A snapshot of environmental iodine and selenium in La Pampa and San Juan provinces of Argentina

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Abstract

Soil and water samples were collected from farmsteads and provincial towns across the provinces of La Pampa and San Juan in Argentina. Inductively coupled plasma mass spectrometry was used for the determination of iodine in water following addition of tetramethyl ammonium hydroxide (TMAH) to 1 % v/v and soils extracted with 5% TMAH. Iodine in agricultural soils was in the range of 1.3 - 20.9 mg/kg in La Pampa located in central Argentina and 0.1 - 10.5 mg/kg in San Juan located in the northwest Andean region of Argentina, compared to a worldwide mean of 2.6 mg/kg for soils >50km from the coast. Mean selenium concentrations for soils from both provinces were 0.3 mg/kg, compared to a worldwide mean of 0.4 mg/kg. The majority of soils were alkaline, although ranged from pH 6.7 to 8.8. The soil organic matter content of soils in La Pampa was 2.5 – 5.9 % and in San Juan 0.1 - 2.3 %, whilst, mobile water extractable soil iodine was 1 - 18 % for La Pampa and 2 - 42 % for San Juan. No simple relationship observed for pH and organic content, but mobile iodine (%) was highest when organic content was low, higher for lower total iodine concentrations and generally highest at pH > 7.5. Water drawn for drinking or irrigation of a variety of crops and pasture was found to range from 52 to 395 µg/L iodine and 0.8 to 21.3 µg/L selenium in La Pampa and 16 - 95 µg/L iodine and 0.6 to 8.2 µg/L selenium in San Juan. The water samples were alkaline between pH 8 and 10. Water-iodine concentrations were highest at pH 7.8 to 8.8 and in groundwaters positively correlated with conductivity. Raw water entering a water treatment works in La Pampa was reduced in iodine content from approximately 50 µg/L in raw water to 1 µg/L in treated drinking water, similar to levels observed in regions experiencing iodine deficiency.

Keywords

Goitre, Iodine deficiency, ICP-MS

Introduction

Approximately 1.9 billion people worldwide were estimated to be at risk of iodine deficiency disorders (IDD) (Benoist *et al.*, 2003). A daily intake of 150 µg of iodine per adult is recommended to prevent IDD (Delange, 1993; WHO, 2004). Below 100 µg/day, a series of thyroid functional and developmental abnormalities occur (Hetzel, 1989. Dunn, 1998), in which symptoms can occur as goitre, hypothyroidism, or impaired mental function in adults. In the fetus, neonates and children IDD can lead to lower levels of thyroid hormones necessary for normal brain development, leading to irreversible brain damage and possible IQ that is 10 to 15 points lower than sufficient iodine intake (ICCIDD, 2009). In addition, physical development can be effected as a result of a range of associated disorders including still birth, congenital anomalies, endemic cretinism or short stature. UNICEF, ICCIDD and WHO reported detailed recommendations for the daily intake of iodine; 90 µg for 0 to 5 year old children, 120 µg for 6 to 12 year old children, 150 µg for adolescents and adults, 250 µg for

pregnant and lactating women (WHO, 2007a). Four methods are commonly used for the monitoring of iodine nutritional status in populations and summarised as: (1) measurement of goitre by the physical inspection of the neck, palpation or thyroid ultrasonography reflects long-term iodine intake (months-years), (2) measurement of urinary iodine (UI) concentrations since 90% or more of ingested iodine is excreted in the urine and provides an indication of recent iodine intake (days), (3) measurement of Thyroid Stimulating Hormone (TSH) in serum, which is elevated when iodine supply is low, particularly in infants, and (4) Thyroglobulin (Tg) in serum which increases due to greater thyroid mass or TSH stimulation and provides an intermediate response (weeks-months). Tg correlates well with UI indications of deficiency and can be simply assayed on dried blood spots. This method also provides a good indication of improved thyroid function after iodine repletion. A more detailed appraisal of these monitoring techniques is described by Zimmerman (2008).

