# Water quality assessment of streams and rivers for irrigation in Southern Continental Patagonia

# Evaluación de la calidad del agua para irrigación en ríos y arroyos de la Patagonia Austral Continental

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# ABSTRACT

This work aimed to analyze and classify the suitability of freshwater sources for irrigation in three large hydrographic regions of Southern Continental Patagonia: Coyle, Serrano, and Gallegos. In these regions, there is a lack of information on the irrigation suitability of surface waters. For this, 74 surface water locations were sampled from 42 watercourses in Santa Cruz province and Magallanes region in Argentina and Chile, during dry and wet seasons between 2017 and 2019. The concentration of ions of agricultural interest was evaluated in the laboratory. The pH ranged between 6.1-9.5 with little seasonal variability. The prevailing ions were Ca<sup>2+</sup> Mg<sup>2+</sup> and HCO<sub>3</sub>, while the lower cation concentration was K<sup>+</sup>. The Sodium Adsorption Ratio was 0.58 ± 0.21 during winter and 0.46 ± 0.15 in summer. Most waters in the region have electrical conductivity values below 250  $\mu$ S/cm and may be categorized as low-salinity waters. We determined no significant hazards for crops, vegetables, and pasture production in terms of the combined salinity and sodicity indicators. However, a potential negative impact on soil structural stability mainly due to Na<sup>+</sup> concentration must be considered for the implementation of suitable irrigation projects.

#### Keywords

agriculture • hydrochemistry • hydrology

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#### RESUMEN

En este trabajo se analizó y clasificó la aptitud de fuentes de agua para riego en tres regiones hidrográficas de la Patagonia Austral (Argentina): Coyle, Serrano y Gallegos. Estas regiones carecen de antecedentes sobre la aptitud de sus aguas para la irrigación. A fin de proporcionar esta información, se analizaron en laboratorio muestras de aguas superficiales de 74 locaciones en 42 cursos de la provincia de Santa Cruz en Argentina y de la región de Magallanes en Chile, durante las estaciones seca y húmeda del año, entre 2017 y 2019. Se evaluó la concentración de cationes y aniones de interés agrícola. Las aguas mostraron un rango de pH entre 6,1 y 9,5 con poca variabilidad estacional. Los cationes predominantes fueron Ca<sup>2+</sup> y Mg<sup>2+</sup> y menor en K<sup>+</sup>, siendo HCO<sub>2</sub>, el principal anión. El SAR se encontró entre 0,58 ± 0,21 durante el invierno y 0,46 ± 0,15 en verano. Con excepción de algunas muestras, la mayoría de las aguas tienen valores de conductividad eléctrica inferiores a 250 μS/cm y pueden catalogarse como aguas de baja salinidad. No se detectaron peligros significativos para la producción de cultivos, hortalizas y pastos en términos de los indicadores combinados de salinidad y sodicidad. Sin embargo, existe un potencial impacto negativo en la estabilidad estructural del suelo debido principalmente a la concentración de Na<sup>+</sup> que debe tenerse en cuenta para la implementación de proyectos de riego.

#### **Palabras clave**

agricultura • hidroquímica • hidrología

### INTRODUCTION

Patagonia occupies a vast territory in southern Argentina and Chile. This includes various heterogeneous ecological areas, mainly because of the diverse edaphoclimatic characteristics that determine the predominance of arid, semi-arid, and very arid bioclimatic zones (1). The grassy and shrub steppes on plateaus and glaciofluvial valleys represent the main features of the landscape. The main socioeconomic activities are extensive sheep and cattle farming and agriculture in irrigated valleys. These environments have been enduring constant degradation for little more than a century since the initial European settlement at the end of the 19<sup>th</sup> century. This process still occurs mainly because of the combination of poor agricultural management practices, livestock overgrazing, and recurrent drought events. In this context, plant communities and agro-productive activities are severely limited by water deficit.

Consumptive use for agricultural production represents the greatest demand for freshwater in the world, with an estimate of 70% globally by 2020 (27) and in Argentina (10). This use is also one of the most inefficient due to overexploitation, lack of reuse, contamination with agrochemicals, low irrigation efficiency, and flooding (24).

Irrigating natural grasslands in river valleys of Southern Patagonia has exerted increasing pressure on the consumptive use of surface water, mainly due to the frequent drought events in recent decades. In arid and semi-arid regions of Patagonia, this practice can significantly improve natural grass yields up to 10-20 times, mainly in wetlands (4). Irrigation to supplement the rainfall in the warm months and the snow melting in early spring arises as an alternative during critical stages of the grasslands growing season and cultivated pastures (15) in traditional dry farming lands. However, irrigation may produce negative environmental impacts. Soil sodicity, salinity or ion toxicity caused by poor management irrigation practices in hazardous situations (25) are some of the greatest environmental pressures of agriculture worldwide (11). Because of these potential negative effects, it is important to better understand of how water quality influences the management of irrigated agriculture.

