Review

The impact of recent volcanic ash depositions on herbivores in Patagonia: a review

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Abstract.   Volcanic tephra (ejected solids) result in varied impacts on ecosystems and livestock production. The recent Puyehue (2011) and Calbuco (2015) eruptions deposited large amounts of tephra in Chile and Argentina, affecting both livestock and wildlife in several ways. Impacts from Puyehue tephra on livestock were attributed initially solely to inanition, rumen blockage, eye problems, increased mechanical tooth wear; water consumption was considered without risk for humans and animals; and toxic effects were discarded. Subsequently, wildlife exhibited pronounced clinical signs of fluorosis and bone level exceeding 10 000 ppm of fluoride by 2014. Livestock including horses, cattle and sheep also had high levels of bone fluorine and clinical fluorosis. Tephra from Calbuco and Puyehue now overlap, containing on average 548 and 352 ppm fluoride, respectively. Dryness and eolic redeposition of tephra particularly east of the continental divide continues to re-expose domestic and wild ruminants. However, fluorosis and other related impacts like hypothyroidism, anaemia, and eosinophilia in ruminants also impact wool production. Although fluoride was discarded by others as a cause for the observed reduction in wool production, the specific effect of fluorosis on reducing wool production is well recognised, and occurs in sheep with less bone fluoride than reported from the Puyehue event. The rapid accumulation of fluoride in herbivores exposed to tephra from Puyehue coincides with reports that upon exposure to fluoride, sheep bone levels increased from 160 to 2300 ppm in only 3 months. The susceptibility of ruminants to fluorosis resides in their food processing: (1) intensive mastication and tephra size reduction, (2) thorough mixing of tephra with alkaline saliva during repeated rumination cycles, (3) water-soluble extraction in the rumen, and (4) extraction in the acidic abomasum. Lastly, the fluorosis may be further exacerbated by regional iodine and selenium deficiencies. Iodine deficiency may increase the incidence of dental fluorosis and the severity of damage, whereas selenium deficiency causes secondary iodine deficiency. Ash depositions from the Puyehue (2011) and Calbuco (2015) volcanic eruptions may cause havoc for wild and domestic animals and the people dependent on them. The negative impact on sheep wool production was thought to be related to reduced forage and tooth wear, but as shown here, there was also a major effect from fluoride intoxication. The recognition of toxic effects such as fluorosis have a strong bearing on diagnosing the types of impacts and selecting appropriate remedy measures aimed at reducing the impacts.

Additional keywords: *Cervus elaphus*, dental fluorosis, livestock, pathology, red deer, tephra.

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Introduction

Volcanic tephra deposition (ejected solid matter) results in a variety of impacts on ecosystems and livestock production systems. The Puyehue-Cordon Caulle volcanic eruption of 2011 (PCCVE) in north-western Patagonia provided a recent case study: it deposited large amounts of tephra in Chile and over ~36 million ha in Argentina (Gaitán *et al.* 2011; Mohr Bell and Siebert 2011), affecting both livestock and wildlife systems. Then in April 2015, the Calbuco volcanic eruption (CVE) deposited some $210 \times 10^6 \, m^3$ of tephra (equivalent to $1 \, t \, m^{-3}$) during the first 2 days in Chile and Argentina (Anon. 2015*a*), and significant amounts of tephra travelled as far as Buenos Aires and southern Brazil (Anon. 2015*b*).