Despite concerted efforts to alleviate IDD in the twentieth century, the incidence of IDD increased by 32 % between 1993 and 2003 afflicting some 2 billion people (WHO, 2004). Moderate to severe endemic goitre due to iodine deficiency has been historically reported in Argentina. Provinces in the north and west of the country, particularly in the Andean foothills have been affected, in particular La Pampa and San Juan, the focus of this study. In Argentina, 90% of the population was estimated to receive iodized salt (WHO 2004, ICCIDD, 2003), as a result of a programme of supplementation since the 1950/60s and resulted in a significant decrease in goitre prevalence in many areas. A relapse of goitre in some regions experiencing goitre rates of 10 to 42% in the 1980s and 1990s. The main reasons for this relapse were poor understanding of the problem, inadequate support for education, enforcement, monitoring, quality control of salt iodisation and poor coordination of agencies involved (ICCIDD, 2009). The World Health Organisation (2007b), estimated the a prevalence of goitre in newborns in Buenos Aires to be 83 % and across provincial states ranging from rates of 4 to 19 % for 5 to 16 year olds according to goitre prevalence and urinary iodine measurements. Goitre prevalence was reported in a study group of school children at rates of 9, 10 and 12%, in San Juan (capital of San Juan province), Punta del Medano (rural) and Colonia Fiscal (rural), respectively. In addition, goitre prevalence was reported to be 11 % in Santa Rosa the capital of La Pampa and 18 % in Altaliva Roca (rural) amongst school children (ICCIDD, 2003). In countries where goitre rates are above 10 % of the population, iodine deficiency is often estimated to be widespread and can have the effect of reducing the national IQ by 10 to 15% (Stewart *et al.*, 2003). In a separate study, Morando *et al.* (2004) stated that although the goitre rates in San Juan province had previously been reported to have been reduced from 30 to 16 % since the introduction of salt iodisation, they had determined that palpable enlarged thyroids or Grade 1 goitre (Lewinski, 2002; WHO, 1994) were present in 10 % of children studied in the towns of Punta del Medano and Colonia Fiscal. Morando *et al* (2004) suggested that the rates of goitre were not due to the ingestion of goitrogenic foods, but likely probable presence of goitrogenic substances in well water or possible gaps in the supplementation of iodine in the diet. Cebrian *et al.* (1993) reported in a comparative study of patients from areas with known high and low arsenic levels in drinking water that reduced absorption rates of iodine by the thyroid gland occurred in individuals with chronic arsenicosis. Arsenic concentrations in Argentinian surface and groundwaters have been reported at well above World Health Organisation recommended limits of 10 µg/L As (WHO, 1993; Smedley *et al.*, 2002, 2005; O'Reilly *et al.*, 2007).

Selenium deficiency may be an important factor in the onset of IDD through the inhibition of thyroid hormone metabolism. Selenoenzyme, type 1 iodothyronine deiodinase influences the production of thyroid hormones, ultimately controlling cellular development, particularly in the

foetus and early infancy (Arthur *et al.*, 1999). A recommended daily intake of 55 to 75 µg per day is recommended to prevent selenium deficiency (WHO, 1996).

Environmental samples are often used by geochemists to estimate the exposure or prevalence of iodine status in a population or region. Soils generally contain 0.01 - 6 mg/kg iodine and in some coastal areas up to 80 mg/kg (Kebata-Pendias, 1984). The weathering of rocks generally contributes little to the soil iodine pool, other than via the important mechanism of governing the physico-chemical properties of the soil formed. Factors that determine the concentration of iodine in soils are the proximity to coast, soil pH, soil organic content and the presence of iron and aluminium oxides in the soil (Fuge, 2005). The majority of iodine found in soils is ultimately derived from the sea and transported through rainfall as CH₃I (for long-range transport), HI or I₂ (Fuge, 2005). The semi-arid region of San Juan in the Argentinian Andes receives on average 100 to 200 mm of rainfall per year and relies on melt water from the Andes (Cabido *et al.*, 1993), compared to La Pampa at approximately 700 mm per year, which falls sporadically mainly in the North East of the province (www.accessmylibrary.com), where water supplies are dependent on boreholes. Whilst San Juan is situated closer to the coast than La Pampa, the Andean mountain range creates a rain shadow over San Juan. Precipitation at altitude can result in the washout of iodine from the atmosphere in regions such as the Andes (Dunn and Van de Haar, 1990) on the Chilean / Pacific coastal side of the Andes, where excessive iodine intake has been reported (ICCIDD, 2009), leaving reduced deposition of iodine through precipitation on the Argentinian side of the Andes. The potential for iodine to become adsorbed by soil components is influenced by some complex factors, including: organic content, often low in mountainous regions due to erosion and closely correlates with the retention of iodine in soils (Watts and Mitchell, 2009, Johnson 2002); the geochemistry relating to the presence of Fe and Al oxides (Fuge, 2005) and the pH of the soil. The sorption of iodide by Fe and Al oxides is greatest under acidic conditions (Fuge, 2005). The majority of soils reported in the literature contain less than 10 % water-soluble iodine, although this may be expected to increase in arid alkaline soils (Fuge, 2005), such as those found in the Argentinian Andes.