Successful irrigation projects involve appropriate quantification and distribution of the required water and adequate control of its quality (5, 11, 25). Currently, only salinity and sodicity hazards combined have caused 23.5% of the total land degradation by irrigation in Argentina, which represents 500.000 ha (9). Therefore, regular monitoring of water quality for irrigation in this region becomes relevant to support decisions on sustainable

use, management, and conservation of both water and soil (15). Although there has been considerable interest in this topic around the globe, there is a lack of studies in Patagonia.

In this study, we analyze and classify the suitability of freshwater sources for irrigation in the southernmost region of the Southern Continental Patagonia. It was carried out from a set of widely used indicators for the detection of sodicity and salinity hazards. We analyzed 148 surface water samples from 42 watercourses in the Santa Cruz province (Argentine) and Magellan region (Chile) during the dry and wet seasons between 2017 and 2019. We evaluated the following indicators: Sodium Adsorption Ratio (SAR), adjusted SAR, Residual Sodium Carbonate, Soluble Sodium Percentage, Standardized Electrical Conductivity, Total Dissolved Solids, Effective Salinity and Potential Salinity.

#### **MATERIALS AND METHODS**

#### Study site

The study area focused on three major hydrographic regions (HR) in Southern Continental Patagonia, covering 57,406.4 km<sup>2</sup> of which 76.1 % is located in Argentina, and 23.9% in Chile (figure 1). The first region, the Serrano River basin (HR11), covers 8,638.8 km<sup>2</sup> with 23.6% located in Argentina, in the upper basin (6). This transboundary system with a predominantly nivo-glacial mixed regime drains into the Pacific Ocean, exhibiting an average annual flow of 2,964.3 hm<sup>3</sup>. About 164.0 hm<sup>3</sup>/year (5.5%) is produced in the Argentine side. The second region, the Gallegos River basin (HR13), is another transboundary territory that flows into the Atlantic Ocean, with an extension of 19,289.1 km<sup>2</sup>, with 63.2 % in Argentina. It also has a predominantly nivo-pluvial mixed flow regime and produces an annual surface runoff of slightly over 1,000 hm<sup>3</sup>. The last region, the Coyle River basin (HR12), extends across 29,424.0 km<sup>2</sup> exclusively in Argentina. Characterized by a mainly nival flow regime it produces an annual runoff of 39.9 hm<sup>3</sup>.



Figure 1. Sampling sites in rivers, streams, and creeks of Southern Continental Patagonia.Figura 1. Sitios de muestreo en ríos y arroyos de la Patagonia Austral Continental.

# Data collection and analysis of Argentine waters

In Southern Patagonia, the main demand for complementary irrigation of crops, pastures, and natural grasslands occurs between late winter and early spring (September and October, corresponding to a wet season for HR12 and HR13, and a dry season for HR11) and late summer (February and March). Fifty-five surface water samples from different locations along 28 watercourses in the Santa Cruz province were collected during the dry and wet seasons. A total of 110 samples were obtained between 2017 and 2019 (figure 1, page XXX). Both sampling moments represent opposite moments of the annual hydrograph.

Watercourses were classified as permanent, intermittent, or ephemeral types according to their annual discharge and the percentage of annual exposure of the channel bed (23). We used a quantitative watercourses classification adapted from Jowett (2020) to contextualize and facilitate the interpretation of results: creeks (mean annual discharge <1 m<sup>3</sup>/s), streams (<5 m<sup>3</sup>/s), and rivers (>5 m<sup>3</sup>/s).

On-site equipment handling procedures, water sampling methods, conditioning for conservation and transport were implemented in accordance with the protocols for water quality sampling suggested by USGS (26). The concentration of ions of agricultural interest was evaluated in the laboratory. Sodium (Na<sup>+</sup>) and Potassium (K<sup>+</sup>) were determined by flame photometry according to standards SM-3500-Na B and SM-3500-K B. Calcium (Ca<sup>2+</sup>) and Magnesium ( $Mg^{2+}$ ) were analyzed by complexometric titration with EDTA at pH 12 using murexide as the indicator for the first case, and at pH 10 with Eriochrome® Black T for the second, according to standard SM-2340-C. The presence of Chloride (Cl<sup>-</sup>) was determined through the standard SM-4500-Cl<sup>-</sup> B; Sulfate (SO<sub>4</sub><sup>2-</sup>) through precipitation with Barium and by turbidimetry monitoring according to SM-4500-SO<sub>4</sub><sup>-2</sup> E standard. Carbonate (CO<sub>3</sub><sup>2-</sup>) and Bicarbonate (HCO<sub>3</sub>) were determined through titration with 0.1 N hydrochloric acid using phenolphthalein and helianthin as indicators, according to standard SM-2320 B. The pH and specific electrical conductivity -ECw- were determined in situ according to SM-4500-H<sup>+</sup> B and SM-2510 B standards, through a calibrated portable probe. The total dissolved solids (TDS) were determined through a gravimetric method on the dry residue according to the SM-2540 C standard.