The tephra deposition has many different impacts on livestock production systems. For instance, following the PCCVE, Easdale *et al.* (2014) listed: (i) direct impact on livestock, such as tephra deposits over the body and entering the fur, eye problems, modifications of nutritional behaviour and tooth wear; and (ii) indirect impacts through the reduction of water and forage availability. However, because volcanic eruptions may emit toxic levels of elements (e.g. Cronin *et al.* 2000, 2003), I suggest an additional impact from these recent eruptions: (iii) toxic effects. There are several mechanisms leading to intoxication, including exposure to volatile toxins, through contamination of water via leaching of tephra and plants with toxic levels resulting from root uptake (Shupe *et al.* 1984), or through the

ingestion of tephra. The latter occurs when grazing animals ingest tephra via grooming (Walton 1988), via large amounts of ingested soil (up to 14% of DM intake in sheep, Healy 1968; or up to 300 g/day in sheep, Cronin *et al*. 2000), and via particles adhering to low-growing forage (particularly characteristic of rangelands), which results in passive absorption (Gregory and Neall 1996; Cronin *et al*. 2000, 2003). Thus, additional impacts from volcanic tephra are based on studies of the chemical composition of tephra and its relationship to animal biochemical alterations.

Chemical aspects of tephra from the PCCVE (2011)

Immediately after the PCCVE, analyses of tephra revealed mainly oxygen, silicon, aluminium, iron, sodium, and potassium (Buteler *et al*. 2011; Hufner and Osuna 2011). Although initial concerns included the intoxication from fluorine (F) or fluorosis, based on previous incidences from other Chilean volcanoes, only F-containing microbubbles that may turn into fluorohydric acid upon contact with water were mentioned in tephra from Argentina (Bermúdez and Delpino 2011). Moreover, water-soluble extracts from tephra revealed low F levels (0.7 ppm; Hufner and Osuna 2011), surface water analyses from both countries revealed low F levels, and overall water consumption was considered without risk for humans and animals (DGA 2012; Wilson *et al*. 2013). However, the analyses of tephra across various sites averaged 548 ppm of F (Flueck 2014).

Although livestock in the affected region became weak and hundreds of thousands died, this was attributed to inanition, rumen blockage, and excessive tooth wear, rather than to known toxic elements (Wilson *et al*. 2013). However, by 2012 the first clear signs of fluorosis in wild herbivores were documented (Flueck and Smith-Flueck 2013a; see below).

Chemical aspects of tephra from the CVE (2015)

The general chemistry was reported to indicate that the tephra was andesitic and with a composition similar to tephra from the PCCVE, and with 18% deposited as particles of less than 8 microns, whereas 100% of suspended particles were less 8 microns (P. D. Gonzalez, cited in Anon. 2015c). Additionally, the tephra was considered non-toxic and that the water supplies would remain potable for humans and livestock (Anon. 2015d, 2015e). However, the tephra was reported to have severely impacted at least 30 000 livestock in one area of Argentina by reducing the available forage base (Anon. 2015f). Finally, an analysis of the tephra for presence of F via extraction averaged 352 ppm of F (NaOH digestion), whereas 29 ppm resulted from water extraction and 204 ppm from HCl digestion (Flueck and Winkel, unpubl. data).

General effects from tephra

The deposition of volcanic tephra, particularly above certain quantities, affects ruminants by physically covering forage plants. In habitats with brush and trees however, browsing may be affected mainly by fine tephra covering the plant parts, perhaps causing changes in foraging behaviour. However, when the forage base consists of only low strata, a tephra layer may effectively prevent access to this forage. This was notorious during winters, when the humid tephra layer froze and produced

a concrete-like layer impenetrable to hoofstock. Such a sudden reduction in the forage base explains the initially reported high mortality rates among livestock, whereas in red deer it affected mainly body condition and reproductive rates, particularly among subadults, which were no longer able to conceive (Flueck and Smith-Flueck 2013a).

Forage plants covered with tephra also explain an increase in tooth wear such that life expectancy was diminished substantially (Flueck 2013; Wilson *et al*. 2013). However, more importantly, animals which were developing teeth already under the influence of excessive F resulted in producing permanent teeth with altered physical qualities, including a reduced hardness, such that the same abrasiveness of tephra caused an even more accelerated tooth wear and concomitant reduction in life expectancy.