The selenium content of the majority of soils is in the range of 0.1 to 2 mg/kg (Kebata-Pendias, 1984), with a world mean of 0.4 mg/kg, but high concentrations of up to 1200 mg/kg have been reported in seleniferous regions (Fordyce 2005). Whilst the total selenium concentrations in soils provide a general overview of environmental status, it is the mobility of selenium rather than the underlying geology that mostly influences the uptake into plants and animals. Selenite is the most stable form, which is more readily adsorbed onto soil particles than selenate. This process is pH dependent, in acidic soils, selenite forms insoluble oxyhydroxide complexes, resulting in selenite being less mobile. Selenate is the most common chemical form in alkaline soils and is generally more mobile and available for uptake by plants (Fordyce 2005).

The Pacific coastal side of the Chilean Andes has been reported to be iodine excessive based on public health studies (WHO, 2004), whilst the global distribution of IDD as illustrated by Dunn & Van der Haar (1990) illustrated the prevalence of IDD occurring across central South America, in mountainous and rain shadow regions, particularly on the Argentinian side of the Andes. Whilst there have been many reports on the iodine status of the Argentinian population through epidemiological studies, this study provides a limited snapshot of the iodine and selenium status of agricultural soils and irrigation and drinking water in the semi-arid Andean western province of San Juan and lower steppe province of La Pampa in central Argentina. This data will contribute to the understanding of the stubborn prevalence of goitre in parts of

Argentina and fill in some gaps in the knowledge of environmental levels of iodine and selenium. The samples were analysed using an inductively coupled plasma mass spectrometer (ICP-MS) for fast and sensitive analyses. For iodine determination, iodine was extracted from soils using an alkaline extraction, whilst waters were spiked with the same alkaline reagent (Watts 2001, Johnson *et al.* 2002, Watts and Mitchell 2009). Selenium measurements were completed following acidification of the waters and total acid digestion of the soils.

Study Sites

The location of towns and rivers sampled for soil and water are illustrated in Figure 1b & c. The study sites in the province of San Juan are located approximately 250 to 380 km from the Pacific coast, with an elevation ranging from 1600 m from Cuesto del Viento in the west to Encon at 500 m in the east. Study sites were located in the north of La Pampa at an elevation of 200 m, located approximately 450 km from the Atlantic coast. Soils were collected from cultivated fields or small vegetable plots, and water was collected from rivers or wells that supplied drinking water for human consumption. The same water supply was often used for animals and the irrigation of cultivated plots. The sites were selected based on their direct interaction with the source-pathway-receptor, via crop production, grazing and drinking water. Details of the sites are as follows:

1. San Juan: Thirteen soils and twenty one water samples were collected from each of the following sites: (1) Rio Blanco - Angualusta (ANG), Cuesto del Viento (CU); (2) Rio Jachal (RJ) - Agua Negra (AN); (3) Rio Huaco - Huaco (HU); and (4) Encon (EN) in the south of the province. All waters were stream or river fed, with the exception of Encon where boreholes were used for water supplies. The soils along the Rio Blanco, Jachal, Huaco and the village of Encon were underlain by continental marine sediments (DNGM, 1964).
2. La Pampa: Fifteen soils and fifteen water samples were collected from farmsteads around the towns of Ingeniero Luigi (LU) and Eduardo Castex (EC). Groundwater samples from these towns were also collected from the respective town boreholes and water treatment plants. Soils from Ingeniero Luigi and Eduardo Castex are underlain by loess up to 200 m in depth, with a thin layer of ash below the surface (DNGM, 1964, Smedley *et al.*, 2005). Volcanic activity has had an important impact on the formation of Pampean loess from the Tertiary and Quaternary periods through to the present day. The last major ash fall was in 2000 from the Copahue volcano (Ibanez *et al.* 2008) and in 1932 Quiza Pu volcano (Zarate *et al.* 1989). The presence of a fine layer of rhyolitic ash in the upper part of the loess soil profile is believed to be derived from the Quiza Pu eruption of 1932 (Smedley *et al.* 2002).

Materials and methods

Water samples (30 ml) were collected and filtered on-site using a 0.45 µm syringe filter. In addition, a composite sample of 0.5 kg of soil was collected with a spade from the top 20 cm layer of soil. Samples were dried in a drying oven at 40°C overnight, disaggregated and sieved using a nylon mesh to <2 mm and then sieved to < 125 µm. Loss on ignition (LOI) was used as an indication of organic matter content in these mainly sandy soils. The LOI of the soils was determined on 1 g (dry weight) of soil and recorded as a percentage of weight. Soil pH was determined on a 10 g (dry weight) soil sample to which 10 ml of 0.01 M CaCl₂ solution had been added. The pH of the soil paste was measured with a standard Orion pH meter. This method generally gives a lower soil pH determination (0.5 U) than water-based methods (Taylor *et al.* 2005).

