



Soluble silicon in differently textured mollisols of Argentina

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ABSTRACT

Soluble compounds of silicon (Si), such as monosilicic acid and polysilicic acid, affect many of the soil chemical and physicochemical properties of the soil. In Argentina the Chaco Pampean Plain is hugely important as it is one of the main areas of global agricultural production. The main objectives of this study were to examine the distribution of the concentration of soluble Si in soils of different genesis of the Chaco Pampean Plain and to evaluate the relationship between the physical and chemical properties of soils and the Si solubility. A soil sampling in the Pampa region was performed; where 12 soil profiles samples were taken at 1.5 m depth. The Si soil levels were separated into two groups. Group A (fine texture) had a high Si content while Group B (coarse texture) was lower. All soils show poorly provided of soluble Si in the surface horizon, but differences were observed in the subsurface. A finer soil with >100 years of an agricultural system had 30/40% less of Si soluble.

Si correlates positively with pH and with clay content. These clays and the phytoliths can be a source or adsorb silicic acid. There is a negative correlation between Si and sand content, so the sandy loam to sandy soils are to suffer the greatest impact of agriculturalization. There is a significant and negative relationship between Si and phosphorus suggesting a competition might exist between these two elements.

Evaluation of Si in these soils is very important due to its relevance in agricultural production worldwide. Si values may directly affect the production since its deficiency may cause crops disease.

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1. Introduction

Silicon (Si) is the second most abundant element in the surface of the earth's crust and in the soil, where it's content is 28.8% (Epstein, 1994; Sposito, 2008). It is present in >370 rock-forming minerals. Being an element of almost all parent materials, Si is one of the basic components in most of the soils (Sommer et al., 2006). However, Matichenkov and Bocharnikova calculated that 210–224 million tons of Si are removed from agricultural soils each year (Haynes, 2014). Likewise, weathering of Si from feldspars and quartz takes place mainly over multi-millennial to million-year timescales. On the other hand, biogenic produced silica (amorphous opal), mainly found in the shells of several different aquatic organisms, is soluble at time-scales ranging from days to years. Although quartz is a major constituent in rocks, quartz does not control silica concentration in solution because of its slow dissolution kinetics ((Miterzky & Cirelli, 2004), Fig. 1).

Hydrated silica represents the second most abundant biogenic mineral after carbonate minerals (Fauteux et al., 2005). Dissolution of the

amorphous Si in terrestrial soils has been shown to control dissolved Si export from catchments dominated by wetlands, forests and grasslands (Clymans et al., 2011a). Si plays a very important role in the carbon global matter cycle. The Si influences the carbon (C) cycle in two ways, first because the CO₂ affects the weathering processes and second it impacts the Si flow into the oceans because diatoms, representing 50% of the biomass of the oceans, need Si for their skeleton (Sommer et al., 2006).

The genesis of the soil can determine its chemical properties, such as the pH and the texture (Heredia, 2014). The variables present in the different horizons, i.e. clay content, may be positively correlated with the concentration of soluble Si (Korndörfer et al., 2004) and this may affect the Si cycle. Soil processes control the dissolution stock and the precipitation of silicate minerals governing the bioavailability of Si. As well, the variability of the rates of Si cycling in terrestrial ecosystems is largely governed by pedogenesis (Cornelis & Delvaux, 2016).

Si in soils comes from three main sources, which are (1) primary minerals inherited from parent material, (2) secondary minerals (crystalline phases) developed through soil formation (mainly clay minerals) and (3) secondary microcrystalline minerals (autogenic quartz, opal). Silicic acid (H₄SiO₄) form is the main component of Si soil solutions, mostly as monomeric silicic acid (Dove, 1995; Drees et al., 1989; Iler,

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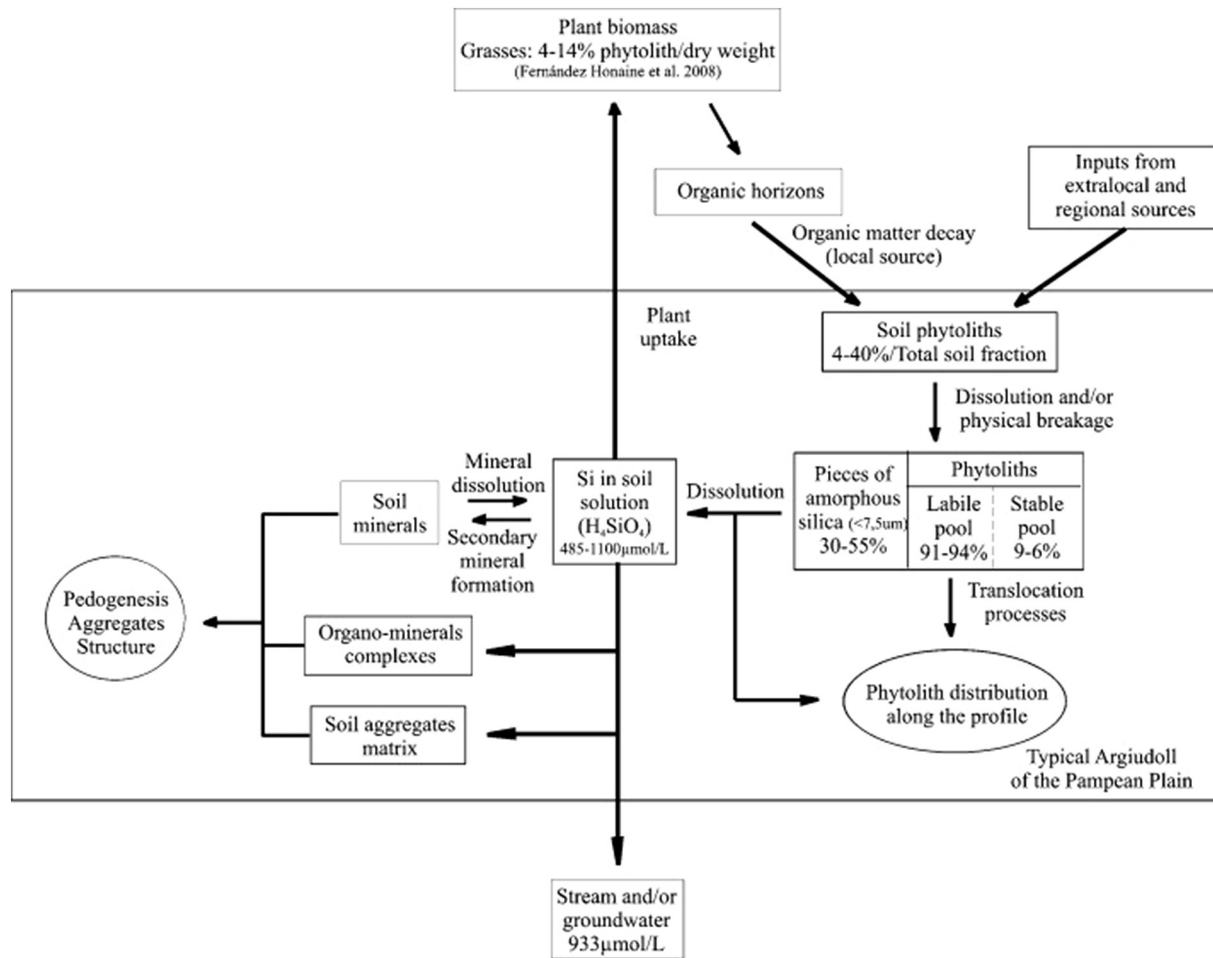