The numerous direct effects of volcanic tephra result in a reduction of body condition in ruminants with subsequent effects on performance. These effects include: (i) reduction of access to forage plants, (ii) mechanically producing excessive tooth wear, (iii) reduction of the physical resistance of teeth due to fluorosis, and (iv) reduction of the stamina via osteopathology, digestive and other health problems.

Fluorosis and skeletal effects

Wild red deer (*Cervus elaphus*) sampled following the PCCVE during the spring of 2012 indicated not only excessive tooth wear, but pathological tooth development in subadults with a pathophysiognomy typical of fluorosis (Fig. 1). Moreover, F levels in bone determined by direct potentiometry using an ion selective electrode ORION 94-09 (Orion Research Inc., Cambridge, MA, USA) revealed bone levels up to 5175 ppm of F, with average bone levels having increased over 38-fold during the first 15.5 months of exposure to tephra (Flueck and Smith-Flueck 2013a). Subsequent research showed that although mothers averaged already 2151 ppm of F, their late-term fetuses had only 20 ppm, indicating a barrier to fluoride transport *in utero*. Additionally, levels among four age classes increased significantly, at an average rate of ~1000 ppm of F/year, and these temporal kinetics of accumulation suggested that the sources of available F were highly effective in causing intoxication (Flueck and Smith-Flueck 2013b). During October–November 2013 additional red deer were analysed, revealing that some animals occupied areas of more intense ingestion of tephra, resulting in an annual accumulation rate of ~3700 ppm of F/year, and with the highest bone concentration having reached 10 396 ppm of F after ~28 months of exposure (Flueck 2014). Bone samples from red deer collected before the PCCVE provided background levels averaging 63 ppm of F in adults, which was similar to the average of 58 ppm of F in bones of other deer stemming from areas not affected by the PCCVE (Flueck 2014).

Consequently we also evaluated livestock species in areas affected by tephra from the PCCVE (Flueck 2013). As expected, livestock also succumbed to the effects of excessive F exposure via tephra. Aside from excessive mechanical tooth wear in adults from the abrasive quality of tephra, subadults exhibited accelerated tooth wear as the new permanent teeth developed under the influence of excessive dietary F (Fig. 2). The analyses
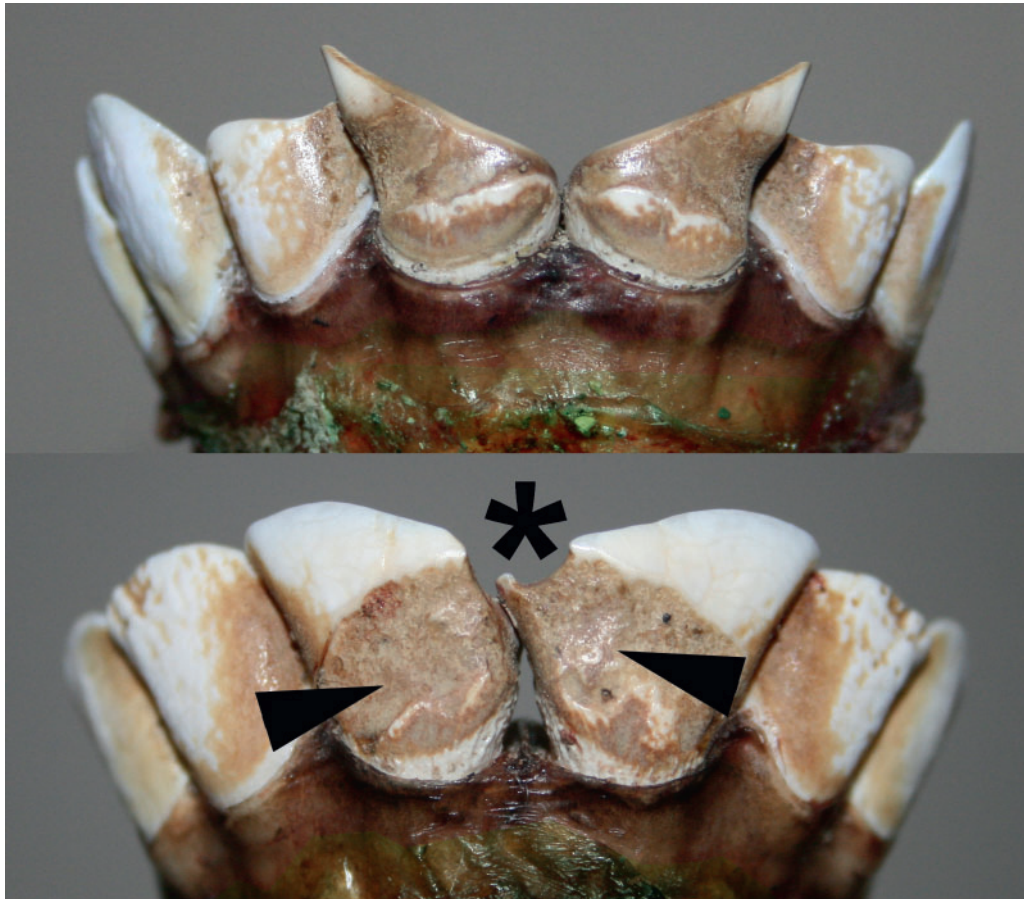
Fig. 1. Typical early lesions caused by fluorosis from the Puyehue-Cordon Caulle volcanic eruption event in red deer.