Iodine determination

The methodology for the measurement of iodine in water and soil is based on the work of Watts and Mitchell (2009). Water samples were spiked with 25 % tetramethyl ammonium hydroxide (TMAH: Sigma Aldrich, Kent, UK) to result in a final solution of 1 % TMAH. For soils, 0.25 g (dry weight) of sample was weighed directly into a 15 ml poly(tetrafluoroethene) bottle to which 5 ml of 5 % TMAH was added and shaken. Sample bottles, with lids loosened, were placed in a drying oven at 70°C for 3 hours, with bottles shaken at 1.5 hours. After 3 hours of heating, 5 ml of deionised water was added and the bottles centrifuged at 2500 rpm for 20 minutes. The supernatant was removed from the top of the sample solution and diluted to a final matrix of 1% TMAH. Soluble iodine was determined by cold water extraction, with 12.5 ml of deionised water and 1.25 g of soil shaken for 15 minutes, centrifuged at 2,500 rpm for 10 minutes and adjusted to a matrix of 1 % TMAH for analysis. Soil preparations for selenium determinations were completed through acid digestion as described by Watts *et al.* (2008). Final solutions were acidified to 1% HNO₃ for selenium determinations. Iodine and selenium were determined in separate analytical runs, owing to the incompatibility of the two matrices. All sample solutions were analysed by an Agilent 7500 ICP-MS instrument (Agilent, Hemel Hempstead, UK). An internal standard of 100 µg/L rhenium in 1 % TMAH was mixed with the sample solution via a t-piece for iodine or 50 µg/L tellurium in 1 % HNO₃ for selenium measurements to correct for signal drift during the analytical run (<1 % signal change in internal standard). Iodine determinations were completed in standard mode as described in Watts and Mitchell (2009) and selenium in collision cell mode, using He as a buffer gas as described in Watts *et al.* (2008). Water certified reference materials NASS-4, IAPSO, SLRS-2 (iodine) and NIST SRM 1643e (selenium) were employed for quality control checks throughout the analytical runs. The accuracy and precision of the method for measuring iodine was evaluated and reported in Watts and Mitchell (2009) using a selection of appropriate soil certified reference materials (CRM). The accuracy of iodine measurements in soil certified reference materials, were within 15% of target values, as were selenium measurements for NIST SRM 2711 for selenium measurements.

Results and discussion

Mean water-iodine concentrations (Table 1) show a substantial difference between the river waters of San Juan and the groundwaters of La Pampa, as summarised by Figure 2 with mean concentrations of 40 µg/L (median of 30 µg/L) in San Juan and 145 µg/L (median of 110 µg/L) in La Pampa. The river waters from the area of San Juan had concentrations which were much higher than other mountainous regions, such as the Himalayas (<1.0 µg/L) with similar topography to San Juan, where goitre has been reported (Day and Powell-Jackson, 1972) or mountainous Afghanistan at 5 to 23 µg/L (Watts and Mitchell, 2009), and are high compared to many river waters cited in the literature (Fuge, 1989). The groundwaters from the loess of La Pampa had iodine concentrations with a lower range than those found by Smedley *et al.* (2005) (median of 229 µg/L, mean 243 µg/L). However, these two datasets are broadly comparable when taken in the context of the range of groundwater concentrations shown in the literature. The exceptions to this are high (mean >300 µg/L) concentrations from similar plain settings in parts of China (Zhao *et al.*, 1998), or where higher iodine concentrations from brines or thermal waters are implicated (Fuge & Johnson, 1986). The high conductivity values observed in most La Pampa waters compared to San Juan are also characterised by generally lower pH values (Table 1). A positive correlation between conductivity and iodine concentration was observed (Figure 3), with a Pearson correlation coefficient of 0.5 ($P < 0.002$). This relationship is controlled by the variable and highly evolved Pampean groundwaters, where the high conductivity reflects the high total dissolved solids. Whilst no simple relationship between aqueous iodine concentrations and pH can be observed, comparison of

data in Table 1 with that of Smedley et al. (2005) for La Pampa, shows that all iodine concentrations $>200 \mu\text{g/L}$ occur in the pH range 7.8 – 8.8. A water treatment plant in Ingeniero Luiggi was set up to remove the high levels of arsenic in groundwater supplies to the town by precipitation with iron hydroxide and reverse osmosis. It would appear that the treatment plant also reduces the iodine content from approximately $50 \mu\text{g/L}$ in the raw water (LU39a) from supply wells to $1 \mu\text{g/L}$ in the treated drinking water (LU39g), resulting in similar levels to IDD prone areas, whilst the waste water (precipitate) contained elevated levels of iodine at $87 \mu\text{g/L}$. Selenium concentrations were also reduced from approximately 3 to $<0.5 \mu\text{g/L}$, comparable to that for waters in selenium deficient regions (Fordyce et al., 2002). An increase in selenium concentration was measured in the waste water at $4.7 \mu\text{g/L}$.