Fig. 1. Silica biogeochemical cycle in the southeastern area of the Pampean Plain (Borrelli et al., 2010).

1979). Polymeric species become stable beginning with $\text{pH} \approx 10$ and the rate of polymerization and depolymerization is slow. (Dietzel, 2000; Dietzel, 2002). Polymeric silicic acid is composed of two or more Si atoms and may appear in different forms, e.g., chains, branching forms, or spherical clusters (Sommer et al., 2006).

Soluble compounds of Si, such as monosilicic acid and polysilicic acid, affect many of the chemical and physicochemical properties of the soil. The monosilicic acid can react with aluminum, iron and manganese in the formation of slightly soluble silicates. Furthermore, under different concentrations, the monosilicic acid can be combined with heavy metals (Cd, Pb, Zn, Hg, etc.) forming soluble complex compounds when the concentration of monosilicic acid is low, and silicates of heavy metals slightly soluble when monosilicic acid concentration is higher in the system. Thus, the application of active Si forms (soluble and extractable Si) offers the possibility of managing the mobility of heavy metals (Matichenkov & Bocharnikova, 2008).

In regards to polysilicic acids, these mainly affect the physical properties of soil because they can bind soil particles. The formation of soil structure occurs through silicates bridging between particles. With increasing polysilicic acids, the degree of soil aggregation, water retention capacity, exchange capacity and the regulatory capacity of sandy soils increases (Matichenkov & Bocharnikova, 2008).

The sequestration of Si in soil clay-sized Fe-oxides can thus affect the Si terrestrial cycle by influencing Si concentration in solution, and hence in waters drained from watersheds. Three major Si reservoirs have been identified. First, Si-rich precipitates (opal, quartz) induce very large uptake of preferentially light Si isotopes. Second, Si uptake by biota favors

the absorption of Si in plants, and diatoms. Third, soil clay-sized components sequester light Si isotopes (Opfergelt et al., 2009).

The soil is the primary source of plant Si and therefore a key reservoir of the Si biological cycling (Cornelis & Delvaux, 2016). The process of Si uptake can be classified as active, passive or rejective, and accordingly plants can be classified as accumulators, intermediates, and excluders. Plants are considered as Si accumulators when the tissue Si concentration is $>10 \text{ g kg}^{-1}$ and as excluders when they have concentrations $<5 \text{ g kg}^{-1}$ (Haynes, 2014). The Si concentration in plants depends primarily on the concentration of silicic acid in the soil solution and it is not correlated with the total Si concentration of the soil (Guntzer et al., 2012). Plants can influence chemical weathering rates by producing various organic ligands and acidity, by affecting the soil water budget through transpiration, and by root uptake of Si (Gérard et al., 2008). Si biocycling may be the most important source of available Si to plants (Guntzer et al., 2012). Biological uptake of Si can enhance silicate weathering by decreasing aqueous silica concentrations. Conversely, the release of Si from dead plant biomass and its decomposition in the organic soil layer leads to an increased phytoliths concentration in the soil and may therefore inhibit the rate of chemical weathering (Gérard et al., 2008).

Phytogenic Si is now recognized as one of the most important sources of Si in soil solution among all soil minerals. It is, however, important to note that phytoliths can be highly resistant to dissolution and may remain in soils for thousands of years, thus, contributing to C sequestration (Haynes, 2014). The biogeochemical C sequestration by phytoliths provides a longer-term opportunity to sequester atmospheric CO_2 (Marxen et al., 2016; Yang et al., 2018). The distribution of

phytoliths through the soil profile is similar to that of carbon and, in some cases, shows a rapid decrease with depth (Guntzer et al., 2012). It has been confirmed that approximately 0.1–6% of organic C could be occluded within phytoliths during its formation process (Yang et al., 2018).

Upon death and decay of the plants, phytoliths become part of the clastic materials, thus being exposed to the same weathering processes that affect the soil minerals. These processes generate surfaces with pores or cavities through which monosilicic acid is released, ready to be reabsorbed by the plants, to remain in the system, to be involved in the formation of secondary minerals (such as clays, allophanes and amorphous silica) or to flow into the underground water (Borrelli et al., 2010).

There are depositions of biogenic silica as opal, which may be found in soils from 3 to 20%. These values mean that opal comprises a significant portion of the Si compounds. There is considerable evidence that the opal phytoliths are very abundant in the regolith of many locations (Clarke, 2003). Biogenic Si can undergo a faster turnover than the silicate minerals depending on the mineral composition of the soil and the amount of phytoliths. In the Pampean Plain, light minerals and compounds of amorphous silica, both of inorganic (vitroclastics) and organic origin (phytoliths), predominate. These represent over 40% of mineral components of the soil (Borrelli et al., 2010).