### Data collection and analysis of Chilean waters

Water quality data publicly available from the Chilean governmental authority (7) was used for 14 creeks, streams, and rivers in 19 different locations, in the same time periods sampled in the Argentine sector. Major cations (Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup>) were determined by atomic absorption spectroscopy according to the standard SM-3111 B. The anions Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, CO<sub>3</sub><sup>2-</sup>, and HCO<sub>3</sub>, the pH and EC were determined through the same procedures used for the Argentine samples.

## Data processing and water quality analysis

All 148 water samples analyzed in the present work (55 from Argentina + 19 from Chile, for each season) showed less than 5% absolute average error in the electroneutrality condition from major ion concentrations. Water types were classified according to their chemical composition and dynamics based on Piper (21).

Four indicators were used to evaluate the sodium hazard. First, the Sodium Adsorption Ratio (SAR), widely used for the suitability of typical irrigation waters (14, 31), constitutes a strong predictor of the soil exchangeable sodium percentage (11, 30). This standard SAR equation was adjusted (SAR<sub>adj</sub>) when alkaline waters contained relatively high concentrations of Mg<sup>2+</sup>, Ca<sup>2+</sup> as well as carbonates (CO<sub>3</sub><sup>-2</sup>) and bicarbonates (HCO<sub>3</sub>). This situation could raise the relative proportion of Na<sup>+</sup> in solution concentrations after precipitation of carbonate salts with Ca<sup>2+</sup> and Mg<sup>2+</sup> (3, 8, 12, 14, 25, 31), particularly in soils of arid environments subject to high evapotranspiration or evaporation rates (1). Weiner (2013) suggests the application of SAR<sub>adj</sub> to water samples with >200 mg/l HCO<sub>3</sub> and pH>8,5. Among different approaches for its calculation, we used one suggested by Lesch and Suarez (2009). A third indicator used was the Residual Sodium Carbonate (RSC), defined by Eaton (1950). Finally, we used the Soluble Sodium Percentage (SSP) to complement the SAR. This is useful for characterizing water hardness (30) to anticipate the long-term negative effects of Na<sup>+</sup> on the soil (22).

Four indicators were used to evaluate the salinity hazard. First, the Standardized Electrical Conductivity -ECw- (in  $\mu$ S/cm) and Total Dissolved Solids -TDS- (in mg/l) were analyzed. Both are highly correlated with the total concentration of soluble salts (31) and, consequently, widely used for the interpretation of the saline hazard in irrigation waters (30). Even in terms of potential sodicity hazard, SAR is best interpreted when analyzed together with ECw (14). Second, the Effective Salinity (ES) defined by Marín *et al.* (2002), is useful when some less soluble salts precipitate in the form of carbonates or sulfates in contact with the soil. Under such circumstances, ECw tends to overestimate the impact of the real salinity. Finally, the Potential Salinity (PS) indicator was used. This is often recommended when soil moisture content drops below 50%, and chlorides and sulfates are the last salts to remain in solution (16, 20). This is a common situation in the summer for Southern Patagonian environments.

The results were analyzed using arithmetic means and standard deviations in different sample groupings, according to hydrographic regions. The Shapiro-Wilks normality test (p<0.05) was conducted before the arithmetic analysis. Specific relationships were established between analytical results and seasonal flows by Pearson's linear correlation coefficient at p<0.05.

### **RESULTS AND DISCUSSION**

#### **Descriptive analysis**

Water temperature plays a critical role in numerous physical and chemical processes essential for the aquatic environment including gas and some ionic compounds solubility, biodegradability of substances, toxicity of chemicals, metabolic activity, nutrient cycles, and primary production (28). During the sampling campaigns, the mean water temperature ranged between 4.9 and 7.6°C in winter and 8.2 to 11.5°C in summer (table 1, page XXX). Extreme values ranged from 0.2 to 14.8°C during winter, with the lowest values occurring in the mountain range (HR11 and southwestern HR12). In contrast, summer water temperatures ranged from 2.1 to 19.9°C, with the highest values found in small creeks and streams in the center of the HR12 and HR13 basins.

Another major controlling variable of chemical processes in aquatic environments is pH (28). All regional waters showed a pH range between 6.1 and 9.5 with little seasonal variability and without a relationship with their flow regimes or annual discharge. The proximity to the western mountain range narrowed pH values to 7.7-7.9 in streams and rivers of the HR11 and tributaries in the upper watersheds of the HR13 basin. Waters become slightly more alkaline in HR12 and eastern watersheds of the HR13 basin (for example in intermittent Los Frailes and ephemeral Coy Inlet streams), with a pH range of 8.1-9.4.