Fig. 2. Typical lesions caused by fluorosis from the Puyehue-Cordon Caulle volcanic eruption event in livestock. The new I1 are already completely worn down as the I2 emerge.

of bones were done on samples stemming from animals that died after about August of 2012 and thus had been exposed to tephra for some 14–15 months. The results revealed that sheep from five different sites averaged 931, 956, 1160, 1604, and 2431 ppm of F, respectively (highest: 3253 ppm); two horses had F levels of 880 and 1198 ppm (Flueck 2013); and two cows had 1067 and 1337 ppm of F (W. Flueck, unpubl. data).

Due to the elevated concentration of F in tephra and the dry conditions and eolic redeposition of tephra particularly east of the continental divide, exposure of domestic and wild ruminants is expected to continue while tephra remains near the surface level of soils (Fig. 3). As a consequence, after 47 months of continuous exposure to PCCVE tephra, a likely first case of skeletal fluorosis was found in a male deer (W. Flueck, unpubl. data). The three available limbs all showed several pathological changes. Articular surfaces were partially eroded, a metacarpal was shorter by 8% and wider by 32%, being strongly curved medially and twisted 25 degrees compared with a normal metacarpal, and several long bones had exostoses on the shaft and distal ends (Fig. 4). This case indicates osseous changes compatible with those described for chronic intoxication with fluoride.

Fluorosis and wool production

Besides the numerous distinct effects of volcanic tephra resulting in reduced body condition and its subsequent effects on performance, there may be a specific biochemical link between fluorosis and wool production. For instance, it is well known that fluorosis causes reduced serum thyroxine and triiodothyronine, and ruminants develop hypothyroidism, anaemia, and eosinophilia of leukocytes (Hillman *et al.* 1979). Fluoride in fact, had been used successfully to treat hyperthyroidism (Zachariassen and Flaten 2009). Fluorosis in sheep also affected lipid peroxidation and caused oxidative stress manifested by increased erythrocyte levels of malondialdehyde and decreased activities of Na^+-K^+ ATPase and glucose-6-phosphate dehydrogenase (Yur *et al.* 2003). Moreover, the literature is replete with references to volcanic tephra reducing wool production in sheep. Ryder (1956) examined wool and skin samples from controls and sheep being dosed with F. The F caused the wool to grow shorter, finer, less crimped and to become less lustrous and less wool grease was produced. Wheeler *et al.* (1985) found clean fleece weight being reduced by 18% in 17-week-old lambs from F administration. Other studies indicate the negative effect of fluorosis on wool production (Peirce 1959; Underwood 1977; Nicholas 2012).

