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Quaternary Research

journal homepage: www.elsevier.com/locate/yqres

Formative pre-Hispanic agricultural soils in northwest Argentina

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ARTICLE INFO

Article history:

Received 30 November 2009

Available online xxxx

Keywords:

Geoarchaeology

Pre-Hispanic agriculture

Pedology

Soil chemistry

Formative Period

Tafi culture

ABSTRACT

Our study area is from an early agricultural archaeological site named "El Tolar" (1st to 9th century AD), located in Tafi Valley (Tucumán, northwest Argentina). The objective was to identify geochemical signatures generated by the sustained agrarian use of soils. Chemical and pedological studies were made in different archaeological contexts. Physical and chemical features, such as bulk density, pH, organic and inorganic phosphorus, and available copper, manganese and iron, were taken into account. The results suggested that a buried paleosol identified was contemporary with the occupation of the site. It also showed characteristics clearly related to pre-Hispanic agrarian production. The concentrations of organic phosphorus and iron in agricultural soils probably reflect the use of fertilizers. The application of geoscience techniques allowed us to obtain important information on their behaviour and socio-economic development. This paper constitutes the first pedogeochemical approach to the study of Argentinean pre-Hispanic agricultural soils.

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Introduction

Many kinds of land use can alter soil properties, and agriculture can cause especially significant changes to soils and landscapes (Sandor and Eash, 1995). Agriculture began in northwestern Argentina around 2500 yr ago. The magnitude and duration of agricultural practices, along with environmental factors, and the natural characteristics and sensitivity to disturbance of the soil can produce different results (Sandor and Eash, 1995).

Agricultural terraces from the Tafi Valley present an excellent opportunity to study soils that have been cultivated during the first millennium after Christ, and may be representative of the earliest agricultural practices in northwestern Argentina. Tafi Valley is located in the heart of the pre-Andean region of northwestern Argentina (Fig. 1). It is a highland valley, and constitutes a key area in the understanding of the earliest agricultural places in the highlands of the region, where agricultural terraces survive until the present day.

First sedentary settlements of the valley started during the Formative Period, between 500 BC and 1000 AD (Olivera, 2001). The socio-cultural system of the Formative Period is characterized by landscape manipulation through early agricultural and pastoral production techniques, and by hunting and gathering practices. Due

to their technical development, small groups of people were sustained in early village settlements (Olivera, 2001).

The most conspicuous settlements of Tafi Valley were characterized and named "Tafi culture" by González and Nuñez Regueiro (1960). There were some important cultural changes after the collapse of this culture. The use of spaces changed, settlements became dispersed and rarer, and satellite villages belonging to the Santa María socio-cultural society (1000 to 1400 AD) were established in the Santa María Valley (Tarragó, 2000).

Our study was focused on Tafi agricultural settlements, especially those at the El Tolar archaeological site (Fig. 1). The socio-cultural development of this entity was based on the exploitation of natural resources through agriculture and animal breeding (i.e. llamas, *Lama glama*) (Berberian et al., 1988). These activities involved the development of sedentarism together with specific agricultural tools, ritual behaviours related to soil (Sampietro Vattuone et al., 2008), and among other practices, improvements in building technologies.

In this context, the purpose of this study was to investigate pedogeochemical features produced by sustained agricultural practices performed during the Formative Period at the El Tolar archaeological site. The main questions revolve around how almost ten centuries of agricultural use under pre-Hispanic techniques introduced modifications in the old occupational surface and soils, and in which ways the original geomorphological units and soils sustained societies.

This paper makes a qualitative comparison of soil properties described from three contextual locations: (a) long-term cultivated sites; (b) contemporaneous residential areas; and (c) a control off-site location, all in the same geomorphological unit.

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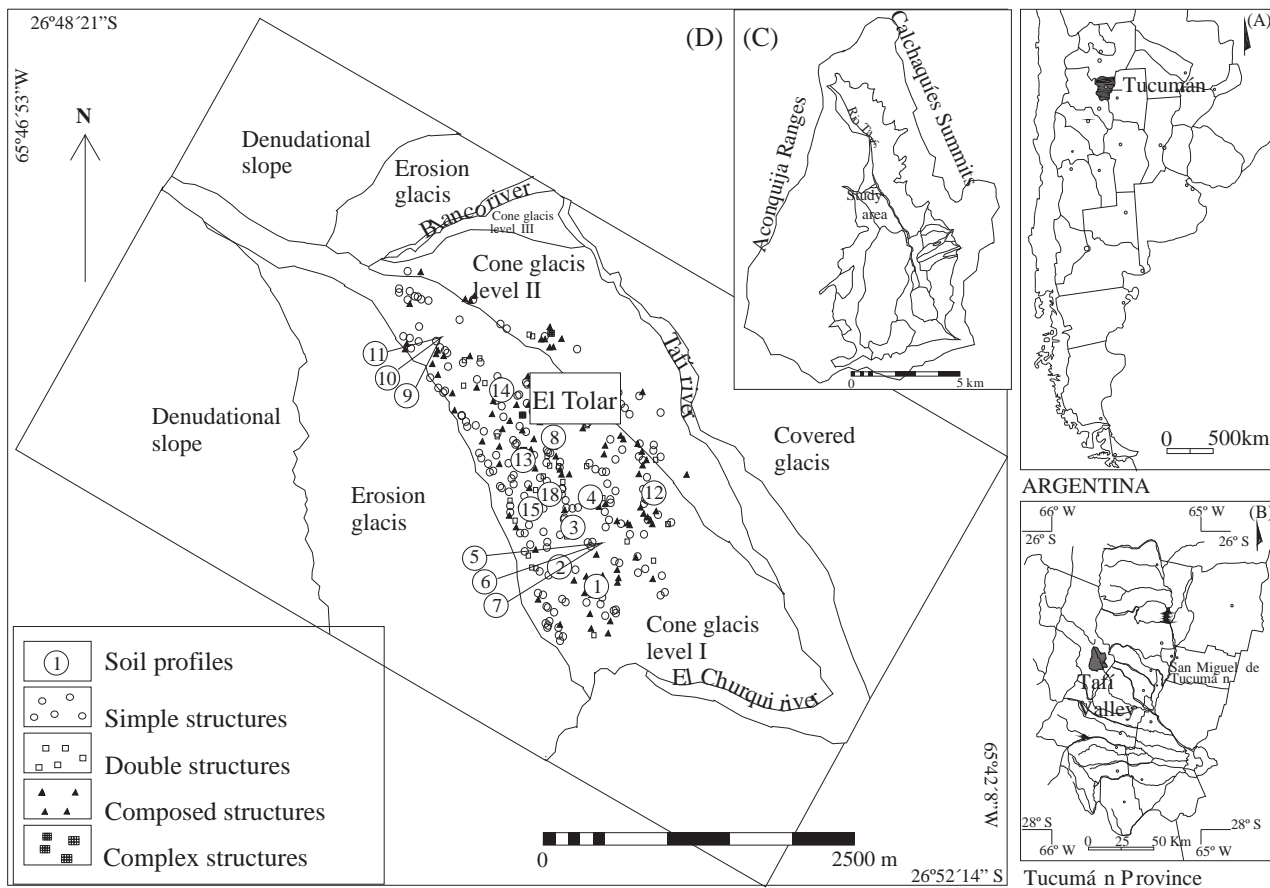


Figure 1. El Tolar archaeological site location. (A) Argentina; (B) Tucumán province; (C) Tafi Valley; (D) El Tolar archaeological site, geomorphology and sampled profile distribution.

The aim was to characterize the human impact on soil, to help understand better the way in which resource management was carried out. In combination with paleoenvironmental data we aim to assess soil productivity under past agricultural techniques, and to postulate on the implications to understand population variability. Moreover, through the application of a theoretical and methodological spectrum derived from pedogeochemical analysis in an archaeological context, it is possible to elaborate an inferential framework for the reconstruction of agricultural behaviour, such as social strategies of the study region. This framework is especially significant in archaeological sites where material features like agricultural field are scarce. With this information and other cultural characteristics, it is possible to improve knowledge on the symbolic aspects of agrarian societies.