Soil concentrations and physico-chemical parameters are given in Table 2, with soil-iodine ranges of 0.05 - 10.5 mg/kg in San Juan and 1.2 - 20.9 mg/kg in La Pampa. However, there are four datapoints, which may represent very localised positive anomalies, rather than being representative of wider soil conditions. The high soil-iodine value for AN01, is thought to arise from proximity to a stream and flooding from iodine-rich waters (Table 1). In addition, soils collected from EC2 S5, EC7 S2 and EC8 S2 were relatively high in iodine ($>4 \text{ mg/kg}$) and in close proximity to water tanks used to store iodine rich groundwater. Otherwise similar soils, collected within 10 to 20 metres of the elevated soil-iodine sites (EC2 S2, EC7 S1, EC8 S1), were generally low ($<2.6 \text{ mg/kg}$), suggesting that leakage from the storage tanks may have resulted in a localised elevation of soil-iodine. When these outliers are excluded the summary values for San Juan are a mean of 1.1 mg/kg (median of 0.35 mg/kg), and a mean of 2.3 mg/kg (median of 2.2 mg/kg) in La Pampa, with a systematic variation between those two areas, which mimics that of the aqueous iodine concentrations (Figure 4). The majority of soils from La Pampa were close to the worldwide geometric mean of 2.6 mg/kg, for inland regions further than 50 km from the coast (Johnson, 2003a), whilst those from San Juan were much lower (Figure 4). Goitre has been reported as prevalent where soils contained mean soil-iodine of 5.4 mg/kg in the UK (Fuge, 1989), 3.1 mg/kg in Sri Lanka (Fordyce *et al.*, 2000), 1.0 mg/kg in China (Fordyce *et al.*, 2003), 2.1 mg/kg in Morocco (Johnson et al., 2002) and 2.4 mg/kg in Afghanistan (Kabul) (Watts and Mitchell, 2009). Whilst these studies were specific surveys rather than representative of countrywide iodine status, they are useful when trying to gauge the soil-iodine status for San Juan and La Pampa, which could be considered to be of poor iodine status, when compared to those values.

Water extractable soil-iodine was 2 to 42 % (mean 19 %) of total iodine in San Juan soils, with five of the thirteen soils above 20 % mobile iodine (Table 2). Soils from La Pampa exhibited 1 to 18 % (mean 6 %) mobile iodine, with the majority of soils $<5 \%$ and just two soils above 10 %. There is little comparable data on mobile iodine, although Johnson *et al.* (2002) reported extractable soil-iodine, using the same method, in Morocco at between 2 to 10 % where bioavailable iodine was considered to be low. The percentage values for San Juan mobile iodine are relatively high compared to the Moroccan data and provide a valuable indication of the bioavailable iodine. However, these values should be taken in context with the actual concentrations of mobile iodine, which are in many cases extremely low ($<0.1 \text{ mg/kg}$). The range of mobile iodine concentrations is very similar despite the difference in percentage values, San Juan 0.01 to 0.93 mg/kg (mean 0.20 mg/kg) and La Pampa 0.04 to 0.94 mg/kg (mean 0.20 mg/kg) (Figure 5).

Whilst increasing mobile iodine (mass) corresponds to increasing total iodine, there is no such relationship with the available mass and percentage iodine data. Soil pH and loss-on-ignition (as a measure of organic carbon) vary systematically between the two regions (Table 2), with generally higher pHs in San Juan (mean of 7.8) compared to La Pampa (mean of 7.2), whilst

the latter has higher organic carbon (loss-on-ignition mean of 3.8 %) than San Juan (mean of 1.0 %). The slightly alkaline pH is likely to have contributed to the low iodine values through poor absorption onto Fe and Al oxyhydroxides and clay minerals. The organic matter content of soils in both areas are low compared to organic rich soils in the UK where total soil iodine is correspondingly higher (Fuge 2005; Watts and Mitchell, 2009). In this study, there is no simple relationship between loss-on-ignition and total iodine, although for the lowest concentrations in both (LOI < 4 % and I < 3 mg/kg) there is a positive linear relationship. An inverse relationship between organic matter and mobile iodine (%) can be seen in Figure 6, the correlation of -0.600 (R^2) for both provinces was observed at a probability level of 0.05 ($P < 0.01$). The majority of organic rich soils probably have a mobile iodine content of less than 10 % of the total, although arid alkaline soils are likely to contain elevated levels of mobile iodine (Fuge, 2005) as is seen for San Juan. No simple relationship was observed between soil pH and the three measures of iodine. However, in these data the higher (> 10 %) mobile iodine falls only in those samples where pH > 7.8, which are also the samples with the lowest loss-on-ignition values (Figure 6), suggesting multi-factorial controls on iodine concentrations and mobility.