The prevailing cations in waters of the three large hydrographic regions (HR) were  $Ca^{2+}$  and  $Mg^{2+}$  with a slight dominance of the former (figure 2, page XXX). Na<sup>+</sup> had similar concentrations to  $Mg^{2+}$  in HR11, prevailing only in a few cases, as in the Don Guillermo stream (concentration over 25.0% between major cations when expressed in meq/l). The lowest concentration between cations was K<sup>+</sup>, with a mean value of 3.8% in meq/l in winter and 2.4% in summer. This distribution of proportions among cations is consistent with most rivers in the world (17). HCO<sub>3</sub><sup>-</sup> was the predominant cation resulting in the Ca(Mg) HCO<sub>3</sub> water type in the Argentine side of HR11 (figure 2, page XXX). Data was insufficient for such analysis in the Chilean side of this basin.

Except for Cl<sup>-</sup>, the average concentrations of different ions tend to be slightly lower during summer compared to winter, with the occurrence of annual peak flows in HR11. In both seasons the proportions of these ions tend to remain unchanged. As stated by Mosley and Row (1981), this suggests the dilution of solutes by run-off and a relatively low concentration of elements contributed by the subsurface flow. This process can be associated with a faster transit of rainwater toward the waterways in the wet season without interacting with soil solutes. This is particularly evident in creeks and streams, rather than rivers.

**Table 1.** Statistics for salinity and sodicity hazard indicators obtained from the analysis of surface water samplesin the most important courses of the Serrano (HR11), Coyle (HR12), and Gallegos (HR13) river basins, between2017 and 2019.

Tabla 1. Estadísticos de indicadores de riesgo de salinidad y sodicidad obtenidas del análisis de muestras deaguas superficiales en los cursos más importantes de las cuencas de los ríos Serrano (HR11), Coyle (HR12) yGallegos (HR13), entre 2017 y 2019.

Indicator	Late winter / Early spring			Late summer		
	HR 11	HR 12	HR 13	HR 11	HR 12	HR 13
Water temperature (°C)	5.4 ± 4.2 (77.2)	7.6 ± 2.8 (37.1)	4.9 ± 2.6 (53.7)	10.2 ± 4.2 (41.2)	8.2 ± 4.0 (48.3)	11.5 ± 2.6 (22.5)
рН	7.7 ± 0.5 (5.9)	8.5 ± 0.2 (2.8)	7.9 ± 0.5 (6.7)	7.7 ± 0.4 (5.8)	8.4 ± 0.5 (5.7)	7.5 ± 0.7 (9.7)
SAR [Ec.1] <sup>a</sup>	0.58 ± 0.21	3.79 ± 8.91	0.78 ± 0.42	0.56 ± 0.15	6.66 ± 20.64	0.84 ± 0.52
	(36.6)	(235.1)	(53.9)	(26.9)	(310.0)	(61.7)
SAR <sub>adj</sub> [Ec.2] <sup>b</sup> ***	nd **	7.87 ± 15.02 (190.9)	1.55 ± 0.53 (34.3)	nd **	17.15 ± 34.41 (200.6)	1.46 ± 0.72 (49.4)
RSC [Ec.3] <sup>c</sup> (meq/l)	0.26 ± 0.39	1.04 ± 1.82	-0.04 ± 0.34	0.03 ± 0.30 *	1.31 ± 3.34	-0.07 ± 0.33
	(148.3) *	(176.0)	(878.7)	(960.0)	(256.0)	(470.2)
SSP [Ec.4] <sup>d</sup> (%)	20.2 ± 8.8	54.2 ± 9.3	31.3 ± 5.5	18.1 ± 6.6	53.0 ± 12.9	30.5 ± 6.5
	(43.8)	(17.1)	(17.7)	(33.9)	(24.4)	(21.4)
ECw ° (µS/cm)	122.1 ± 69.8	554.6 ± 986.6	209.6 ± 195.7	168.8 ± 130.9	1,249.4 ±	245.8 ± 217.7
	(57.1)	(177.9)	(93.3)	(77.6)	3.609.8 (288.9)	(88.6)
TDS <sup>f</sup> (mg/l)	96.8 ± 49.3	343.2 ± 639.5	145.0 ± 131.0	113.3 ± 46.4 *	749.3 ± 8.91	165.6 ± 141.0
	(50.9) *	(186.3)	(90.3)	(41.0)	(235.1)	(85.1)
ES [Ec.5] <sup>g</sup> (meq/l)	0.6 ± 0.2 (36.7) *	4.3 ± 10.8 (248.3)	0.9 ± 0.8 (87.4)	0.6 ± 0.4 * (68.7)	11.1 ± 36.6 (330.5)	1.1 ± 1.1 (94.3)
PS [Ec.6] <sup>h</sup> (meq/l)	0.4 ± 0.1 (36.1)	2.9 ± 7.7	0.8 ± 0.8	0.3 ± 0.1 *	10.4 ± 36.8	0.8 ± 0.9
	*	(261.3)	(102.7)	(52.2)	(355.4)	(118.7)

Data are presented as mean values ± standard deviation and the percentage of variation coefficient between brackets.