This paper constitutes one of the first systematic approaches oriented to the determination of the alterations introduced by humans into pre-Hispanic soils by the effect of Formative agricultural activities. This information is also relevant to modern problems in soil and water conservation of semi-arid environments because this approach transcends local geographical and cultural conditions.

Study area

Tafi Valley is located between 26°45' and 26°58' South latitude, and 65°39' to 65°48' West longitude (Fig. 1). It is an elongated tectonic basin with a total surface area of 450 km². The valley bottom is located between 1800 and 2500 meters above sea level (masl), with a medium slope of 18.8% oriented north/south (Bolsi et al., 1992).

The present climate is semi-arid, with mean annual precipitation between 400 and 550 mm. The mean annual temperature is about 13.1°C (Sesma, 1987). The surface of the valley is predominantly

grassland, which makes archaeological structures easily visible on aerial photographs.

Our focus in this valley is the El Tolar archaeological site (26°48'21" to 26°52'14" South latitude; 65°42'8" to 65°46'53" West longitude). It is located on the piedmont of the Aconquija Ranges (Sampietro and Sayago, 1998) (Fig. 1). This area is currently used for extensive cattle ranching.

Geomorphologically, it is a cone glacia, defined by Viers (1976) as an accumulation glacia with the shape of a cone or fan. It is possible to distinguish three major debris-flow depositional events from aerial photographs. These show differences in spatial distribution and morphogenetic characteristics. The oldest is the most extensive, marking the climax of periglacial conditions (Sampietro and Sayago, 1998). Its altitude ranges between 2200 and 2800 masl.

Tafi as a socio-cultural entity

Tafi settlements were recognized as an early socio-cultural entity from northwestern Argentina, (Ambrosetti, 1897; Lafone Quevedo, 1902; Bennett et al., 1948). A clear definition of Tafi settlements as "Tafi culture" was made in the 1960s, after the first systematic archaeological digs were made (González and Nuñez Regueiro, 1960). The archaeological record helped define this culture through its lithic sculptures (menhirs and stone masks), settlement pattern (circular stone enclosures isolated or associated around a central patio forming residential units, in some cases these residential units are agglomerated forming villages), agricultural structures, and a ceremonial mound (Casas Viejas archaeological site – El Mollar) (Berberian et al., 1988; Tartusi and Nuñez Regueiro, 1993; Sampietro Vattuone, 1994, 2002).

Radiocarbon analyses established that these settlements are inside the period regionally known as Formative, from 2296 ± 70 ^{14}C yr BP (Y888) (González, 1965) to 1140 ± 50 ^{14}C yr BP (CSIC586) (Berberían et al., 1988). This period was characterized by the appearance of early agricultural settlements in northwestern Argentina.

The sedentarism, typical of this Formative society was always culturally influenced from other Andean regions, like the Bolivian highlands (Tartusi and Nuñez Regueiro, 1993) and northern Chile (Domínguez Bella and Sampietro Vattuone, 2002).

Some artefacts associated with Tafi culture were also found outside the valley: at the El Portugués stream on the Tucumán plain (Heredia, 1975; Nuñez Regueiro and García Azcárate, 1996); at El Infiernillo, in association with Ciénega ceramic (Caria et al., 2006); at La Ciénega valley, associated with Candelaria ceramic (Bernasconi de García and Baraza de Fonts, 1985; Cremonte, 1996); and at Medina valley, on the east side of Tucumán Province (Krapovickas, 1968).

Paleoenvironment and plant resources

The environment in which Formative cultures were developed allowed us to understand the potential management of space and resources. Even though there was climatic variability in each region, each human group took unique adaptive decisions in response to similar environmental conditions.

The first agricultural populations appeared in the Argentinean Meridional Puna (3000–2500 BP) (Olivera et al., 2004) as well as in Tafi Valley (2300–1100 BP) (González and Nuñez Regueiro, 1960; Berberían et al., 1988). This period was paleoenvironmentally characterized by the presence of wetter and warmer conditions than today (Sampietro Vattuone, 1999; Tchilinguirian and Olivera, 2000; Olivera et al., 2004). These conditions favored the rise of earliest agricultural centres of the region. According to pollen (Garralla, 1999) and pedological data (Sampietro Vattuone, 1994; Sampietro and Sayago, 1998; Sayago et al., 2001; Sampietro Vattuone, 2002), these conditions persisted until around 875 ± 20 ^{14}C yr BP (Garralla, 1999). After that, pollen evidence indicates a shift to a relatively drier period. This was contemporaneous with the abandonment of the Formative settlements of the valley, while in the Southern Puna, new technological agricultural criteria were incorporated through artificial irrigation in areas with inclined slopes (Tchilinguirian and Olivera, 2000; Olivera et al., 2004) (Fig. 2).

An important feature of these Formative societies was the use of both wild and domesticated plant resources. Squash cultivation was very common in the lowland pre-Andean region, with maize, beans and peanuts being typical from middle altitudes, while quinoa and potatoes were typical in the highlands. Maize was the most important species for this period (Oliszewski, 2004). Remains of Chilean palo

verde (*Geoffroea decorticans*), black and white carob tree (*Prosopis nigra* and *P. alba*), beans (*Phaseolus vulgaris*) and maize (*Zea mays*) were found in Formative settlements from Tafi Valley (Carrizo et al., 1997).

El Tolar archaeological site

The first systematic archaeological research at El Tolar archaeological site was performed by Sampietro Vattuone during the 1990s. It occupies around 13.9 km², with residential structures dispersed among walled agricultural terraces, and an irrigation system that allowed the management of flowing water over the entire geomorphological unit (Sampietro Vattuone, 1994; Sampietro and Sayago, 1998). The partial excavation of a household unit, together with its building characteristics, and a radiocarbon date (1560 ± 35 ^{14}C yr BP), determined that the settlement belonged to the Tafi culture (Sampietro Vattuone, 2002; Sampietro and Vattuone, 2005).

The human occupation of El Tolar was favored by a good water supply from the Blanco River, and a relatively smooth slope (between 8 and 13%, SE exposed) (Sampietro and Sayago, 1998). Agricultural walled terraces were constructed to control or attenuate erosive processes and to favor slope stabilization (Sampietro Vattuone, 2002). Sampietro Vattuone (2002) simplified the building classification into two major categories: agricultural structures and circular rooms (Fig. 2). The first category included “despedres” (elongated mounds formed by removing stones from agricultural fields) and agricultural terraces (walls constructed perpendicular to the slopes). The second category could be divided into: simple circular rooms (one isolated structure), double circular rooms (two rooms with the same shape and dimensions constructed together), composite units (one big circle surrounded by smaller ones forming a household unit), and complex units (two or more big circles together with smaller ones forming a network where it was impossible to define restricted units). These structures are distributed as shown in Figure 1.

Settlement abandonment was related to human pressures (such as demographic pressure and food availability), together with environmental changes (especially a decrease of flowing water) registered in the late occupational period (Sampietro Vattuone, 2002).

