulative proportion	0.425	0.626	0.743

DO dissolved oxygen, T temperature, EC electrical conductivity, TS total solids, COD chemical oxygen demand, Tur turbidity, N total N, NO<sub>3</sub>-N nitrate-nitrogen, NH<sub>4</sub>-N ammonium-nitrogen, PO<sub>4</sub><sup>3</sup> phosphate, SO<sub>4</sub><sup>2</sup> sulphate



**Fig. 7** Three-dimensional plot for the first three principal components (comp. 1–3) for which loadings were plotted. *DO* dissolved oxygen, *T* temperature, *EC* electrical conductivity, *TS* total solids, *Tur* turbidity, *Ntot* total nitrogen, *NO3* NO<sub>3</sub>-N, *NH4* NH<sub>4</sub>-N, *PO* PO<sub>4</sub><sup>3-</sup>, *SO4* SO<sub>4</sub><sup>2-</sup>

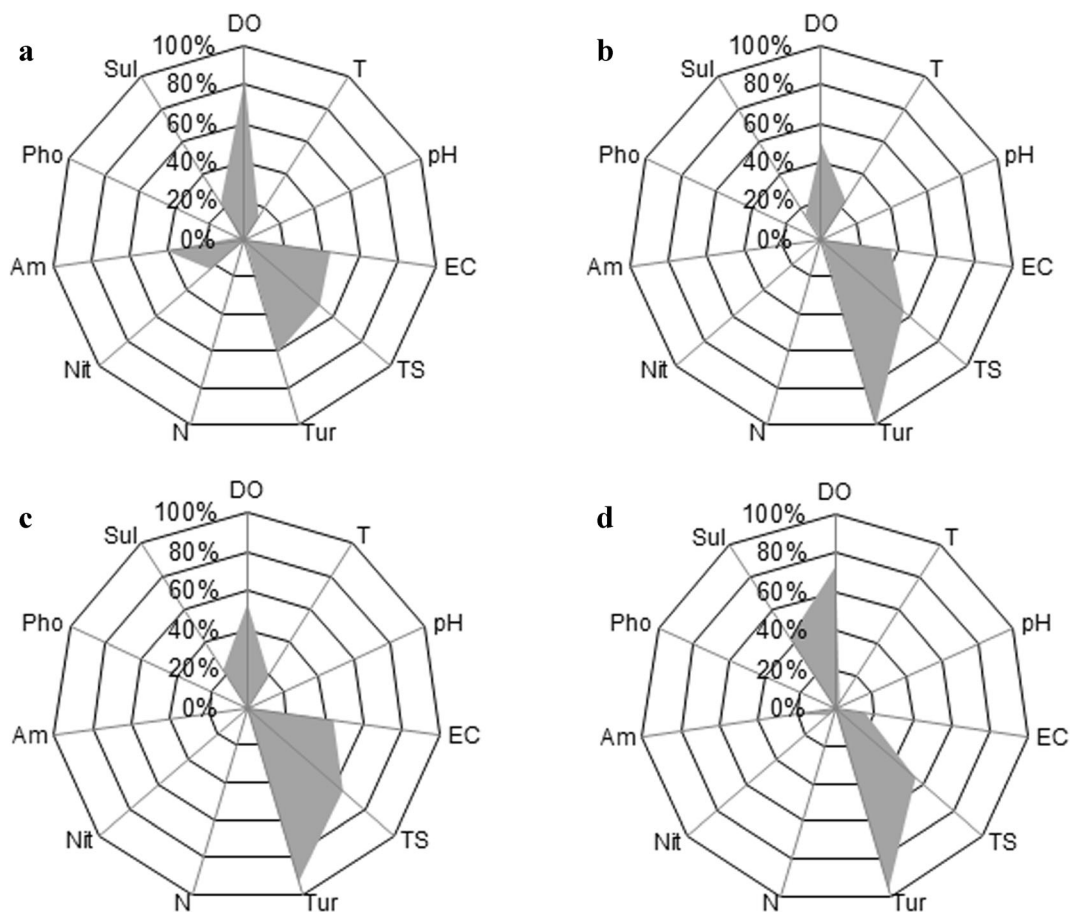
The second component had major loadings for NO<sub>3</sub><sup>-</sup>N, SO<sub>4</sub><sup>2-</sup> (negative vectors), and pH and temperature (positive vectors) (Table 7). This component suggests that while NO<sub>3</sub>-N and SO<sub>4</sub><sup>2-</sup> concentrations in the channels increased, temperature and pH decreased. During winter, when the temperature was obviously low, the concentrations of NO<sub>3</sub>-N and SO<sub>4</sub><sup>2-</sup> in the drainage channels increased due to the increased water availability (Fig. 7).