<sup>a</sup> Sodium Adsorption Ratio; <sup>b</sup> Adjusted Sodium Adsorption Ratio; <sup>c</sup> Residual Sodium Carbonate; <sup>d</sup> Soluble Sodium Percentage; <sup>e</sup> Specific Electrical Conductivity; <sup>f</sup>Total Dissolved Solids; <sup>g</sup> Effective Salinity; <sup>h</sup> Potential Salinity; <sup>\*</sup> Only valid cases in the Argentine sector due to unavailable data from the Chilean sector in transboundary basins HR11 and HR13. \*\* No data in range for calculation (HCO<sub>3</sub> >200 mg/l). \*\*\* Only cases with HCO<sub>3</sub> >200 mg/l.

Los datos se presentan como valores medios ± desviación estándar y el coeficiente de variación porcentual entre paréntesis.

<sup>a</sup> Relación Adsorción de Sodio; <sup>b</sup> Relación Adsorción de Sodio ajustada; <sup>c</sup>Carbonato de Sodio Residual; <sup>d</sup> Porcentaje de Sodio Soluble; <sup>e</sup> Conductividad Eléctrica Específica; <sup>f</sup> Sólidos Totales Disueltos; <sup>g</sup> Salinidad Efectiva; <sup>h</sup> Salinidad Potencial; \* Solo casos válidos en el sector argentino debido a faltante de datos en el sector chileno en las cuencas transfronterizas RH11 y RH13. \*\* Sin datos en el rango de cálculo sugerido (HCO<sub>3</sub> > 200 mg/l). \*\*\* Solo casos con HCO<sub>3</sub> > 200 mg/l.



Data available only for Argentine basins. / Datos solo disponibles para la porción Argentina de las cuencas transfronterizas.

**Figure 2.** Piper diagram for winter waters (left) and summer waters (right). **Figura 2.** Diagrama de Piper para muestras de agua de invierno (izquierda) y de verano (derecha).

> Also, in HR13, most of the waters did not have a prevalent cation between  $Ca^{2+}$  and  $Mg^{+2}$ . Na<sup>+</sup> was the second most important cation (30.5 and 31.1% in meq/l for winter and summer, respectively) while  $Mg^{2+}$  occupied the third place (22.7 and 23.6% in meq/l for winter and summer, respectively). Few samples showed a dominance of chlorinated water type in both seasons. This occurred, mainly, in small steppe creeks and streams near the seacoast, like in Ci-Aike (over 40% in meq/l Cl<sup>-</sup>) and Los Frailes (over 50% in meq/l Cl<sup>-</sup>), both of intermittent stream type (figure 2). A similar pattern of concentrations occurred with the remaining anions without seasonal variation, in which the bicarbonate type dominated. The hydrochemical facies of these waters are a combination of the Ca(Mg)HCO<sub>3</sub> type and a mixed type (figure 2).

> There was no dominant type among the cations in HR12 samples. However, Na<sup>+</sup> was the most prevalent (over 40.0% in meq/l), followed by Ca<sup>2+</sup> (between 30.9 and 31.9% in meq/l) and Mg<sup>2+</sup> (23.1 and 26.0% in meq/l). There was a tendency for Na<sup>+</sup> to prevail in short ephemeral coastal watercourses towards the east of this HR, with extreme values of 74.7% in meq/l in De Las Casas and 94.1% in meq/l in Coy Inlet. Bicarbonate waters are dominant in this region which determined the existence of facies mainly of the Ca(Mg)HCO<sub>3</sub> type and the Na(K)HCO<sub>3</sub> mixed type (figure 2). Only few samples were corresponded to a chlorinated type.

Although large rivers cross the extensive Patagonian steppes, like Coyle and Gallegos, with a high evapotranspiration rate during summer, there was no evident change in ion concentrations along river courses to the sea. Likewise, there is no clear dominance of  $Ca^{2+}$  or  $Mg^{2+}$  in the upper basins or tributaries. This suggests a relatively uniform lithology along watercourses that determines a homogeneous distribution of major element concentrations (17).