The pedological sequence identified at the study area is represented by three superimposed edaphic cycles. The present topsoil is represented by an A/AC/C sequence. The second cycle, the pre-Hispanic settlement surface, is represented by a well-developed paleosol, with illuvial features, relatively thick horizons, carbonate micro-concretions, and clay coatings. Carbonate micro-concretions and clay coatings are more abundant close to agricultural terrace walls, showing their role in the retention of soil moisture, probably associated with irrigation practices. The absence of a 2A horizon in all

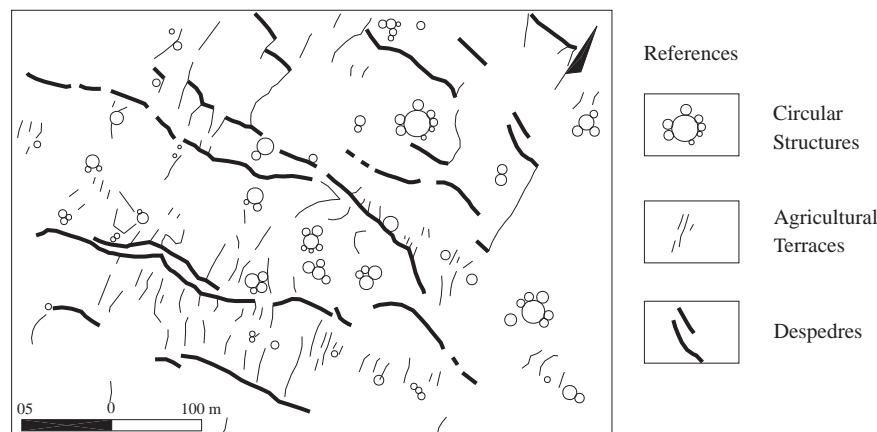


Figure 2. Detail of a section of El Tolar archaeological site.

profiles was interpreted as the result of natural erosion processes (hydric and/or eolic) accelerated by human activity on soils in the transition to present soil (Sampietro and Sayago, 1998; Sampietro Vattuone, 2002). Previous pedogeochemical studies showed alterations in available phosphorus content of the agricultural paleosol, while inside residential units this component tended to remain stable (Sampietro Vattuone, 2001, 2002). Finally, the third pedological cycle represents a pre-occupational epoch and does not have any identified archaeological features.

Materials and methods

The complexity of geological soil parent materials, soil processes, and potential anthropogenic modifications made it necessary to choose a sample extraction/decomposition technique that was compatible with the specific objectives of the analysis. To identify past human agricultural soil modifications we selected techniques that allowed the establishment of available forms of soil micronutrients focused on features related to anthropogenic modifications. Nevertheless, the debate about what constitutes the most appropriate extraction technique for geoarchaeological studies is an ongoing one (e.g. Entwistle et al., 2000; Middleton, 2004).

Eighteen test pits were made in different archaeological contexts (agricultural terraces, household units, and one control test pit without superficial archaeological evidence) inside the cone glacis unit. We considered the geomorphological unit as a sample unit because it represents a basic environmental entity, which is adequate to infer resource availabilities and the extrapolation of paleopedological, paleoclimatic, lithostratigraphic, and geochronological data for the entire geomorphological unit (Sayago and Collantes, 1991; Sampietro Vattuone, 2001).

Twelve test pits were located in agricultural terraces (profiles 1 to 12), five were inside the patios of residential units (profiles 13 to 17), and one profile (representative of off-site conditions) was inside the same geomorphological unit (profile 18). Soil descriptions were made according to the procedures outlined by Soil Taxonomy (Soil Survey Staff, 1999). The central part of each soil horizon was sampled for laboratory analyses.

Chemical analyses were carried out on profiles 8 to 13, 17, and 18. Thirty-two samples were obtained. Bulk density (BD) (method of parafined clod), porosity (estimated using the previous parameter and the real density of the sample), pH, texture (Bouyoucos, 1936), organic matter, and carbon (C) inferred from organic matter contents (Walkley and Black, 1946) (Table 1). Available key macronutrients (phosphorus (P) and calcium (Ca)), and micronutrients (iron (Fe), copper (Cu), and manganese (Mn)) were also determined (Buckman and Brady, 1977).

Bulk density is considered here as a proxy of tillage effect on the soil. In fact, soil compaction increases bulk density and decreases pore volume (Kooistra and Tovey, 1994). If bulk density becomes too high, it can limit plant root growth; can lead to aeration stress on soil (Stepniewski et al., 1994); diminishes soil temperature and produces changes in biological processes (Brussaar and Van Faassen, 1994) such as increases in denitrification (Linn and Doran, 1984), and loss of mycorrhizal fungi (Ellis, 1998). For these reasons bulk density is frequently identified as an indicator of soil quality (USDA-NRCS, 1996a,b) and included in many minimum data sets (Logsdon and Karlen, 2004). Due to the wide influence that bulk density could have over different aspects of soils, it could be taken as a sensitive indicator of soil quality (USDA-NRCS, 1996a,b). Variables like parent material, soil texture, the crop being grown, and land management history are influencing bulk density and finally will affect the growth and development of cultivated plants. High bulk-density values reflect

Table 1

Results obtained from soils physical and chemical analysis (BD: bulk density; AP: available phosphorous; OP: organic phosphorous).

Sample	Depth cm	BD	Porosity %	pH	Texture	Organic matter %	Calcium ppm	AP ppm	OP ppm	Iron ppm	Manganese ppm	Copper ppm	
Profile 8	A	0-13	1.19	37.6	5.07	Sandy loam	9.41	448	161	7353	48.75	14.75	9
	2B	13-25	1.54	36.9	5.35	Sandy loam	4.8	420	186	14744	15.54	8.52	23
	2BC	25-50	1.50	38.5	6.29	Sandy loam	4.46	762	167	4588	11.18	0.49	0.7
Profile 9	A	0-19	1.52	41.9	5.74	Sandy loam	7.34	600	149	10497	22.55	1.94	2.8
	2B	19-29	1.83	24	6.39	Sandy loam	4.53	512	149	7186	11.18	1.11	0.3
	2BC	29-48	2.2	9.8	6.66	Sandy loam	1.81	576	211	6051	10.12	2.65	200
Profile 10	2C	48-70	1.6	34.4	7.13	Sandy loam	1.25	384	254	2486	11	1.85	1
	A	0-18	1.21	42.3	5.81	Sandy loam	6.18	480	136	20869	20.91	4.33	28
	2AB	18-40	1.35	43.7	6.13	Sandy loam	4.6	576	130	19456	11.44	4.06	17
Profile 11	2B	40-56	1.47	38.4	6.48	Sandy loam	2.74	576	174	3770	7.26	3.40	28
	2C	56-70	1.99	22.8	6.87	Sandy loam	1.43	400	223	11557	7.2	2.75	41
	A	0-16	1.55	29.5	5.78	Sandy loam	5.63	448	87	4743	10.76	3.12	9.7
Profile 12	2AB	16-28	1.37	42.4	6.19	Sandy loam	4.6	576	124	21471	11.48	2.89	63
	2BC	28-42	1.52	37.1	6.67	Sandy clay loam	3.01	642	130	13733	9.9	2.67	37
	3B	42-55+	1.51	39.1	6.9	Sandy clay loam	1.24	512	100	7800	8.77	4.25	0
Profile 13	A	0-5	1.4	33	5.68	Sandy clay loam	6.8	722	180	17019	21	6.20	0
	AC	5-17	1.37	41.9	5.4	Sandy clay loam	4.74	496	100	16610	16.06	5.86	0
	2A	17-27	1.26	46.6	6.22	Sandy clay	4.46	770	68	16678	9.24	2.40	0
Profile 17	A	0-21	1.25	33.1	5.56	Clay	5.39	420	143	26108	28.12	7.46	0
	BC	21-40	1.54	36.8	6.44	Sandy clay	2.53	576	62	19511	0.02	1.23	0
	2AB	40-59	1.36	44.4	6.73	Sandy clay	1.81	682	62	23926	3.33	0.76	29
Profile 18	2B	59-90	1.46	43.6	7.11	Sandy clay	0.84	448	124	16622	2.31	0.39	2
	A	0-9	0.88	41.3	5.4	Sandy loam	7.96	898	192	16101	16.8	2.73	0
	AC	9-20	1.37	38.2	6.41	Sandy loam	3.05	706	174	17906	4.41	2.63	54
Profile 18	2A	20-35	1.22	36.4	7.48	Sandy loam	1.43	898	242	15990	2.31	1.19	0
	2B	35-95	1.41	43.3	7.61	Sandy loam	1.05	642	87	4991	1.35	0.67	0
	3B	95-1.3+	1.62	35.7	6.86	Sandy loam	0.74	820	198	15556	2.36	0.67	0
Profile 18	A	0-10	1.4	18.1	5.63	Sandy loam	7.41	898	161	3410	50.43	8.90	0
	AB	10-20	1.55	32.3	6.46	Sandy loam	3.98	898	112	17087	13.44	1.85	23
	B	20-60	1.52	37.4	6.94	Sandy loam	1.74	820	167	3590	4.18	1.23	9.8
	BC	60-75	1.48	39.8	7	Sandy loam	1.18	682	105	5227	2.36	0.64	0
2AB	75-90+	1.5	40.9	7.01	Sandy loam	0.84	620	130	20237	2.36	0.81	0	

soil compaction affecting soil properties, especially by reducing infiltration and nutrient cycling, and increasing runoff with soil erosion and soil losses (Logsdon and Karlen, 2004).