There is no accepted threshold figure in the literature for defining an iodine deficient environment, or what sample media that measurement should be made in. The comparison of data from a range of studies is often the most appropriate approach, encompassing a combined approach to determining medical and environmental parameters in order to provide remediation strategies. However, it is common that such parameters are defined separately and compared against IDD regions reported in the literature. Soils in San Juan (mean 1.1 mg/kg) and La Pampa (mean 2.3 mg/kg) can be considered as an iodine poor environment since the concentrations are below reported values in regions afflicted by IDD. This is not the case with the aqueous iodine concentrations in either region. San Juan, where the median value is 39 µg/L exceeds most data in comparison to other studies of aqueous iodine (Fuge, 1989), including those where symptoms of IDD are not recognised. Concentrations of iodine in the more highly evolved groundwaters of the Pampean Plain are very high in relation to literature values from outside this region (Fuge, 1989) but, unless appropriately treated, these waters are widely recognised to contain arsenic and other potentially hazardous trace elements at concentrations which may be detrimental to health (Smedley et al., 2005; O'Reilly et al., 2007).

Mean water-selenium concentrations were 1.8 µg/L in San Juan, generally low compared to 2 to 19 µg/L reported by Fordyce (2005) for Argentinian surface waters. A mean water-selenium concentration of 6.4 µg/L in La Pampa, follows the pattern for higher groundwater concentrations compared to surface water reported by Hem (1992), due to greater contact time for rock-water interactions. The majority of water samples (Table 1) were significantly higher than selenium deficient waters reported by Fordyce *et al.* (2000) in Sri Lanka and China (2003) at less than 0.1 µg/L. Mean soil-selenium concentrations (Figure 2) of 0.3 mg/kg in San Juan and 0.3 mg/kg in La Pampa were marginally lower than the worldwide mean of 0.4 mg/kg (Fordyce, 2005) and soils reported by Fordyce *et al.* (2000) for Sri Lanka at 0.1 to 5.2 mg/kg. Argentinian soils in this study are generally greater in selenium content than reported threshold values of <0.125 mg/kg for deficient soils and <0.125 to 0.175 mg/kg for marginally deficient soils (Fordyce *et al.*, 2003), with the exception of just three samples. Although, total soil-selenium values of 0.1 to 0.6 mg/kg have been considered deficient, since these concentrations have been reported in soils where selenium deficiency has been prevalent in livestock (Fordyce, 2005). No relationship of total selenium with either pH or soil organic matter was observed for data in this study.

Conclusion

Argentinian environmental samples were largely considered to be selenium sufficient, through comparison with reported studies from other parts of the world. Water-iodine concentrations were greater than literature values for IDD areas. The highest concentrations were measured in pH 7.8 to 8.8 and in groundwaters positively correlated with conductivity, also demonstrated by Smedley *et al.* (2005). However, many of the soils were consistent with iodine deficient areas at <3.1 mg/kg (Fordyce *et al.*, 2003). Stewart *et al.* (2003) raised concerns over the direct correlation of total soil-iodine to the prevalence of IDD. Rather there is a need to understand the bioavailable fraction in order to better understand the factors that influence IDD. No simple relationship occurred between total iodine or selenium with pH and soil organic matter content. Soluble (mobile) soil-iodine was elevated in San Juan soils (mean 19 %) in comparison to La Pampa (6 %), likely due to the slight differences in organic matter of 1.0 and 3.8 % (mean LOI), respectively. Mobility as a percentage of the total iodine was highest when soil organic matter were low, higher for lower total iodine concentrations and generally highest when the pH was greater than 7.5. Soils are influential in the nutritional status of humans and animals. Geochemical mapping can stimulate investigations into the cause of diseases and aid the planning of public health corrective responses (Abrahams, 2006). Mitigation strategies, such as the common practice of salt iodisation in Argentina or direct supplementation are often patchy (Morando *et al.*, 2004). Localised mitigation strategies have been proposed for the improvement of soil-iodine, such as crop biofortification (Xiao-E *et al.*, 2007), addition of Chilean iodine rich nitrate fertilisers, soil improvement through addition of organic matter (Aston and Brazier, 1979; Johnson 2003b) or iodination of well water or irrigation water (Maberley *et al.*, 1981; Elnager *et al.*, 1997; Lim, *et al.* 2006). The influence of iodine rich irrigation water was observed in soils sampled close to iodine rich rivers subject to spring flooding in San Juan or in close proximity to groundwater storage tanks in La Pampa. Whilst the majority of waters contained elevated levels of iodine, careful attention should be given to population status resulting from raw water treated for arsenic removal that was iodine sufficient, such as in Ingeniero Luiggi where concentrations of <5µg/L iodine in treated drinking water is consistent with IDD prone areas. The high iodine content of San Juan waters and high mobility of what are low soil iodine concentrations are also worthy of further study, particularly when considering the prevalence of goitre in San Juan province reported by Morando *et al.* (2004).