# Sodicity (alkali) hazard

The soluble salts present in the soil or in the irrigation water contribute to the increase the salinity of the soil solution. Similarly, when these salts involve exchangeable Na<sup>+</sup>, they contribute to the increase of Na<sup>+</sup> relative saturation, given its more persistent nature in soils (25). Excess of sodium salts represents a toxicity hazard for sensitive plant species, it negatively affects the soil permeability and hydraulic conductivity and, therefore, it alters soil structure aggregation with the consequent unavailability of water for crops intake (15, 31). Na<sup>+</sup> hazard in soils is more complex to establish than the water sodicity hazard because of several interacting factors, such as soil texture (28), electrical conductivity, and rate of sodium adsorption during soil watering (25).

Serrano (HR11) and Gallegos (HR13) regions exhibited lower levels of SAR than Coyle (HR12). In HR11, the mean SAR ranged from  $0.58 \pm 0.21$  during late winter and  $0.56 \pm 0.15$  in summer (table 1, page XXX). This is a small difference despite the contrasting seasonal flows in rivers and streams, which can reach mean annual values as low as  $0.01 - 2.0 \text{ m}^3/\text{s}$  (Don Guillermo and Chorrillo streams) and  $2.5 - 30.0 \text{ m}^3/\text{s}$  (Vizcachas, Baguales, Las Chinas and Paine rivers) or higher, up to  $120.0 - 380.0 \text{ m}^3/\text{s}$  (Grey and Serrano rivers), all of them being of permanent type. The only extreme values were observed in Don Guillermo stream waters with SAR ranging between 0.92 and 1.06, depending on the season. Low mean SAR values were also found in HR13, ranging from  $0.78 \pm 0.42$  in winter and  $0.84 \pm 0.52$  in summer, with a few exceptions in the San José creek, a minor tributary located in the upper portion of the system (SAR=2.40). Relatively high values were observed in Los Frailes and Ci Aike creeks (SAR=2.61), which represent intermittent courses in the eastern portion of HR13. Regardless of the ECw, these SAR values were always located in the S1 category, which represents a low sodium hazard for irrigation (figure 3) (25, 31).



Figure 3. Salinity and sodicity combined hazards in surface waters from the three HR in the winter (left) and in the summer (right), through the Wilcox plot (23).

HR12 showed the highest mean regional SAR values, with great spatial variability. The average SAR ranged between  $3.79 \pm 8.91$  for winter and early spring and  $6.66 \pm 20.64$  for summer, with spatial variabilities between 235 to 310%, respectively. The highest SAR values were recorded in the ephemeral waters of Coy Inlet Creek, located at the mouth of the Coyle River, where it meets the sea (39.9 and 83.9 for winter and summer, respectively), and in the Fabre creek, located in the central section of HR12 (5.9 and 3.8 for winter and summer, respectively). Coy Inlet creek water exhibited an extremely high sodium hazard (>S4), exceeding the scale proposed by USDA (25). Furthermore, a few streams such as the Fabre creek and the De Las Casas stream reached a medium sodium hazard category S2 (figure 3). This condition, combined with fine-textured soils, high cation exchange capacity, and restricted drainage, typical situations in this region, represents a high risk for several crop species (31). Excluding these extreme cases, the mean SAR of waters in this basin ranged from 1.55  $\pm$  1.52 in winter to 1.34  $\pm$  0.94 in summer.

**Figura 3.** Riesgos combinados de salinidad y sodicidad en aguas superficiales de las tres RH, según el esquema de Wilcox (23), durante invierno (izquierda) y verano (derecha).

In general terms, there were significant strong positive correlations between the mean season flows and SAR values for HR11 and HR13. The predominant nivo-glacial mixed regime type in HR11 rivers, streams, and creeks showed two hydrograph peaks from late winter to mid-spring, and a maximum in late summer. In HR13, the nivo-pluvial mixed flow regime presented two hydrograph peaks: one moderate from late autumn to early winter, and a maximum from late winter to mid-spring. In both cases, seasonal peak flows correlated with higher SAR values in terms of  $m^3/s$  determined in gauging stations. For HR11, the correlation was 0.847 ( $r^2$ = 0.717, p-value <0.05) in 32 valid cases, while for HR13 correlation was 0.825 ( $r^2$ = 0.681, p-value <0.01) in 49 cases. A valid case consisted of the existence of a flow record at the same site as a sample collection. No statistical significance was detected for HR12 water samples between seasons (0.639,  $r^2$ = 0.406, p-value=0.114). The predominantly nival regime produces a strong peak flow between late winter to mid-spring, with minimum flows during the rest of the year, and most creeks and small streams dry out during the warmest months.

No HR11 samples met the requirements proposed by Weiner (2013) to implement the SAR<sub>adj</sub>. Although the mean SAR<sub>adj</sub> value was 25% higher in water samples from HR13 with >200 mg/l HCO<sub>3</sub> than the mean standard SAR values both remained in the S1 sodicity hazard category. In HR12 water samples SAR<sub>adj</sub> emphasized the sodium character of waters with high concentration of bicarbonates, especially in creeks and streams such as Coy Inlet, Fabré, and De Las Casas, all of them ephemeral types. The sodium hazard categories in these sites were between S2 and S4 (from high to very high), with extreme SAR<sub>adj</sub> values up to 44.8 in winter and 87.4 in summer, slightly above the standard SAR indicator. Despite these cases, most samples were classified, in terms of SAR<sub>adj</sub>, within the S1 category (low hazard) with an average of 11% higher than standard SAR values.