Another important feature to evaluate soil quality is the organic matter content, which is also related to soil bulk density (USDA-NRCS, 1996a,b). Soil organic matter (soil carbon) can significantly affect bulk density and the potential for compaction by influencing soil water retention (Hudson, 1994). In addition, soil organic matter usually has lower particle density than minerals, which may reduce overall soil bulk density. It also provides a carbon and energy source for soil microbes, and stabilizes and holds soil particles together, thus reducing the hazard of erosion. This aids the growth of crops by improving soil ability to store and transmit air and water (USDA-NRCS, 1996a,b). Nutrients such as nitrogen, phosphorous, and sulphur are needed for the growth of plants and soil organisms, and are better retained in soils with low bulk density. When soils are tilled, organic matter decomposes more rapidly because of changes in water, aeration, and temperature conditions. The amount of organic matter lost after tilling native grasslands varies according to the kind of soil, but most organic matter is lost within the first ten years. Losses are higher with aerobic decomposition. The amount of soil organic matter is controlled by a balance from additions of plant and animal material and losses from their decomposition. Both addition and losses are strongly controlled by management activities (USDA-NRCS, 1996a,b).

Soil pH is also an indicator of soil quality. It influences the solubility of nutrients and also affects the activity of micro-organisms responsible for breaking down organic matter and most chemical transformations in the soil. Soil pH thus affects the availability of several plant nutrients. A pH range of 6 to 7 is generally most favorable for plant growth because most plant nutrients are readily available in this range (USDA-NRCS, 1996a,b).

Among macronutrients phosphorus (P) is an archaeologically significant indicator of human activity among agricultural and pre-agricultural societies. Few elements left by humans are as ubiquitous, sensitive, and persistent as an indicator of human activity as P (Holliday and Gartner, 2007). Human activity can strongly redistribute P in soils. Plants take up P from soils. They can be eaten by animals or harvested. The animals themselves can be moved or used; they can be housed and thus concentrate P in a particular area. Dung residues can be collected and used as manures, respread over fields, or they may be used as a fuel, as walling material, or ignored. As part of an economic system, P is very mobile, and its importance lies in the strong fixative powers of the soil. When P enters the soil system it is relatively immobile compared to other elements concentrated by human activities (Bethel and Máté, 1989). Phosphorus can be found in several different kinds of compounds. Here available P refers to the fraction of P compounds that are easily extractable with weak acids and normally used by plants to growth. This fraction is especially important for agroecosystems, its presence in soils normally depends on the characteristics of parent material and is easily removed by continuous harvesting. Total P refers to organic and inorganic P containing compounds that persist and are fixed in soils for an extended period of time. The difference between the values of available P and total P gives us an estimation of organic P content of samples. All these values allow us to make inference of the range of anthropic activities.

Micronutrients like copper (Cu), zinc (Zn), manganese (Mn), iron (Fe), molybdenum (Mo), and boron (B) are essential for plant growth. These elements, also named heavy metals, may be toxic to plants at high concentrations. Micronutrients are either inherited from soil parent material or inputs through human activities in an agroecosystem. Repeated use of metal-enriched chemicals, fertilizers, and organic amendments such as manure may cause variations in their concentrations. Both deficiency and toxicity of trace elements occur in agroecosystems, so the knowledge of their presence and concentra-

tion can be used to diagnose soil contamination or deficiency in micronutrients (Zhenli et al., 2005).

Prehistoric anthropogenic activities can influence inputs of micronutrients through the use of fertilizers, organic manures, food processing and storage, irrigation, and the moisture conditions.

Outputs of micronutrients from agroecosystems include crop harvest, losses by leaching, surface runoff, and gaseous emissions. In this context crop harvest accounts for a large proportion of outputs according to the type of soil, crop variety, and climate conditions (Zhenli et al., 2005).

It is remarkable that only a small proportion of micronutrients in soil are often bioavailable. The mobility and availability of micronutrients are controlled by many of the chemical and physical qualities of parent soil, that is why it is important to check bulk density, porosity, texture, and pH.

Available P was determined by the molybdenum blue method (Fiske and Subbarow, 1925). Total P was determined with the same method, after a sample digestion with sulphuric acid (Fiske and Subbarow, 1925). Organic P was estimated by the difference between these values. Phosphorus can be stable over centuries in soils, though it tends to be quickly associated with other soil elements (Terry et al., 2000). Calcium was determined by the EDTA Na₂ (ethylenediaminetetraacetic acid disodium salt) and murexide (Sampietro and Vattuone, 2005).

Available iron was determined by soil extraction with ammonium acetate-acetic acid and reduction with hydroxylamine chlorhydrate. Optical density was read at 508 nm in a Beckman DU 650 spectrophotometer (Roldán et al., 2005). Available copper was determined by soil extraction with ammonium acetate-acetic acid and treatment with EDTA Na₂ and ammonium citrate. Then, it was titrated with cresol red and ammonium hydroxide. To separate and eliminate the organic phase, sodium diethyldithiocarbamate and carbon tetrachloride were added. Optical density was read in a spectrophotometer at 440 nm in a Beckman DU 650 spectrophotometer (Roldán et al., 2005). Manganese was determined in soil samples by treatment with neutral ammonium acetate. After oxidation of the organic matter with hydrogen peroxide, the optical density was read in a spectrophotometer at 540 nm (Roldán et al., 2005).

Results

In general terms, pedological descriptions showed that all profiles are composed by two cycles: the modern soil and a paleosol. The modern soil is thinner in the cone-glacis apex, showing an A, A/C, C sequence, of about 13 to 19 cm depth. In the middle part of the geomorphological unit, the modern soil attains a thickness between 40 and 80 cm (Fig. 3).

In the 12 profiles from the agricultural terraces (profiles 1 to 12), the 2A horizon is eroded, while in the profiles from residential units (13 to 17), it is still identifiable, even when it appears to be deeply altered by anthropic activity, probably due to the fact that it was the room floor (Table 1).

Cultural findings (such as eroded ceramic potsherds included in the matrix of soils, occupational floors, and walls from agricultural terraces), help us infer that the most important pedological features representative of the agricultural pre-Hispanic practices are on the paleosol.

Superficial bulk density ranges between 0.88 g/cm³ and 1.55 g/cm³ while in the upper paleosol horizons ranges between 1.22 g/cm³ and 1.83 g/cm³. Bulk density values reflecting the limit between soil and paleosol horizons and values increase gradually with depth. These indicate, along with porosity values, some compaction.