Si deficiency produces weak plants, growth, development and reproduction are abnormal, and plants are more susceptible to metal toxicity, pests and diseases (Doncheva et al., 2009).

In Argentina, the Chaco Pampean plain is hugely important as it is one of the main areas of global agricultural production and there are

very few studies of Si in soils. Several authors have studied the importance of biogenic silica and its effect on soil physical properties (Pecorari et al., 1990; Pecorari et al., 1991; Peinemann & Ferreiro, 1972). Cosentino (Cosentino, 2002) evaluated the contribution of phytoliths to light silt fractions which were found to have a negative effect on the soil structure.

But there are no studies in Argentina on soluble and available Si soils and its direct impact on the nutrition of crops or on the burden of ions that can reach aquifers or surface water bodies.

The main objectives of this study were to examine the distribution of the concentrations of soluble Si in soils of different genesis of the Chaco Pampean Plain and to evaluate the relationship between the physical and chemical properties of soils and Si solubility.

2. Materials and methods

2.1. Site and sampling

Soils sampling was performed in the Pampa region during 2012–2013. The soil samples consisted of 12 soil profiles which were taken in duplicates at 1.5 m depth and come from composite samples. Samples were obtained at different locations of the province of Buenos Aires: 25 de Mayo, (25 M), S53°28,762' W60°07,601'; Balcarce, (Ba), S37°45,798' W58°17,845'; Ferré, (Fe), S 34°06',008' W61°08,381'; Las Armas, (LasA) S37°05,603' W57°52,478'; Pergamino (Pe) S 33°53.397' W60°34.412'; Trenque Lauquen, (TL) S35°58,378' W62°45,956'; in the Santa Fe province: Las Rosas, (LR) S32°29,539' W61°34,046'; in Córdoba: Manfredi,



Fig. 2. Map of Argentina and soil sampling distribution.

Table 1
Physical and chemical characteristics of soil surface horizons.

ID	Coordinates	Province	pH	TC	CEC	Sand	Silt	Clay	Taxonomy classification
			1:2,5	g/kg	cmol _c /kg	%	%	%	
25 M	S53°28,762' W60°07,601'	Bs. As.	6.7	12.9	14	54.8	38.6	6.6	Thapto Argic Hapludolls
Fe	S 34°06',008' W61°08,381'	Bs. As.	6.5	25.22	23.1	28.2	57.7	14.1	Typic Argialbolls
Pe	S 33°53,397' W60°34,412'	Bs. As.	5.65	22.1	25.3	20	47.5	32.5	Typic Argialbolls
LasA	S37°05,603' W57°52,478	Bs. As.	5.3	55.5	14.1	33.2	62.5	4.3	Typic Natraquolls
LR	S32°29,539' W61°34,046'	Santa Fé	5.2	17.36	21.4	4.3	93.9	1.8	Typic Natraquolls
TL	S35°58,378' W62°45,956'	Bs. As.	6.2	8.8	14	69.2	24.3	6.6	Acuic Hapludolls
Ba	S37°45,798' W58°17,845'	Bs. As.	4.9	38.1	30	33.6	57.2	9.3	Typic Argialbolls
Mn	S31°51,422' W63°44,926'	Córdoba	6.4	13.68	18.7	14	69.3	16.8	Typic Hapludolls
AN	S36°32'29.7'' W63°59'27.3''	La Pampa	6.9	4.01	8	84.7	13.8	1.6	Entic Hapludolls
IAL	S35°22'33.7'' W63°41'8.2''	La Pampa	6	6	7.6	82.5	12.6	5	Entic Hapludolls
IAML	S35°22'37.9'' W63°41'4.3''	La Pampa	6.1	9.82	9.5	70.2	22.3	7.5	Entic Hapludolls
IAB	S35°22'53.8'' W63°41'6.4''	La Pampa	5.9	7.83	11	68.8	23.7	7.5	Entic Hapludolls

(Mn) S31°51,422' W63°44,926'; towns in La Pampa: Anguil (AN) S36°32'29.7' W63°59'27.3' and Intendente Alvear (IA). Samples from IA were taken in three land scape positions: upper (IAL) S35°22'33.7' W63°41'8.2'', middle (IAML) S35°22'37.9''W63°41'4.3'' and lower (IAB) S35°22'53.8'' W63°41'6.4''. All the soils are from agricultural systems, in rotation wheat/maize/soya.

The climate of the region is humid (700–1000 mm/year) and mild, isotherm 16 (INTA, 2008). The parent material was identified as Pampean Loess and Post Pampean loess (Frenguelli, 1955a; Frenguelli, 1955b).

2.2. Soils analysis

Sample soils were classified using the soil taxonomy (Soil Taxonomy, SSS, 2014) and they were analyzed for total carbon (TC) (Walkley& Black), TN (Kjeldahl), water pH (potentiometric), extractable phosphorus (P) (Kurtz and Bray 1), exchangeable cations and cation exchange capacity (CEC, Ammonium Acetate method 1 N pH 7) (Sparks, 1996), electrical conductivity (EC) (conductimetry) and texture (Bouyoucus method) (Klute, 1986).

Soluble Si was extracted with water. The extraction procedure was as follows: 1) after removing plant roots, 6 g of fresh soil was placed into 100 mL plastic vessels; 2) 30-ml of water was added to each vessel; 3) after 1 h shaking, a sample was filtered, and a clean extract was analyzed for soluble monosilicic acid. To quantify, the Govett (yellow procedure silicomolybdic acid) and Weaver et al. (blue procedure silicomolybdic acid) (Sparks, 1996) colorimetric methodology was used. It was decided to use this methodology because others gave a lot of variabilities. All the samples had two replicas.

Statistical correlation and regression analysis were conducted to establish the relationship between all the variables analyzed with the Infostat program (Di Rienzo et al., n.d.).

Table 2
Physical and chemical characteristics of soil subsurface.