**Water characterisation**

Water characterisation results for the 2011–2012 season in the MAI, NAR and TIN channels, showing the percentage of total samples exceeding the maximum permissible standards for each measured variable, are presented in Fig. 6. The MAI channel showed values above the maximum permissible standards for DO, temperature, EC, TS, turbidity, SO<sub>4</sub><sup>2-</sup> NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> concentration. The percentage of samples exceeding the maximum permissible standards for NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> was considerable (41 and 24 %, respectively). On the other hand, the CLC channel showed values above the maximum permissible standards for DO, EC, TS, turbidity and NH<sub>4</sub><sup>+</sup> (Fig. 8). As a result, no channel can be classified as irrigation class 1 according to Chilean standards.

Previous studies performed in Chile mainly evaluated the NO<sub>3</sub>-N dynamics in basins instead of general water quality variables. In order to establish the water quality parameters for a basin, DGA (2004) performed an analysis of data from different sources and reported levels for the nearest river (Tinguiririca) of EC between 200 and 300 μS cm<sup>-1</sup> without seasonal fluctuation; pH between 7.0 and 7.5; DO about 9.5 mg L<sup>-1</sup> without seasonal fluctuation and SO<sub>4</sub><sup>2-</sup> between 52 and 60 mg L<sup>-1</sup> without seasonal fluctuation. Based on this analysis, DGA (2004) classified the water quality of Tinguiririca River as class 0, “Best”. These results differ from the findings for drainage channels in the present study, but obviously these are not comparable due to differences in scale. Similarly, we found that in the pristine reference site, the water quality variables fell within class 0, with pH ranging from 7 to 8 and mean values (*n* = 10) of EC 135 μS cm<sup>-1</sup>, DO 12 mg L<sup>-1</sup>, TS 129 mg L<sup>-1</sup> and turbidity 2.9 NTU without seasonal fluctuation. We could not find any previous data with which to compare our water quality results for drainage channels in the central valley of Chile.

Regarding NO<sub>3</sub>-N, Iriarte (2007) made a risk classification for the *Cachapoal* basin, located on the northern edge of the Tinguiririca River basin and concluded that the watershed represents a medium to high risk of lixiviation, with Inceptisols having a high risk. He also found that the majority of the samples taken (63 % from 59 samples collected along *Cachapoal watershed*) from rivers (4), irrigation channels (27), shallow wells (10) and deep wells (18) in that basin contained NO<sub>3</sub>-N concentrations above the standard of 10 mg L<sup>-1</sup>. Another study, conducted by Golembeski (2004), found high NO<sub>3</sub>-N concentrations (>10 mg L<sup>-1</sup>) in all wells (17 in total) sampled in the Tinguiririca basin. In contrast, Ribbe et al. (2008), in a study performed in a basin in the *Valparaíso* Region, reported that levels of NO<sub>3</sub>-N remained between 2 and 10 mg L<sup>-1</sup> during the season 2004/2005. However, the N fertilisation rates of fruit trees (150 kg N per hectare per year), horticulture (152 kg N per hectare per year) and greenhouse crops (256 kg N per hectare per year) in the Valparaíso Region are generally lower (152, 150 and 276 kg N per hectare per year, respectively, according to Ribbe et al. 2008) than the rates applied to maize fields in the O’Higgins Region. Finally, Donoso et al. (1999) showed with a simulation study of the Chilean Central Valley that NO<sub>3</sub>-N contamination is high, particularly contamination of the groundwater. However, those authors did not find