Paleosol pH values vary between 5.35 and 7.61. Acidity decreases in depth tending to neutrality, without discontinuities among pH levels in the interface between soil and paleosol (Table 1). Texture and

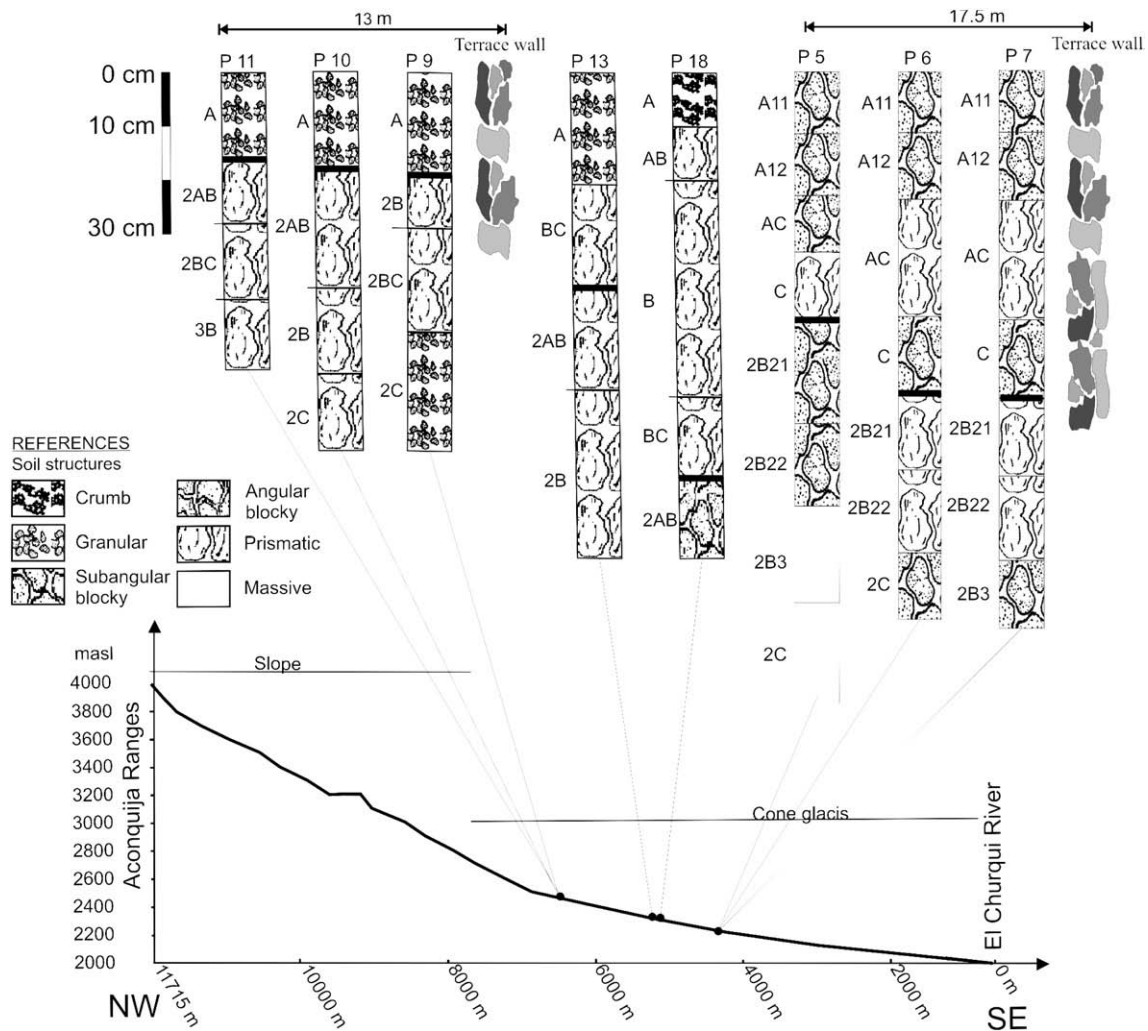


Figure 3. Profiles described on the cone glacis. Detail of structure and soil deepness along geomorphological unit and in relation with terrace walls.

pH show constant values through all described profiles (5.07–7.61 for pH and sandy clay to sandy loam for texture).

The percentage of organic matter and carbon values decline with depth; but there were no significant changes between soil and paleosol, or between agricultural and residential profiles. However, organic matter values of the profiles described in the apex of the cone glacis vary between 4.53 and 4.8%, which is relatively higher than equivalent horizons of the middle part of the geomorphological unit (between 0.84 and 1.81%) (Table 1; Fig. 4). Organic matter values are also accompanied by bulk density variations: in all profiles as organic matter decreases, the latter increases (Fig. 4).

Agricultural paleosol surfaces showed that available phosphorus values oscillate between 62 and 254 ppm, increasing in depth. In residential profiles, available phosphorus values are between 68 and 242 ppm (Table 1). Organic phosphorus values range between 15,990 and 16,678 ppm in paleosol surfaces of the residential units, and between 7186 and 23,926 ppm in agricultural profiles. Organic phosphorus values diminished with depth, showing a significant difference between the superficial horizons of agricultural paleosol and the subjacent ones (Table 1).

Available calcium concentrations are higher in the paleosol of the household profiles (770 ppm mean value) than in the paleosol of the agricultural profiles (546 ppm mean value). The value obtained in the control profile is 620 ppm, overlapping with the range of values in the agricultural profiles. Higher concentrations

of this element are found in illuvial horizons of all profiles (Table 1).

Available iron, copper, and manganese are found in small amounts in all studied profiles. In the pre-Hispanic soils iron values are between 1.35 and 15.54 ppm, manganese between 0.39 and 8.52 ppm, and copper between 0 and 63 ppm, with a very high value of 200 ppm in profile 9 (2BC horizon). In general the quantity of iron and manganese diminishes in depth without significant changes in the paleosol profile section. However, both elements were in higher concentrations in the apex of the cone glacis (Fe: 10.5 ppm, and Mn: 2.9 ppm mean values) than in the middle part of the geomorphological unit (Fe: 2.3 ppm, and Mn: 0.8 ppm mean values). Copper is almost undetectable in all residential profiles, while it is represented in small quantities in agricultural terraces (Table 1).

Profiles 9 to 11 were excavated inside the same agricultural terrace but at different distances from the terrace wall (Fig. 3). Profile 9 was separated from profile 11 around 13 m. In addition to the similar traits shared in all studied profiles, there are some interesting differences among profile 9 (near to terrace wall) and profiles 10 and 11. Profile 9 shows uniform organic phosphorus values in the illuvial horizons (2B and 2BC). Manganese and copper values increased in the 2BC horizon. This horizon also shows more compaction and a prismatic structure (Table 1; Fig. 3). In the same horizons of profiles 10 and 11, micronutrients are not concentrated in the illuvial horizons and the organic phosphorus distribution is irregular.