ID	Coordinates	Province	pH 1:2.5	TC g/kg	CEC cmol _c /kg	Sand %	Silt %	Clay %
25M	S53°28,762' W60°07,601'	Bs. As.	8.1	0.66	19.1	59.3	18.3	22.5
Fe	S 34°06',008' W61°08,381'	Bs. As.	6.6	4.03	22.6	21.6	49.3	29.1
Pe	S 34°06',008' W60°34,412'	Bs. As.	6.16	3.86	23.6	22.5	35	42.5
LasA	S37°05,603' W57°52,478	Bs. As.	8.4	2.58	29.8	27.4	53.5	19.1
LR	S32°29,539' W61°34,046'	Santa Fé	6.7	3.6	27.9	2.1	56.1	41.8
TL	S35°58,378' W62°45,956'	Bs. As.	8	0.88	9.3	76.9	19.1	4.1
Ba	S37°45,798' W58°17,845'	Bs. As.	6.6	1.55	16.2	48.6	32.2	19.3
Mn	S31°51,422' W63°44,926'	Córdoba	8.2	1.61	15.7	15.7	70	14.3
AN	S36°32'29.7'' W63°59'27.3''	La Pampa	7	1.71	7.3	85.6	12.8	1.6
IAL	S35°22'33.7'' W63°41'8.2''	La Pampa	6.3	2.59	10.5	81.6	13.4	5
IAML	S35°22'37.9'' W63°41'4.3''	La Pampa	6.2	3.42	11.3	73.8	18.7	7.5
IAB	S35°22'53.8'' W63°41'6.4''	La Pampa	6.6	3.55	10.2	71.6	21	7.5

3. Results and discussion

3.1. Sampling sites

Fig. 2 shows the localities where the samples were taken. All of them were obtained in Argentina, in the provinces of Buenos Aires, Córdoba, La Pampa and Santa Fe.

3.2. Physical and chemical soil data

All the soils correspond to Mollisols order. Physico-chemical values of the surface soils horizons are presented in Table 1.

The pH of the soil surface varies between very acid to slightly acidic (5,2 to 6,9). Soil texture ranges from sandy loam to silt loam. The grain size is related to soil parent materials in each region. The total carbon content (TC) is very well provided as in the case of soil LasA (55,5 g/kg), and poorly provided in AN (4,01 g/kg). This is probably related to reduced precipitation and plant biomass. The soil CEC varied between low to moderate values according to texture and TC.

Physicochemical values of subsurface horizons of soils evaluated are shown in Table 2. These values were determined at the depth where the B horizon begins (accumulation horizon), which ranged between 60 and 80 cm in depth. Subsurface soils ranged from slightly acid to moderately alkaline pH (6,16 to 8,2), showing a texture from sandy loam to silty clay. On the other hand, TC diminishes (0,66 to 4 g/kg) and CEC had a low variability in comparison with the superficial horizon.

3.3. Soil silicon analysis

3.3.1. Distribution profile

The Si soil levels were separated into two groups (Figs. 3 and 4). Comparing these groups to each other, group A (Fig. 3) had a high Si content while Group B (Fig. 4) was lower. Group A had a concentration

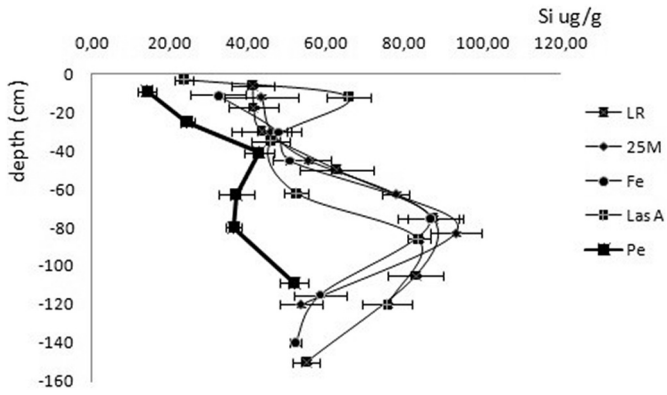


Fig. 3. Si distribution in the soil profile (group A), bands are standard error. Fig. 4. Si distribution in the soil profile (group B), bands are standard error.

from 20 µg/g to 100 µg/g. On the other hand, group B had a concentration from 20 µg/g to 40 µg/g. The two groups were separated by the silicon content and by its texture. The standard error was lower than 10%. Matichenkov and Bocharnikova (Matichenkov & Bocharnikova, 2008) classifies soils according to the concentration of Si identifying four classes with regards to their availability. The first class applies to well provide soils, where no fertilization is required, which are soils that contain values higher than 40 µg/g of available Si. On the other hand, there are poorly provided soils, where fertilization with Si is necessary, and these soils contain between 20 and 40 µg/g of available Si. If the soils have between 10 and 20 µg/g of available Si they are deficient soils, where Si fertilizers have a stable and significant effect on all crops and increase soil fertility. Finally, there are soils with very deficiency where the lack of Si has a negative effect on productivity and which are the soils that contain <10 µg/g of available Si (Clymans et al., 2011b; Matichenkov & Bocharnikova, 2008; Struyf et al., 2010). Song et al. (Song et al., 2014) wrote, Si is not an essential nutrient but it is a beneficial element against abiotic or biotic stress.

In Fig. 3 group A, the soils have been classified texturally as silty loam or clay loam, therefore they are fine textured Mollisols. The soluble Si content in surface horizons ranges from 15 to 40 µg/g of soil reaching a maximum of 100 µg/g at 80 cm depth. These findings agree with the results of Keller et al. (2012). They found at depth, amorphous Si may increase due to phytoliths translocation.

In Fig. 4, group B, soluble Si content remains relatively constant with an increasing profile depth. Profile values ranged from 15 to 30 µg/g in the surface with a maximum value of 40 µg/g for most soils except IAB. Most of these soils have been classified texturally as sandy or sandy loam, which are coarse textured Mollisols.