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Tables and Figures

Table 1: Iodine and selenium concentrations for water samples.

Location	Site details	Iodine (µg/L)	Selenium (µg/L)	pH	Conductivity (µS/cm)
San Juan – Surface waters (Except Encon)					
ANG 03 Angualusta	Rio Blanco Above CU 01	55	1.3	8.6	1505
ANG 04 Angualusta	Rio Blanco Above CU 01	44	0.6	8.1	1350
ANG 05 Angualusta	Rio Blanco Above CU 01	52	0.9	8.6	1295
CU 01 Cuesto del Viento	Dam – Rodeo	60	0.9	8.8	na
RJ 01 Rio Jachal	Below CU 01	29	8.2	8.8	1475
RJ 02 Rio Jachal	Above Rio Caracol input	62	0.9	8.8	1473
RJ 03 Rio Jachal	Below Rio Caracol input	63	0.8	8.8	1457
RJ 04 Rio Jachal	Below San Roque	46	0.9	8.9	1495
RJ 05 Rio Jachal	Niquivil	58	0.9	8.8	1532
RJ 06 Rio Jachal	Tucunuco	95	1.1	8.6	1960

AN 01 Agua Negra	Spring water	48	2.1	7.8	2215
HU 02 Huaco	Rio Huaco – above Huaco	30	3.3	8.8	2506
HU 03 Huaco	Rio Huaco – centre Huaco	16	2.6	8.6	2220
HU 04 Huaco	Rio Huaco – below Huaco	23	2.4	8.7	2215
EN 08 Encon	Garden, centre of village – tap	28	<0.5	9.6	1248
EN 09 Encon	Garden 300 m from centre - well	27	<0.5	9.7	1221
EN 10b Encon	Centre – well	30	0.7	9.6	1352
EN 10c Encon	Centre – storage before filtration	16	<0.5	9.6	1254
EN 10a Encon	Centre – filtered	17	<0.5	9.2	1101
EN 11 Encon – 10 km S.East	Borehole – 300 m deep	16	<0.5	9.7	1390
EN 12 Encon – village garage	Borehole – 15m deep	29	<0.5	9.7	1046
La Pampa – Groundwaters					
EC 51	Campo Vidile – well 7 m deep	64	<0.5	8.6	767
EC 52a	Campo Marchisio well	104	14.8	8.3	>3999
EC 52c	Campo Marchisio well	112	14.5	8.2	>3999
EC 53	Campo Nelso well	88	2.6	9.9	>3999
EC 54	Campo Nelso well	102	3.1	9.7	>3999
EC 55	Campo Macagno well	108	5.4	8.8	>3999
EC 56a	San Juan Bautista well	212	4.4	8.7	2514
EC 56b	San Juan Bautista house	219	1.6	8.7	2491
EC 56c	San Juan Bautista well	223	5.5	8.7	2495
EC 57	Campo Coralís well	316	6.2	8.7	2610
EC 58	Campo Perez well	110	21.3	8.0	>3999
EC 59a Treatment works	Raw Input	395	6.2	8.2	3120
EC 59c Treatment works	Treated after reverse osmosis	148	4.3	8.2	3254
EC 60	Town Borehole	262	8.2	8.5	3494
EC 61a	Town Borehole	148	5.9	8.6	3478
EC 8 S2 Campo El Laurel	Borehole	219	9.9	8.4	>3999
LU 40	Borehole: 25 m deep	97	5.5	8.6	2620
LU 41	Borehole: 25 m deep	63	5.3	8.7	2640
LU 42	Borehole: 25 m deep	79	0.8	8.6	1120
LU 39a Treatment works	Raw water	52	2.9	8.6	2202
LU 39b Treatment works	Raw water mixed wells	61	4.0	8.7	2155
LU 39c Treatment works	Addition of Chloride	60	3.7	8.6	2145
LU 39d Treatment works	Residual waste- reverse osmosis	87	4.7	8.5	3655
LU 39e Treatment works	Water after reverse osmosis	1.4	<0.5	8.5	9
LU 39f Treatment works	Mineralised with salts	7	<0.5	8.5	11
LU 39g Treatment works	Drinking water	1.2	<0.5	8.7	50

Table 2: Iodine and selenium concentrations for soils.