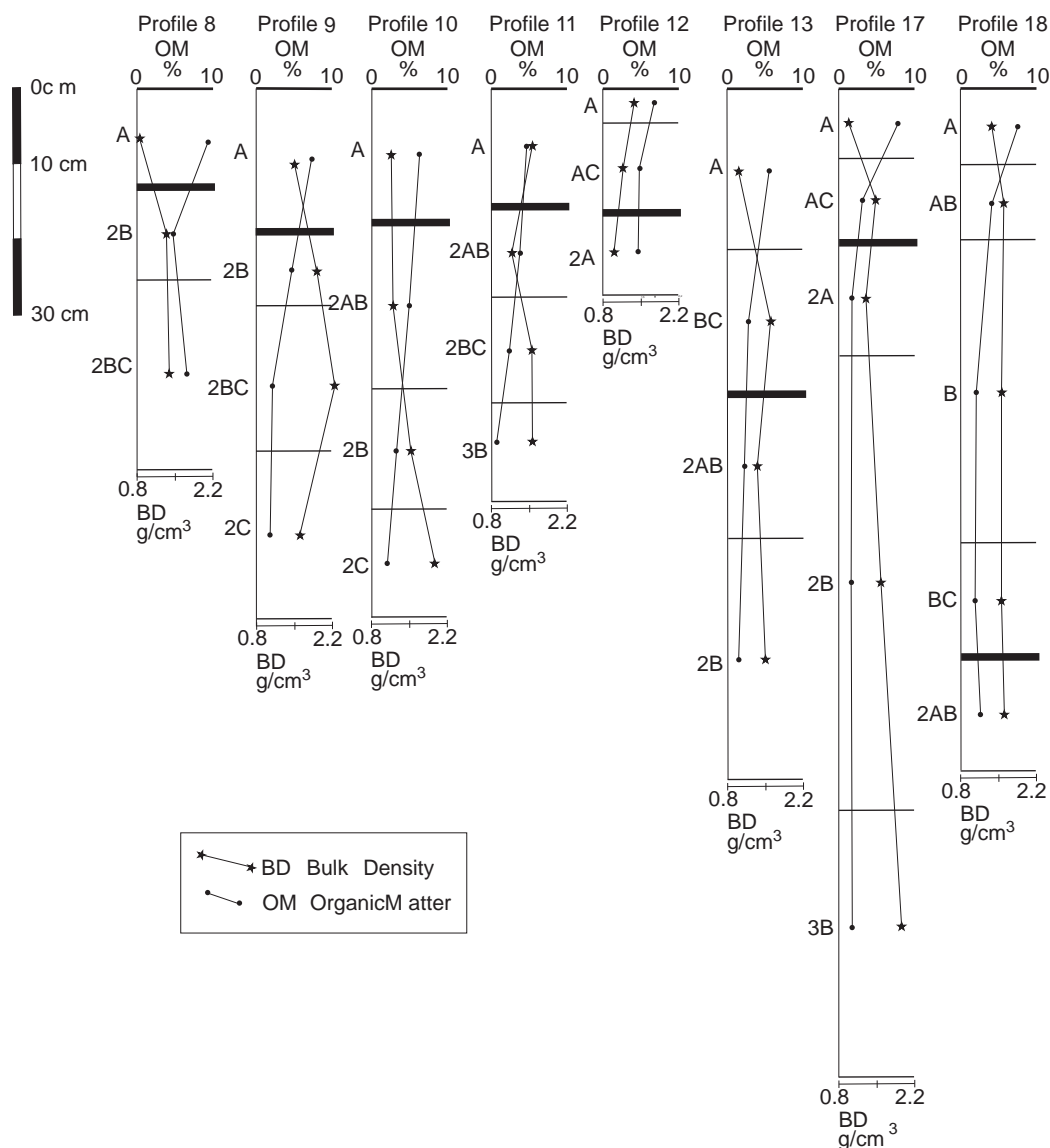


Figure 4. Relationship between BD and organic matter.

Discussion

Many physical and chemical variables were considered for this study, with soil texture and pH relatively constant across the entire geomorphological unit. In general terms both characteristics are important elements for soil fertility for agricultural purposes. Some features were modified by anthropic activities on an extended scale. Soil profiles from the apex of the geomorphological unit showed a greater concentration of organic matter than in the middle part. Stevenson (1982) determined that increasing aeration of soils produced by tillage, together with the rupture of aggregates, exposes organic matter to aerobic conditions after cultivation, and stimulates microbial activity, accelerating its decay. On the other hand, microbial activity could be stimulated by the increase of dry/wet cycles of soil farming and the practice of irrigation as suggested by Sampietro Vattuone (2002). The content of organic matter of superficial horizons of the present soil is equivalent over the entire geomorphological unit. Consequently, the variation in organic matter content registered in the paleosol does not correspond to microclimatic conditions but to pre-Hispanic use characteristics.

When organic matter decays, it liberates nitrogen, carbon and organic phosphorus among other elements. Under adequate humidity conditions, carbon and nitrogen are rapidly available to plants (Buckman and Brady, 1977), while organic phosphorus remains in a non-available fraction and remains stable in the profile. Organic phosphorus constitutes a very reliable indicator of human activity because its decay is very slow (Bohn et al., 1993). Human activity also produces soil enrichment of other elements, like calcium, copper, iron, and manganese, as a result of the accumulation of organic and inorganic debris (Entwistle et al., 2000).

In general, the dynamic of the concentration of available and organic phosphorus throughout the study profiles is related to the source of each compound. Organic phosphorus comes from organic debris deposited in soil surface, while available phosphorus has its origin in soil parental material (Schlezinger and Howes, 2000). In the selected area of study, the available phosphorus variability is not as great as seen in previous works (e.g. Sampietro Vattuone, 2002). On the contrary, it is present in all horizons of the described profiles within the agricultural terraces. Comparatively, the available phosphorus contents of paleoedaphic horizons from residential profiles had the same range as the control profile, where the concentration of

this element increases with depth. This is the expected distribution, considering that the origin of this element is the parent material and that it is highly mobile due to illuvial processes (Schleziinger and Howes, 2000). On other hand, the concentration of this element tends to diminish quickly in agricultural soils if they are not treated with organic manure (Terry et al., 2000). Accordingly, the organic matter found in agricultural areas could be due to the addition of fertilizers, while its presence in households could be the product of organic debris which is incorporated incidentally.

Very high concentrations of organic phosphorus were found in pre-Hispanic surfaces of agricultural paleosols. Its concentration was slightly lower in profiles described from inside the residential units. The loss of the 2A horizon in some profiles may be a product of tillaging and natural erosive agents, and occurred before the paleosol was buried. High concentrations of organic phosphorus in illuvial horizons of these profiles could result from the anthropic addition of fertilizers. A similar response of this element was recorded in archaeological sites such as Piedras Negras (Guatemala) (Terry et al., 2000) and Cape Cod (USA) (Schleziinger and Howes, 2000).

The concentration of calcium is high in residential structures, and is probably because the areas are used to process and consume food, as well as areas with bone evidence (see Sampietro and Vattuone, 2005).

Finally, micronutrients (Fe, Mn, and Cu) are found in small quantities, probably for the same reasons as organic matter. These are non-toxic and available as plant nutrients in agricultural soil profiles. Available Fe and Mn are higher in concentration in the apex of the geomorphological unit, as is organic matter. Micronutrient cations (Fe, Mn and Cu) are much more soluble, and they are assimilated under lightly acidic conditions (Buckman and Brady, 1977). The interaction between soil pH and aeration is very important for plant growth. Poorly drained acid soils frequently contain toxic quantities of Mn and Fe (Buckman and Brady, 1977). The presence of Cu in agricultural profiles and its absence in residential ones, together with the high concentration of organic phosphorus in the surface of pre-Hispanic soils, and the existence of appreciable concentration of available P in agricultural profiles, suggest the possibility of the use of organic fertilizers to the maintenance of farming soils. The evidence suggests that pre-Hispanic soils (or paleosols) were suitable for crops supplying the highest nutrient availability and without evident toxic levels.

The walls of the agricultural terraces favor nutrient concentration that tends to be mobilized by infiltration. In this study, where samples were taken near to the retaining walls, available phosphorus values are high while the content of organic phosphorus, calcium and organic matter are relatively low. All data shows that terrace wall locations have a strong influence over pedogeochemical processes. Illuvial features are more intense close to terrace walls improving macro and micro nutrient concentrations, but also increasing bulk density and compaction.

Conclusions

The archaeological site El Tolar reveals spatial changes in environmental parameters over time (T). The distribution of archaeological features in space is evidenced by the agrarian appropriation made over the surface of the cone glacis geomorphological unit. The presence of structures is related to pre-Hispanic agrarian use such as agricultural terraces and “despedres” and is accompanied by circular structures which were fundamentally storage and household activity spaces. The pedological characteristics of the 18 soil profiles are in general agreement with studies made by Sampietro and Sayago (1998) and Sampietro Vattuone (2002). Soil profiles are composed by a poorly developed soil which is underlain by a well-defined paleosol. In some cases it is possible to recognize a third paleoedaphic cycle associated with the pre human-activity period. Paleoclimatic oscillations in the late Holocene redistributed human activities and changed the nature of the characteristics of the soil/paleosol sequence (Sampietro and Sayago, 1998; Sampietro Vattuone, 2002).