**Fig. 8** Radial charts of water quality. The grey area indicates the percentage of the total number of samples that exceeded the standard. (a) MAI channel (including both points), (b) NAR channel (idem), (c) TIN channel, (d) CLC channel (including both

points). *DO* dissolved oxygen, *T* temperature, *EC* electrical conductivity, *TS* total solids, *Tur* turbidity, *N* total nitrogen, *Nit*  $\text{NO}_3^-$ -N, *Am*  $\text{NH}_4^+$ -N, *Pho*  $\text{PO}_4^{3-}$ , *Sul*  $\text{SO}_4^{2-}$

values of  $\text{NO}_3^-$ -N exceeding the permissible standards for the O'Higgins Region. Although the problem of  $\text{NO}_3^-$ -N pollution was clearly proven in those studies, once again the scale of the present study differed, so no comparison is possible. However, the high levels of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  found in drainage channels in this study suggest that there was a high risk of non-point source N pollution from maize cultivation during the study period, especially in the MAI and CLC channels.

To date, practically no studies of  $\text{PO}_4^{3-}$  pollution have been performed in the central valley of Chile. Pizarro et al. (2010) evaluated the P dynamics in a nearby river named Rapel, but found that trend were not conclusive. In our study,  $\text{PO}_4^{3-}$  concentrations exceeding the maximum permissible standards were not observed, but the grab water non-continuous monitoring used in the study did not allow high runoff events,

possibly causing sediments and associated P loss to drainage channels, to be captured.

Overall, great emphasis must be placed on good agronomic management of fields neighbouring drainage channels, including accurate calculation of N and P fertiliser rates (Najera et al. 2015) and establishment of suitable mitigation measures, such as vegetated buffer strips (Salazar et al. 2015).

## Conclusions

The nitrogen (N) and phosphorus (P) balances for three maize fields in a river basin in central Chile indicated a high risk of N and P non-point source pollution, when N and P surplus were estimates in values ranging from 232 to 1466 kg N per hectare and from 105 to 720 kg P per

hectare. Particularly, the maize fields with pig slurry had the highest N and P surplus. Elevated levels of  $\text{NH}_4\text{-N}$  and  $\text{PO}_4^{3-}$  in the drainage channels were usually observed during the winter period, which were related to the pig slurry applications, while  $\text{NO}_3^-$  concentrations did not show a clear tendency.

It was found that the  $\text{NH}_4\text{-N}$ ,  $\text{PO}_4^{3-}$  and total N loadings are associated with slurry application increasing the EC, TS and COD and decreasing DO parameters. In addition, no channel can be classified as irrigation class 1 according to Chilean standards because had a number of samples exceeding the maximum permissible standards, mainly for  $\text{NH}_4^+$  and  $\text{NO}_3^-$ .

The results suggest that excessive slurry applications during the winter, when the soil is moist, more rainfall occurs and watertables are at shallow depth, create a very high risk of N and P runoff to drainage channels. Overall, great emphasis must be placed on good agronomic management of fields neighbouring drainage channels, including accurate calculation of N and P fertiliser rates and establishment of suitable mitigation measures.

**Acknowledgments** We thank Professor María Adriana Carrasco, Dr. Julio Haberland and Dr. Víctor García de Cortázar from the University of Chile for giving valuable advice and suggestions on the manuscript.

#### Compliance with ethical standards

**Funding** This study was funded by FONDECYT de Iniciación 2011 project N°11110464 and by Universidad de Chile project U-Inicia 11/09.

**Conflict of Interest** The authors declare that they have no competing interests.

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