Therefore, soils in group A contain more Si than those in group B. According to Matichenkov's soils Si classification (2008), surface soils in

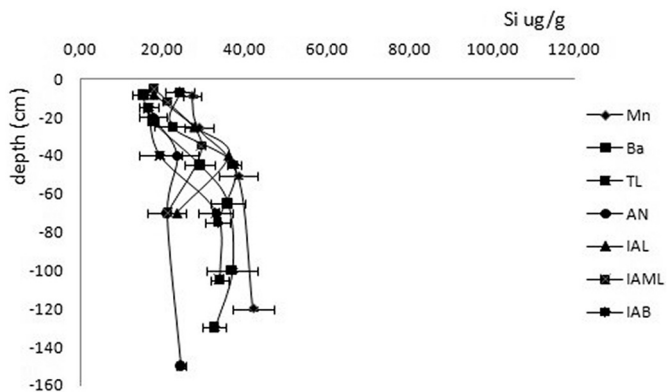


Fig. 4. Si distribution in the soil profile (group B), bands are standard error.

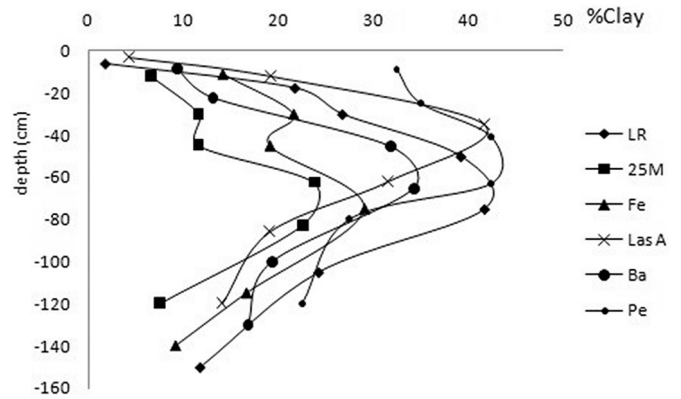


Fig. 5. Clay distribution in the soil profile (group A).

group A and group B would be classified as soils poorly provided. But this changes in depth because soils in group A, fine textured, have values >40 µg/g and they are well provided with this element. However, the group B, coarse textures, contained the same Si content in the surface as in depth. Possibly soils in group A have a subsurface Si reserve and therefore the coarse soils may have less Si available.

In previous studies, our work team found that coarse-textured Hapludolls soils in Buenos Aires province are poorly deficient in soluble Si with superficial values ranged between 13.3 µg/g to 30.1 µg/g soil matching with group B (Chirkes et al., 2012).

A very interesting result was found in group A. The profile Pe had 30 or 40% less soluble Si than the other profiles of the same group. Pe is a soil with >100 years of agricultural system, so it could be happening that the different crops in all these years absorbed a great quantity of soluble Si from the soil. Then, with the exports, those amounts of Si can be lost. As these soils are not fertilized with Si, it could be a limiting element in the future as has been discussed by Clymans et al. (Clymans et al., 2011b) and Struyf et al. (Struyf et al., 2010). The concentration of amorphous silica is lower in cultivated soils compared to natural ecosystems where plant Si is not exported (Guntzer et al., 2012). Haynes (Haynes, 2014) sustained that since the continual removal of Si in the harvested product is promoting desilication of soils, the addition of fertilizer Si may become a more common practice for a wide range of crops in the future. This way, cumulative manure amendment may increase the content of available Si in soils either directly- through manure available Si input- or indirectly through mineralization and transformation of other noncrystalline Si forms released from manure degradation (Song et al., 2014).

3.3.2. The relationship between Si and edaphic variables

The maximum Si value in all soils for group A could correspond to the maximum clay content (Fig. 5) while the low Si concentration

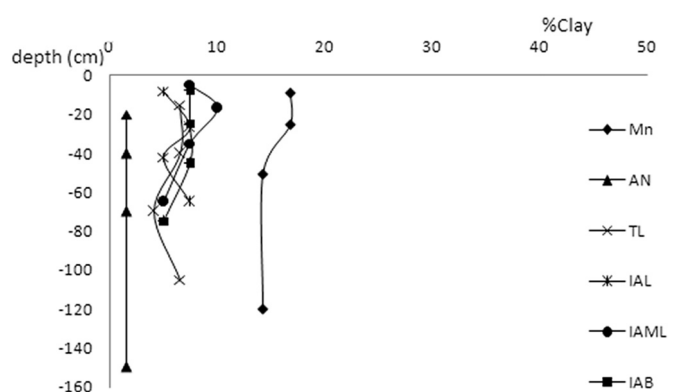


Fig. 6. Clay distribution in the soil profile (group B)

Table 3
Correlation between edaphic components for soil of group A

	Si	pH 1:2.5	C.E.	TC	TN	P	CEC	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	Sand	Silt	Clay
Si	1	0,02	0,3	0,01	0,01	0,19	0,42	0	0,04	0,84	0,03	0,86	0,92	0,89
pH 1:2.5	0,41**	1	0,03	0	0	0	0,04	0	0	0,01	0,02	0,02	0,02	0,88
C.E.	-0,19	0,4	1	0,25	0,19	0,36	0,09	0,38	0	0	0,09	0,84	0,86	0,95
TC	-0,54**	-0,57**	0,24	1	0	0,18	0,27	0,08	0,03	0,53	0,19	0,68	0,19	0,12
TN	-0,5**	-0,55**	0,27	0,99	1	0,3	0,26	0,08	0,04	0,6	0,17	0,73	0,22	0,13
P	-0,27	-0,67**	-0,19	0,28	0,22	1	0,9	0,21	0,04	0,16	0,48	0,01	0	0,48
CEC	0,17	0,42**	0,34*	-0,23	-0,23	-0	1	0,08	0	0	0	0,01	0,35	0
Ca ²⁺	0,51**	0,72**	0,16	-0,36**	-0,36**	-0,3	0,4**	1	0	0,07	0	0,31	0,45	0,63
Mg ²⁺	0,38**	0,8**	0,5**	-0,44**	-0,41**	-0,4**	0,8**	0,62	1	0	0	0,83	0,47	0,44
Na ⁺	-0,04	0,66**	0,82**	-0,13	-0,11	-0,3	0,7**	0,33	0,8**	1	0,02	0,91	0,48	0,36
K ⁺	0,39**	0,45**	0,31	-0,27	-0,28	0,15	0,75*	0,5	0,7**	0,42**	1	0,05	0,14	0,4
Sand	-0,17	0,43**	0,04	-0,09	-0,07	-0,5**	-0,5**	0,19	0,04	0,02	-0,4**	1	0	0,03
Silt	0,08	-0,43**	-0,03	0,27	0,25	0,6**	0,19	-0,1	-0,1	-0,1	0,27	-0,8**	1	0,19
Clay	0,19	-0,03	-0,01	-0,32	-0,31	-0,2	0,6**	-0,1	0,14	0,17	0,16	-0,38**	-0,2	1

n = 31. The cases with * correlate with a value of significance of $p < 0.1$ and **correlate with a value of significance of $p < 0.05$.