Cultural findings made during the excavations, belonging to the Formative Period, include some eroded ceramic fragments (found in the matrix of the present soil), occupational floors (identified inside households in the transition between soil and paleosol), and agricultural terrace walls (constructed over pre existing surface but now paleosol). From a chronological point of view, all these findings, together with its stratigraphic position, help establish that the paleosol surface was the Formative settlement surface. Thus we consider that the most representative features of pre-Hispanic agricultural use must be measured on the paleosol.

At the study site strictly natural paleopedological features were texture (sandy loam) and pH (5.35 to 7.61). However these formed a base of nutrient bioavailability which favored agricultural land use across the geomorphological unit.

Considering each profile independently, the percentage of organic matter diminishes in depth. Taken together, it is possible to verify that paleosols from profiles located in the apex of the geomorphological unit have higher percentages of this component (4.53 and 4.8%) while in the middle part of the unit they just reach 1.81%. This is not a response to the altitudinal gradient but is accompanied by an increase in the bulk density values as shown in Figure 4.

In terms of anthropic use throughout time this distribution of features is a product of the effect of soil tillage during long periods of time in the middle area of the archaeological site, located in the central part of the geomorphological unit as shown in Figure 1, where land use exposes organic matter to decomposition and thus favoring soil compaction.

Available calcium concentration is lower in agrarian than in household profiles, probably because of the processing of a continuum of harvests. Available phosphorus values are similar in all analyzed contexts.

Organic phosphorus is an important indicator of human activity due its ubiquity, persistence, and stability over time. Values suggest the use of manure during agricultural production especially considering that the values from residential areas, where more human activities of any kind are concentrated, are lower than in the areas of agricultural exploitation. The high values are reached in profiles where 2A horizons are eroded, showing that erosion processes begun before the site was abandoned.

Available micronutrients (iron, copper, and manganese) are in small quantities in the entire geomorphological unit. Iron and manganese show more bioavailability in the apex of the geomorphological unit, probably because they are bound with organic matter.

In summary, it is possible to demonstrate through this work that the adequacy of pre-Hispanic space use for agricultural purposes during the Formative phase begun with the construction of structures, such as agricultural terraces, that affected superficial runoff and illuviation processes in the micro spaces generated by each agricultural terrace, generating nutrient concentration and deeper soils against terrace walls. On the other hand, manures were used to improve soils, as evidenced by the high concentration of organic phosphorus. Both activities modified physicochemical characteristics of the paleosol. Among the negative effects of tillage it was possible to identify organic matter loss, lower bioavailability of micronutrients, 2A horizon erosion and compaction in the middle area of the archaeological site where occupation and land use was more intensive.

There is no doubt that the use of the geochemical tools enabled the discovery of important new information. These data allowed us to improve the knowledge of socio-economic development of pre-Hispanic Formative settlements.

Acknowledgments

We want to thank the geologist Maria Elena Puchulu (Pedology laboratory, Faculty of Natural Sciences, National University of Tucumán), and Mrs Graciela Sánchez who help us with figure

drawing. Financial support was provided by Nacional Research Council (CONICET), CIUNT (National University Council), and ANPCyT from Argentina.