Location	Site details	Iodine (mg/kg)	Selenium (mg/kg)	pH	LOI (%)	Mobile Iodine (mg/kg)	Mobile Iodine (%)
San Juan							
ANG 03 Angualusta	Above Dam- CU01	0.30	0.30	8.0	1.1	0.07	25
CU 01 Cuesto del Viento	Dam – Rodeo	0.26	0.46	7.8	0.1	0.05	18
RJ 02 Rio Jachal	Above Rio Caralaco	1.63	0.52	7.7	1.6	0.22	13
RJ 03 Rio Jachal	Below Rio Caracol input	0.39	0.40	8.4	1.3	0.17	42
RJ 04 Rio Jachal	Below San Roque	0.74	0.27	7.8	0.9	0.02	2
RJ 05 Rio Jachal	Niquivil	0.29	0.25	7.6	0.5	0.07	23
RJ 06 Rio Jachal	Tucunuco	0.52	0.33	7.8	0.7	0.08	15
AN 01 Agua Negra	2m from stream	10.47	0.29	7.3	1.1	0.93	9
HU 02 Huaco near Rio Huaco	Above Huaco – 10 m on bank	4.76	0.65	7.8	1.6	0.74	16
HU 03 Huaco near Rio Huaco	Centre Huaco - 10 m on bank	0.13	0.25	8.0	0.5	0.05	35
HU 04 Huaco near Rio Huaco	Below Huaco – 10 m on bank	0.12	0.18	7.9	1.0	0.03	23
EN 08 Encon	Garden, centre of village	4.20	0.21	6.7	2.3	0.19	4
EN 09 Encon	Garden, 300m from centre	0.05	0.12	8.8	0.9	0.01	15

La Pampa							
EC1 S1 Campo Don Santiago	Soil near water tank	3.65	0.31	6.5	3.3	0.09	2
EC1 S2 Campo Don Santiago	Garden soil	2.18	0.23	6.5	7.7	0.05	2
EC2 S1 San Juan Bautista	Garden soil	1.21	0.21	7.1	2.1	0.06	5
EC2 S2 San Juan Bautista	Garden soil	1.97	0.26	6.9	2.6	0.14	7
EC2 S4 San Juan Bautista	Garden soil	1.40	0.14	6.8	3.7	0.13	9
EC2 S5 San Juan Bautista	Soil near water tank	4.62	0.20	9.1	2.4	0.82	18
EC2 S6 San Juan Bautista	Soil beneath garden tap	1.79	0.20	7.9	3.2	0.29	16
EC2 S7 San Juan Bautista	Soil from field	2.53	0.23	6.9	3.3	0.08	3
EC4 S1 Eduardo Castex	From waterworks	2.27	0.19	7.1	3.7	0.08	3
EC4 S2 Eduardo Castex	Urban garden	2.94	0.24	7.1	3.8	0.05	2
EC6 S1 Campo Brizio	Soil next to well	2.52	0.26	6.6	2.8	0.08	3
EC6 S2 Campo Brizio	Soil from field	1.91	0.26	6.9	2.7	0.04	2
EC7 S1 Campo Gomez	Vegetable plot	3.34	0.26	7.5	5.9	0.04	1
EC7 S2 Campo Gomez	Soil near water tank	20.93	0.71	8.7	5.7	0.94	4
EC8 S1 Campo El Laurel	Garden soil	2.12	0.29	6.7	2.9	0.15	7
EC8 S2 Campo El Laurel	Soil next to well	4.04	0.21	7.5	4.5	0.21	5

Figure 1: (a) Argentina and the (b) San Juan and (c) La Pampa provinces, prepared courtesy of Mr Paul Lappage, British Geological Survey, 2008.

Figure 2: Summary of iodine and selenium concentrations in waters. Box-and-whisker plots show the inter-quartile range as the box, with the median as a horizontal line in the box and the mean as a square symbol. The whiskers locate the 5th and 95th percentiles of the data.

Figure 3: Relationship between conductivity and iodine in waters.

Figure 4: Summary of iodine and selenium concentrations in soils. see Figure 2 for description of the box-and-whisker plot symbols.

Figure 5: Mobile soil-iodine / -selenium concentrations compared to percentage values. see Figure 2 for description of the box-and-whisker plot symbols.

Figure 6: Relationship between organic content of soils and (%) mobile soil-iodine.