observed in group B could be associated with low clay content (Fig. 6). These values match with the results of Ma and Takahashi (2002). They measured the bioavailable Si in a soil profile under a cultivated field and they reported soluble Si concentrations in a paddy field increasing with depth. They interpreted these results as a pH effect, the pH increased with depth and the concentration of Si too. The profiles from group A have an increase in pH with depth too, so we could conclude the same although the regression had a low R² and a low correlation.

On the other hand, Borrelli et al. (Borrelli et al., 2008) also studied the content of phytoliths (particles of hydrated amorphous silica, SiO₂·nH₂O) in a soil of the Pampa and its relationship with vegetation cover. They found higher Si values in the forest than in the pasture and in each profile the Si content decreased from the surface level to subsurface soil levels.

Si levels also varied with the pH, TC and P content (Tables 3 and 4). Si concentration increased with pH (Tables 3 and 4) and similar findings for TC were described by Mostafa and Lall (Mostafa & Lall, 2014).

A competition between P and Si might exist for exchange sites on clay particles possibly via ligands, according to Tallberg et al. (Tallberg et al., 2008). This competition seemed to be more evident in group B (Table 4).

3.3.3. Correlations with studied edaphic variables

Correlations analyses are shown in Tables 3 and 4 between the studied edaphic variables Korndörfer et al. (Korndörfer et al., 2004) and Sparks (Sparks, 2003) found that as the pH increases the releases of Si desorption to the solution is promoted. The results of the present study agree with those observations. Those authors also mentioned that when the pH increases, there is a great

conversion of polysilicic acid (insoluble Si) to monosilicic acid (soluble Si). Different authors have described the relationship between pH increase and dissolution of Si increase (Bergna, 1994; Lindsay, 1979). Lindsay (Lindsay, 1979) mentioned that a pH >8.5 silicates are ionized with a significant contribution to the total Si solution. A negative correlation existed between Si and TC (Tables 3 and 4), so the main Si source is the inorganic soil fraction. Frayssé et al. (Frayssé et al., 2006) suggested that the major part of Si released in solution during plant litter degradation originated from phytoliths and not from the organic matter.

A positive correlation existed between Si and clay content. Korndörfer and his colleagues (2004) found that soluble Si seems to increase with the clay content. In our soils, the presence of a very well developed and enriched in clay minerals (22–38%) B horizon (Group A) could provide the condition for secondary silica precipitation (Borrelli et al., 2010). Grauer-Gray and Hartemink (Grauer-Gray & Hartemink, 2018) in a raster sampling found the distribution of Si was uniform in the Mollisol at 0–40 cm depth, but below 40 cm depth, the distribution of Si was irregular, with sharp horizontal changes in concentration occurring in multiple depth intervals. This coincides with what happens in the Hapludoles of this work but does not coincide with the Argiudoles. Gérard et al. (Gérard et al., 2008) suggested that Si concentrations in capillary solution are mainly biologically controlled (62%) with respect to geochemical contributions from K-feldspar dissolution (38%). So, phytoliths could play an important role in the silica cycle being an important source of Si in these soils, like in different environments around the world (Farmer et al., 2005).

Table 4
Correlation between edaphic components for soils of group B

	Si	pH 1:2.5	C.E.	TC	TN	P	CEC	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	Sand	Silt	Clay
Si	1	0	0,38	0,02	0,02	0,04	0,98	0,01	0	0,64	0,55	0,27	0,45	0,16
pH 1:2.5	0,53**	1	0,25	0	0	0,03	0,05	0	0,05	0,57	0,88	0,91	0,84	0,57
C.E.	-0,17	-0,22	1	0	0	0,35	0,04	0,48	0,83	0,83	0,13	0,33	0,18	0,59
TC	-0,44**	-0,66**	0,72	1	0	0,16	0	0,99	0,56	0,54	0,12	0,04	0,02	0,57
TN	-0,42**	-0,66**	0,7	1	1	0,22	0	0,93	0,68	0,49	0,1	0,03	0,02	0,43
P	-0,39**	-0,4**	0,18	0,26	0,23	1	0,2	0,07	0	0,05	0,27	0,39	0,66	0,11
CEC	0	-0,36**	0,38**	0,65**	0,68**	-0,2	1	0,01	0	0,33	0,02	0	0	0
Ca ²⁺	0,46**	0,51**	0,13	0	0,02	-0,3*	0,44	1	0	0,98	0,01	0	0	0
Mg ²⁺	0,52**	0,35**	-0,04	-0,11	-0,08	-0,5**	0,56	0,66	1	0,74	0,05	0	0,01	0
Na ⁺	0,09	0,11	-0,04	-0,12	-0,13	0,36**	-0,2	0	-0,1	1	0,1	0,3	0,25	0,6
K ⁺	0,11	-0,03	0,29	0,29*	0,31*	0,21	0,42	0,46**	0,36**	0,3*	1	0,03	0,08	0,05
Sand	-0,29*	0,02	-0,18	-0,39**	-0,4**	0,16	-0,8**	-0,7**	-0,7**	0,2	-0,4**	1	0	0
Silt	0,15	0,04	0,25	0,43**	0,43**	-0,1	0,62**	0,72**	0,49**	-0,2	0,33*	-0,96**	1	0,01
Clay	0,26	-0,11	-0,1	0,11	0,15	-0,3	0,76**	0,51**	0,79**	-0,1	0,35**	-0,73**	0,49**	1

n = 30. The cases with * correlate with a value of significance of $p < 0.1$ and **correlate with a value of significance of $p < 0.05$.