When irrigation water contains enough carbonates and bicarbonates to precipitate Ca<sup>2+</sup> and Mg<sup>2+</sup> calcium and magnesium, a small proportion of Na<sup>+</sup> may be enough to cause initial symptoms of soil sodification (8). Applying the classification suggested by Wilcox *et al.* (1954), mean RSC values less than 1.25 meq/l in both seasons and from the three hydrographic regions determined that waters are safe for irrigation (table 1, page XXX). HR12 waters showed a mean RSC value of  $1.04 \pm 1.82$  in winter and  $1.31 \pm 3.34$  in summer. However, Fabré creek, sections of Brazo Norte of Coyle river and the unified Coyle river (convergence of all its tributaries in the HR12) had marginal waters (between 1.25 and 2.5 meq/l). De Las Casas stream and Coy Inlet creek, both of ephemeral type, showed RSC>2.5 meq/l, rendering them unsuitable for irrigation.

Most waters in the HR11 basin had SSP values below 35.0%, qualifying as good to excellent quality for irrigation according to Wilcox (1955), with no potential hazard for soil physical properties or plant growth (22). The average SSP for these waters was between 20.2  $\pm$  8.8% in winter and 18.1  $\pm$  6.1 in summer (table 1), with an exceptional SSP value of 53.5% in the lower Serrano river. A similar situation was observed in HR13 (mean SSP of 31.3  $\pm$  5.5 in winter and 30.5  $\pm$  6.5 in summer) and HR12 waters, which showed the highest mean SSP with 54.2  $\pm$  9.3 in winter and 53.0  $\pm$  12.9 in summer (table 1, page XXX). In both HR, most water samples qualified as good to permissible for irrigation purposes. HR12 waters showed the highest SSPs average in the region.

#### Salinity hazard

Diagnosis and classification of the total concentration of soluble salts in irrigation waters, may be adequately expressed in terms of ECw (25, 30). Except for a few samples, most waters in the region had ECw values below 250  $\mu$ S/cm and may be categorized as low salinity waters (C1), according to Wilcox (1955). Such waters can be used for crop irrigation in a great variety of soils without great risks of developing salinity problems. This is particularly evident in rivers and streams of HR11, with an average of 122.1 ± 69.8  $\mu$ S/cm in winter, and 168.8 ± 130.9  $\mu$ S/cm in summer (table 1, page XXX). Few cases in this basin, such as Don Guillermo (Argentine) and Chorrillo (Chile) streams, showed higher sodium hazard levels up to the C2 category (ECw<750  $\mu$ S/cm), (figure 3, page XXX). This corresponds to medium salinity waters, which can be used for irrigation of crops with moderate tolerance to salinity in soils with good drainage (30). Increasing ECw levels tend to mitigate negative sodium effects on soils but it can simultaneously induce crop stress by degrading the quality of the available water via salinization (14).

Similarly, in HR13 waters mean ECw was 209.6 ± 195.7  $\mu$ S/cm and 245.8 ± 217.7  $\mu$ S/cm in winter and summer, respectively. About 69% of samples were below 250  $\mu$ S/cm in both seasons (C1) and 28% were within C2 (<750  $\mu$ S/cm) (figure 3, page XXX). Los Frailes and Ci Aike (two small intermittent streams in the final stretch of the HR13 near the seacoast) and SanJosé (a small creek of the permanent type in the upper basin that receives strong discharges from extractive coal mining since the 1960s) reached a C3 category (from 750 to 2,250  $\mu$ S/cm).

Coy Inlet and De Las Casas intermittent streams, in HR12, were the only C4 waters in the region, with an ECw of 4,440 and 14,760  $\mu$ S/cm, a high salinity not suitable for irrigation of intolerant crops. Excluding these sections from a global analysis, mean ECw values in this basin ranged from 276.9 ± 160.8  $\mu$ S/cm in winter to 348.7 ± 232.7  $\mu$ S/cm in summer (table 1, page XXX), qualifying closer to HR11 and HR13 waters although slightly higher. A 48.6% water of samples from H12 were C1, 37.1% were C2 and 8.6% were C3 (figure 3, page XXX).

The relationship between sodicity and salinity hazards is more complex in soil than in water. While increasing salinity and sodicity in water involve crop irrigation restrictions, the long-term negative impact on soil occurs when increasing sodicity coincides with decreasing salinity (3, 25, 30). High Na<sup>+</sup> concentration leads to soil sodicity, increasing the susceptibility to crusting, runoff, erosion, and poor aeration, as well as the deterioration of soil hydraulic properties which can be counteracted with increasing salinity (21).