References

- Ambrosetti, J.B., 1897. Los monumentos megalíticos del valle de Tafí (Tucumán). *Boletín del Instituto Geográfico Argentino* 18, 1–3.
- Bennett, W.C., Bleiler, E., Sommer, F., 1948. Northwest Argentine archaeology. *Publications in Anthropology* 38, 5–78.
- Berberián, E.E., Nielsen, A.E., Argüello de Dorsch, E., Bixio, B., Spalletti, L.A., Salazar, J.A., Pillado, E.L., 1988. Sistemas de Asentamiento Prehispánicos del Valle de Tafí. Córdoba. Argentina.
- Bernasconi de García, M.T., Baraza de Fonts, A.N., 1985. Estudios arqueológicos del valle de la Ciénaga (departamento Tafí, provincia de Tucumán). *Anales de Arqueología y Etnología* 36–37, 117–138.
- Bethel, P., Máté, I., 1989. The use of soil phosphate analysis in archaeology: a critique. In: Henderson, J. (Ed.), *Scientific Analysis in Archaeology and its Interpretation*. U.C. L.A. Institute of Archaeology, Los Angeles, pp. 1–29.
- Bohn, H.L., Macneal, B., O'Connor, G.A., 1993. Química del Suelo. Grupo Noriega, México.
- Bolsi, A.S.C., Madariaga, M., Batista, A.E., 1992. Sociedad y naturaleza en el borde andino: el caso de Tafí del Valle. *Estudios Geográficos* 53, 383–417.
- Bouyoucos, G.J., 1936. Direction for making mechanical analysis of soils by the hydrometer method. *Soil Science* 42, 225–230.
- Brussaer, L., Van Faassen, H.G., 1994. Effects of compaction on soil biota and soil biological processes. In: Soane, B.D., Van Ouwerkerk, C. (Eds.), *Soil Compaction in Crop Production*. Elsevier, New York, pp. 215–235.
- Buckman, H.O., Brady, N.C., 1977. *Naturaleza y Propiedades de los Suelos*. Montaner y Simon, Barcelona.
- Caria, M.A., Martínez, J.G., Oliszewski, N., 2006. Geomorfología y arqueología de la quebrada del río de Los Corrales (Infiernillo-Tafí del Valle-Tucumán-Argentina). 3rd Congreso Argentino de Cuaternario y Geomorfología, Universidad Nacional de Córdoba. Argentina.
- Carrizo, J., Cano, S.F., Soler Nixdorff, M.M., 1997. Recursos vegetales comestibles en el valle de Tafí durante el período Formativo: análisis arqueobotánico del sitio Casas Viejas — El Mollar (S Tuc Tav 2). 12ve Congreso Nacional de Arqueología Argentina, Universidad Nacional de Córdoba.
- Cremonte, M.B., 1996. Investigaciones Arqueológicas en la Quebrada de la Ciénega (Dto. Tafí Tucumán). PhD dissertation, Universidad Nacional de La Plata, Argentina.
- Domínguez Bella, S., Sampietro Vattuone, M.M., 2002. Collar vedas from the Tafí culture, Tucumán (Argentina) (I millennium AD). Raw materials characterization and provenance. 33rd International Symposium on Archaeometry. Amsterdam.
- Ellis, J.R., 1998. Post flood syndrome and vesicular–arbuscular mycorrhizal fungi. *Journal of Production Agriculture* 11, 200–204.
- Entwistle, J.A., Dodgshon, R.A., Abrahams, P.W., 2000. An investigation of former land-use activity through the physical and chemical analysis of soils from the Isle of Lewis, Outer Hebrides. *Archaeological Prospection* 7, 171–188.
- Fiske, C.H., Subbarow, Y., 1925. The colorimetric determination of phosphorus. *The Journal of Biological Chemistry* 66, 375–400.
- Garralla, S., 1999. Análisis polínico de una secuencia sedimentaria en el Abra de El Infiernillo, Tucumán, Argentina. 1st Congreso Argentino de Cuaternario y Geomorfología, Universidad Nacional de Córdoba.
- González, A.R., 1965. Nuevas fechas de la cronología arqueológica argentina obtenidas por el método de radiocarbono (¹⁴C). *Revista del Instituto de Antropología* 2–3, 289–297.
- González, A.R., Nuñez Regueiro, V.A., 1960. Preliminary report on archaeological research in Tafí del Valle, N.W. Argentina. 34th Internationalen Amerikanisten Kongressen, Germany.
- Heredia, O.R., 1975. Investigaciones arqueológicas en el sector meridional de las selvas occidentales. *Revista del Instituto de Antropología* 5, 73–132.
- Holliday, V.T., Gartner, W.G., 2007. Methods of soil P analysis in archaeology. *Journal of Archaeological Science* 34, 301–333.
- Hudson, B.D., 1994. Soil organic matter and available water capacity. *Journal of Soil and Water Conservation* 49, 189–194.
- Kooistra, M.J., Tovey, N.K., 1994. Effects of compaction on soil microstructure. In: Soane, B.D., Van Ouwerkerk, C. (Eds.), *Soil Compaction in Crop Production*. Elsevier, New York, pp. 91–111.
- Krapovickas, P., 1968. Arqueología de Alto Medina, provincia de Tucumán, República Argentina. *Rehue* 1, 89–124.
- Lafone Quevedo, S.A., 1902. Viaje a los menhires en Intihuatana de Tafí y Santa María en octubre de 1898. *Revista del Museo de La Plata* 11, 121–128.
- Linn, D.M., Doran, J.W., 1984. Effect of water-filled pore space on carbon dioxide and nitrous oxide production in tilled and nontilled soils. *Soil Science Society of America Journal* 48, 1267–1272.
- Logsdon, S.D., Karlen, D.L., 2004. Bulk density as a soil quality indicator during conversion to no-tillage. *Soil & Tillage Research* 78, 143–149.
- Middleton, W.D., 2004. Identifying chemical activity residues on prehistoric house floors: a methodology and rationale for multi-element characterization of a mild acid extract of anthropogenic sediments. *Archaeometry* 46, 47–65.
- Nuñez Regueiro, V.A., García Azcárate, J., 1996. Investigaciones arqueológicas en el Mollar, dpto. Tafí del Valle, pcia. de Tucumán. 11st Congreso Nacional de Arqueología Argentina, Universidad de San Rafael, Mendoza.
- Oliszewski, N., 2004. Estado actual de las investigaciones arqueobotánicas en sociedades agroalfareras del área valliserrana del noroeste argentino (0–600 d. C.). *Relaciones de la Sociedad Argentina de Antropología* 29, 211–227.
- Olivera, D.F., 2001. Sociedades pastoriles tempranas: el Formativo Inferior del Noroeste argentino. In: Berbarián, E.E., Nielsen, A.E. (Eds.), *Historia Argentina Prehispánica*. Editorial Brujas, Argentina, pp. 83–126.
- Olivera, D.E., Tchilinguirian, P., Grana, L., 2004. Paleoambiente y arqueología en la puna meridional argentina: archivos ambientales, escalas de análisis y registro arqueológico. *Relaciones de la Sociedad Argentina de Antropología* 29, 229–247.
- Roldán, J., Sampietro Vattuone, M.M., Vattuone, M.A., 2005. Técnicas analíticas para el estudio de los suelos de sitios agrícolas prehispánicos. 1st Congreso Argentino de Arqueometría.
- Sampietro, M.M., Sayago, J.M., 1998. Aproximación geoarqueológica al conocimiento del sitio arqueológico “Río Blanco”. Valle de Tafí. Tucumán (Argentina). *Cuadernos del Instituto Nacional de Antropología y Pensamiento Latinoamericano* 17, 257–274.
- Sampietro Vattuone, M.M., 1994. Uso del espacio y manejo prehispánico de suelo y agua en el cono del río Blanco. Tafí del valle. Undergraduate dissertation, Universidad Nacional de Tucumán, Argentina.
- Sampietro Vattuone, M.M., 1999. Propuesta para un modelo climático del Formativo en el valle de Tafí. 13th Congreso Nacional de Arqueología.
- Sampietro Vattuone, M.M., 2001. Geoambientes y sitios arqueológicos formativos en el valle de Tafí (Noroeste-República Argentina). *Cuadernos del Instituto de Antropología y Pensamiento Latinoamericano* 19, 599–611.
- Sampietro Vattuone, M.M., 2002. Contribución al conocimiento geoarqueológico del valle de Tafí Tucumán (Argentina). PhD dissertation, Universidad Nacional de Tucumán, Argentina.
- Sampietro Vattuone, M.M., Neder, L., Roldán, J., Vattuone, M.A., 2008. Mother Earth: soil and people relationships during the prehispanic period (Northwest Argentina). *World Archaeology* 40 (2), 190–205.
- Sampietro, M.M., Vattuone, M.A., 2005. Reconstruction of activity areas at a Formative household in northwest Argentina. *Geoarchaeology* 20, 337–354.
- Sandor, J.A., Eash, N.S., 1995. Ancient agricultural soils in the Andes of southern Peru. *Soil Science Society of America Journal* 59, 170–179.
- Sayago, J.M., Collantes, M.M., 1991. Evolución paleogeomorfológica del valle de Tafí (Tucumán, Argentina) durante el Cuaternario Superior. *Bamberger Geographische Schriften* 11, 109–124.
- Sayago, J.M., Sampietro, M.M., Caria, M.A., 2001. Los efectos de la anomalía climática medieval sobre las culturas del Formativo y su relación con los futuros cambio climáticos en el noroeste argentino. 3rd Reunión Nacional de Geología Ambiental y Ordenación del Territorio and 1st Reunión de Geología Ambiental y Ordenación del Territorio del Área del MERCOSUR.
- Schleizinger, D.R., Howes, B.L., 2000. Organic phosphorus and elemental ratios as indicators of prehistory human occupation. *Journal of Archaeological Science* 27, 479–492.
- Sesma, J.P., 1987. Geología del Cuaternario y geomorfología aplicada en el Valle de Tafí. Undergraduate thesis, Nacional University of Tucumán. Argentina.
- Soil Survey Staff, 1999. *Keys to Soil Taxonomy*. Pocahontas Press, Blacksburg, VA.
- Stepniowski, W., Gliniski, J., Ball, B.C., 1994. Effects of compaction on soil aeration properties. In: Soane, B.D., Van Ouwerkerk, C. (Eds.), *Soil Compaction in Crop Production*. Elsevier, New York, pp. 167–169.
- Stevenson, F.J., 1982. *Humus Chemistry: Genesis, Composition, Reactions*. John Wiley Ex Sons Inc.
- Tartusi, M.R.A., Nuñez Regueiro, V.A., 1993. Los centros ceremoniales del NOA. *Publicaciones del Instituto de Arqueología* 5, 1–48.
- Tarragó, M.N., 2000. Chacras y pukara. Desarrollos sociales tardíos. In: Tarragó, M.N. (Ed.), *Los pueblos originarios y la conquista: Nueva Historia Argentina*, Editorial Sudamericana, pp. 257–342.
- Tchilinguirian, P.I., Olivera, D.E., 2000. Aportes edáficos para el estudio de campos agrícolas arqueológicos Bajo del Coypar, provincia de Catamarca. *Cuaternario y Ciencias Ambientales* 4, 51–55.
- Terry, R.E., Hardin, P.J., Houston, S.D., Nelson, S.D., Jackson, M.J., Carr, J., Parnell, J., 2000. Quantitative phosphorus measurement: a field test procedure for archaeological site analysis at Piedras Negras, Guatemala. *Geoarchaeology* 15, 151–166.
- USDA-NRCS, 1996a. Soil quality information sheet. *Soil Quality Indicators: Organic Matter*, pp. 1–2.
- USDA-NRCS, 1996b. Soil quality information sheet. *Soil Quality Resource Concerns: Compaction*, pp. 1–2.
- Viers, G., 1976. Geomorfología. Oikos-Tai, España.
- Walkley, A., Black, L., 1946. An examination of the degradational method for determining soil organic matter and proposed modification of the cromic acid titration method. *Soil Science* 37, 29–38.
- Zhenli, L.H., Yang, X., Stoffella, P.J., 2005. Trace elements in agroecosystems and impacts on the environment. *Journal of Trace Elements in Medicine and Biology* 19, 125–140.