For cations, Si correlated positively with almost all elements but it doesn't have a correlation with sodium. This could show that the soil would have magnesium and calcium silicate.

The negative correlation between Si and sand content is consistent with the results described above, the Group B soils have more sand being coarse textured and they therefore contain less soluble Si than group A. This finding is expected since this Si in the sandy soil is not very reactive (quartz) and therefore it is poorly soluble (Sommer et al., 2006).

Evaluation of Si in these soils is very important due to its relevance in agricultural production worldwide. Si values may directly affect the production since its deficiency may cause crops disease.

Growing interest of Si study is dimensioned in the increasing number of papers addressing this topic. The rise in Si-deficient soils may find a solution by means of fertilization with Si which may increase its performance and would improve the physiological conditions of crops.

4. Conclusions

All soils are poorly provided of soluble silica superficially probably due to the activity of the plants and the formation of phytoliths. The finer soils texture (group A) are well provided in the subsurface while coarse texture (group B) contained the same Si content in the surface as in depth. The silicates clays present in the subsurface horizons (group A) may release or adsorb silicic acid.

Si correlates positively with pH and with clay content. On the other hand, Si correlates negatively with TC, P and sand content.

As sand content increases, the Si soluble content decreases, so the sandy loam to sandy soils are to suffer the greatest impact of agriculturalization.

There is a significantly negative relationship between Si and P suggesting a competition might exist between these two elements.

Finally, a finer soil (Pe) with >100 years of an agricultural system had 30/40% less soluble Si.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi: <https://doi.org/10.1016/j.geodrs.2018.e00191>. These data include the Google map of the most important areas described in this article.