In contrast to the relatively low sodium hazard of waters for crop irrigation, the SAR analysis indicates an important potential for negative impacts on soil stability. In general, most water samples were found at the likely permeability hazard threshold based on the SAR/ECw relationship (figure 4). During early spring, with the beginning of complementary irrigation season, 100% of water samples in HR11, 89.5% in HR12, and 90.2% in HR13 demonstrated a possible permeability hazard. More than 50.0% of the total water samples in the region were under the curve of high risk of dispersion probability (curve A). During summer, the HR12 waters maintained a similar proportion of samples in the potential (likely) probability hazard category (89.5%), with a slight decrease in the samples from HR11 (91.2%) and HR13 (84.3%).



A, B, C, threshold functions of potential impacts on soil. / A, B, C, funciones umbral de impacto potencial en el suelo.

**Figure 4.** Relationship between SAR and ECw of irrigation water for prediction of soil structural stability in the three HR during late winter and early spring (left) and late summer (right). Adapted from ANZECC and ARMCANZ (2000) and Feitz and Lundie (2002).

**Figura 4.** Relación entre SAR y ECw en agua de riego para la predicción de la estabilidad estructural del suelo en las tres RH, entre fines de invierno y principio de primavera (izq.) y finales del verano (der.). Adaptado de ANZECC and ARMCANZ (2000) y Feitz and Lundie (2002).

There were statistically significant strong positive correlations between seasons and the ECw for both HR11 and HR13, with higher values during summer. In the case of HR11, the correlation value was 0.693 ( $r^2$ = 0.481, p-value <0.01) and for HR13, correlation was 0.819 ( $r^2$ = 0.671, p-value <0.01). No statistical significance was detected for HR12 water samples between seasons despite a high correlation coefficient (0.847,  $r^2$ = 0.717, p-value=0.128).

The average ES values for the HR11 and HR13 samples were  $0.6 \pm 0.2$  meq/l and  $0.9 \pm 0.8$  meq/l respectively, during late winter and early spring, and  $0.6 \pm 0.4$  meq/l and 1.1  $\pm$  1.1 meq/l during summer (table 1, page XXX). Except for Los Frailes and Ci Aike (lower HR13) and San José (upper HR13) with some seasonal sodicity and salinity restrictions, the effective salinity hazard was low for all the remaining water samples (ES<3 meq/l), according to Palacios and Aceves (1970). ES values in these cases were not particularly high (ES<5 meq/l), but enough to be classified as conditioned waters for use in irrigation (20). The Potential Salinity (PS) indicator shares the same ranges that ES (PS<3 meq/l are good irrigation waters, PS between 3-15 meq/l conditioned waters and PS>15 meq/l not recommended waters for use). All the waters analyzed in HR11 and HR13 were classified with the PS indicator similarly to ES (table 1, page XXX).

With average values above 4.3 meq/l in winter and 11.1 meq/l in summer, the ES in HR12 waters were slightly higher than those found in HR11 and HR13. This situation is comparable to the PS indicator, with averages of 2.9 and 10.4 meq/l for both HR, respectively. In general, there is a high proportion of good water for irrigation in the region (ES and PS<3 meq/l) except for few isolated streams and creeks with conditioned-type waters (ES and PS between 3-15 meq/l) such as De Las Casas (lower basin), Cañadón Fabré (middle basin), some sections of the Pelque stream (upper basin) and the main course of the Coyle river (the most important one of the HR12 in terms of annual flow). PS and ES values >15 meq/l were only registered in the Coy Inlet creek (lower HR12), which makes water not recommended for irrigation.

#### **CONCLUSIONS**

Results from this study indicate that most water samples from the three basins pose no significant salinity and sodicity hazards for irrigating crops, vegetables, and pastures. Exceptions include a few temporary streams and creeks. However, a significant proportion of water samples showed a potential negative impact on soil structural stability, from the beginning of the irrigation season (late winter to early spring) to the end of the growing season (late summer). Both saline and sodium hazards of irrigation water may re-transform the pre-existing soil solution through interactions with soil physics and chemistry mainly by precipitation of salts. These potential hazards must be considered during the planning and operating of irrigation schemes in arid and semiarid regions. This is particularly important where overuse through inefficient irrigation practices is common. The potential combined negative effects of the use of these waters for irrigation, in relation to regional soils, need further studies for the implementation of suitable irrigation projects.

#### SUPPLEMMENTARY MATERIAL

https://docs.google.com/document/d/1CHISvNHhFHmVz4kenuVC0089W1BHCAva/ edit?usp=sharing&ouid=111310786017351827239&rtpof=true&sd=true

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