References

- Bergna, H., 1994. *The Colloid Chemistry of Silica*. American Chemical Society, Washington, p. 695.
- Borrelli, N., Osterrieth, M., Marcovecchio, J., 2008. Interrelations of vegetal cover, silicophytolith content and pedogenesis of typical Argiudolls of the Pampean Plain, Argentina. *Catena* 75, 146–153.
- Borrelli, N., Osterrieth, M., Marcovecchio, J., Alvarez, M.F., 2010. Silica content in soil solution and its relation with phytolith weathering and silica biogeochemical cycle in typical Argiudolls of the Pampean Plain, Argentina—a preliminary study. *J. Soils Sediments* 10, 983–994.
- Chirkes, J.D., Azate, R., Heredia, O.S., 2012. Silicio en hapludoles bajo uso agrícola (CACS. Mar del Plata).
- Clarke, J., 2003. The occurrence and significance of biogenic opal in the regolith. *Earth Sci. Rev.* 60, 175–194.
- Clymans, W., Govers, G., Wesemael, B., Meire, P., Struyf, E., 2011a. Amorphous silica analysis in terrestrial runoff samples. *Geoderma* 167–168, 228–235 (a).
- Clymans, W., Struyf, E., Govers, G., Vandevenne, F., Conley, D.J., 2011b. Anthropogenic Impact on Amorphous Silica Pools in Temperate Soils. *Biogeosciences* 8, 2281–2293 b.
- Cornelis, J.T., Delvaux, B., 2016. The functional role of silicon in plant biology. *Soil processes drive the biological silicon feedback loop. Funct. Ecol.* 30, 1298–1310.
- Cosentino, 2002. Limos de baja densidad: impacto sobre el comportamiento físico de los suelos de la región pampeana. *Ciencia del Suelo* 20 (1), 9–16.
- Di Rienzo J.A., Casanoves F., Balzarini M.G., Gonzalez L., Tablada M., Robledo C.W. *InfoStat* versión 2010. Grupo InfoStat, FCA, Universidad Nacional de Córdoba, Argentina.
- Dietzel, M., 2000. Dissolution of silicates and the stability of polysilicic acid. *GeochimCosmochim* 64, 3275–3281.
- Dietzel, M., 2002. In: Stober Bucher, K. (Ed.), *Interaction of polysilicic and monosilicic acid with mineral surfaces*, pp. 207–235 Kluwer, Netherlands.
- Doncheva, Sn., Poschenrieder, C., Stoyanova, Z.L., Georgieva, K., Velichkova, M., Barceló, J., 2009. Silicon Amelioration of Manganese Toxicity in Mn-Sensitive and Mn-Tolerant Maize Varieties. *Environmental and Experimental Botany.* 65 pp. 189–197.
- Dove, P. M., 1995. Kinetic and Thermodynamic Controls on Silica Reactivity in Weathering Environments, in White, A. F., Brantley, S. L. (Eds): *Mineralogy Society of America*, Washington, DC. pp. 235–290.
- Drees, L.R., Wilding, L.P., Smeck, N.E., Sankayi, A.L., 1989. Silica in soils: Quartz and disordered silica polymorphs. Chap 19. In: Dixon, J.B., Weed, S.B. (Eds.), *Minerals in Soil Environments*. SSSA Book Series N 1. Madison, WI, pp. 913–974.
- Epstein, E., 1994. The anomaly of silicon in plant biology. *Proc. Natl. Acad. Sci. U. S. A.* 91, 11–17.
- Farmer, V.C., Delbos, E., Miller, J.D., 2005. The role of phytolith formation and dissolution in controlling concentrations of silica in soil solutions and streams. *Geoderma* 127, 71–79.
- Fauteux, F., Rémus-Borel, W., Menzies, J.G., Bélanger, R.R., 2005. Silicon and plant disease resistance against pathogenic fungi. *FEMS Microbiol. Lett.* 249, 1–6.
- Frayse, F., Cantais, F., Pokrovsky, O.S., Schott, J., Meunier, J.D., 2006. Aqueous reactivity of phytoliths and plant litter: Physico-chemical constraints on terrestrial biogeochemical cycle of silicon. *J. Geochem. Explor.* 88, 202–205.
- Frenguelli, J., 1955a. *Loess y Limos Pampeanos*. Facultad de Ciencias Naturales y Museo, Universidad Nacional de La Plata. Serie técnica y didáctica. 7 pp. 1–88 (La Plata).
- Frenguelli, J., 1955b. *Loess y limos pampeanos. Serie técnica y didáctica del Museo de La Plata*, N. p. 7.
- Gérard, F., Mayer, K.U., Hodson, M.J., Ranger, J., 2008. Modelling the biogeochemical cycle of silicon in soils: Application to a temperate forest ecosystem *Geochimica et Cosmochimica Acta.* vol. 72 pp. 741–758.
- Grauer-Gray, J.G., Hartemink, A.E., 2018. Raster sampling of soil profiles. *Geoderma* 318, 99–108.
- Guntzer, F., Keller, C., Poulton, P.R., McGrath, S.P., Meunier, J., 2012. Long-term removal of wheat straw decreases soil amorphous silica at Broadbalk. *Rothamsted Plant Soil* 352, 173–184.
- Haynes, R., 2014. A contemporary overview of silicon availability in agricultural soils. *Rev. J. Plant Nutr. Soil Sci.* 177, 831–844.
- Heredia, O.S., 2014. *Edafología, bases y aplicaciones ambientales argentinas*, capítulo 3.3. Editorial Facultad de Agronomía. p. 628.
- Iler, R.K., 1979. *The Chemistry of Silica*. Wiley, New York, p. 896.
- INTA, 2008. Serie 1996-2006 S. Gómez. Base de datos agroclimáticos I.C. y A.C.I.R.N.
- Klute, A., 1986. *Methods of soil analysis. Part 1 2nd ed Agron Monogr 9. ASA and SSSA*, Madison, W. I., p. 1986.
- Korndörfer, G.H., Pereira, H.S., Nolla, A., 2004. Análise de silício: solo, planta e fertilizante. Grupo de pesquisa "Silício na agricultura" Boletim técnico n° 3. p. 23.
- Lindsay, W.L., 1979. *Chemical Equilibria in Soils*. Wiley-Interscience Publication, p. 449.
- Marxen, A., Klotzbücher, T., Jahn, R., Kaiser, K., Nguyen, V., Schmidt, A., Schädler, M., Vetterlein, D., 2016. Interaction between silicon cycling and straw decomposition in a silicon deficient rice production system. *Plant Soil* 398, 153–163.
- Matichenkov, V.V., Bocharnikova, E.A., 2008. Silicon deficiency and functionality in soils, crops and food. *Proc Second Intern. Conf. "Ecobiology of Soil and Compost"*, pp. 207–213 Spain, Tenerife.
- Mitzky, Cirelli, 2004. Silica dynamics in pampean lake (lake Chascomús, Argentina). *Chem. Geol.* 203, 109–122.
- Mostafa, A., Lall, R., 2014. Soil carbon and silicon pools across an un-drained topo sequence in Central Ohio. *Catena* 120, 57–63.
- Opfergelt, S., De Bournonville G., Cardinal, D., Andre, L., Delstanche, S., Delvaux, B., 2009. Impact of soil weathering degree on silicon isotopic fractionation during adsorption onto iron oxides in basaltic ash soils. *Cameroun Geochimica et Cosmochimica Acta* 73, 7226–7240.
- Pecorari, C., Guerif, J., Stengel, P., 1990. Fitolitos en los suelos pampeanos argentinos: influencia sobre las propiedades físicas determinantes de los mecanismos elementales de la evolución de la estructura. *Ciencia del suelo* 8, 135–141.
- Pecorari, C., Guerif, J., Stengel, P., 1991. Fitolitos en los suelos pampeanos argentinos: influencias sobre las propiedades físicas determinantes de los mecanismos elementales de la evolución de la estructura. INTA, Instituto nacional de tecnología agropecuaria. Centro regional Buenos Aires Norte, estación experimental agropecuaria Pergamino. Informe técnico N°, p. 260.
- Peinemann, N.Y., Ferreira, E., 1972. Fitolitos: sílica gel natural. *Anales de edafología y agrobiología. Consejo Superior de Investigaciones Científicas. Tomo XXXI N° 11 y 12.* pp. 1011–1026 (Madrid).
- Soil Taxonomy, 2014. *A Basic System of Soil Classification for Making and Interpreting Soil Surveys*.
- Sommer, M., Kaczorek, D., Kuzyakov, Y., Breuer, J., 2006. Silicon pools and fluxes in soils and landscapes—a review. *J. Plant Nutr. Soil Sci.* 169, 310–329.

- Song, Z., Wang, H., Strong, P., Shan, S., 2014. Increase of Available Soil Silicon by Si-Rich Manure for Sustainable Rice Production. *Agronomy for Sustainable Development*. Springer, pp. 813–819.
- Sparks, D.L., 1996. *Methods of Soil Analysis. Part 3. Chemical Methods*. Vol. 677.
- Sparks, D.L., 2003. *Environmental Soil Chemistry*. 2nd Edition. Academic Press, p. 351.
- Sposito, G., 2008. *The Chemistry of Soils*. Second edition. Oxford University Press, Inc, p. 329 ISBN 978-0-19-531369-7.
- Struyf, E., Smis, A., Van Damme, S., Garnier, J., Govers, G., Van Wesemael, B., Conley, D.J., Batelaan, O., Frot, E., Clymans, W., Vandevenne, F., Lancelot, C., Goos, P., Meire, P., 2010. Historical land use change has lowered terrestrial silica mobilization. *Nat. Commun.* 1, 1–7.
- Tallberg, P., Tréguer, P., Beucher, C., Corvaisier, R., 2008. Potentially mobile pools of phosphorus and silicon in sediment from the Bay of Brest: Interactions and implications for phosphorus dynamics Estuarine, Coastal Shelf Sci. 76, 85–94.
- Yang, X., Song, Z., Liub, H., Van Zwietenc, L., Songd, A., Haoa, Lie, Zhanga, X., Wang, H., 2018. Phytolith accumulation in broadleaf and conifer forests of northern China: Implications for phytolith carbon sequestration. *Geoderma* 312, 36–44.