The period of wool growth in sheep ends in late winter (August–September) in the area affected by the PCCVE, which occurred on 4 June 2011. The next shearing thus took place 3–4 months after this tephra fallout, yet fluoride was discarded as a cause for the observed reduction in wool production (Easdale *et al.* 2014), although overt fluorosis in that region had been described in wild and domestic herbivores including sheep (Flueck and Smith-Flueck 2013*a*, 2013*b*; Flueck 2013, 2014). The rapid accumulation of F in herbivores exposed to tephra

Fig. 3. Ecotonal landscape in the Patagonian study area. Although known for commonly strong eolic conditions, this was a 'calm' day without westerlies: this turbulence is due to daily thermal wind patterns, which shift ashes in any direction.
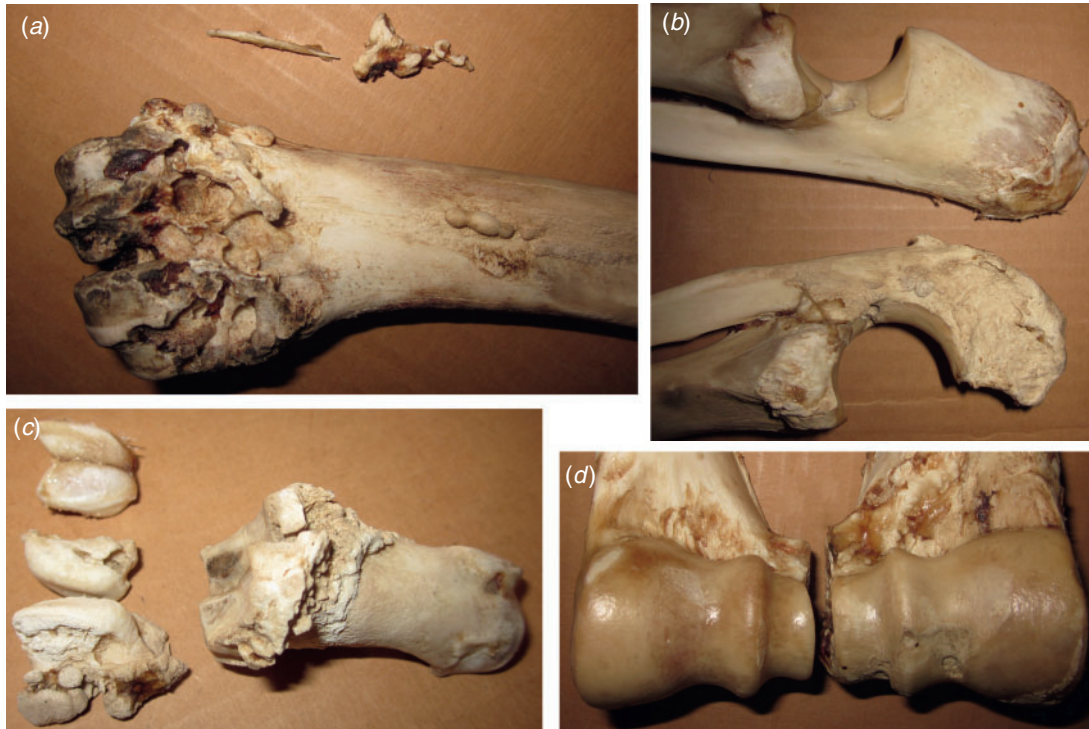
Fig. 4. A likely first case of skeletal fluorosis in deer. A few of the pathologies: (*a*) deformed metacarpal with exostoses and calcified tendons, (*b*) ulna with various pathologies next to a normal one, (*c*) proximal sesamoid bones and first phalange with exostoses, (*d*) distal humerus with exostoses and eroded articulation next to normal one.

from PCCVE (Flueck 2014) is consistent with the results of Grace *et al.* (2007) who reported that sheep bone F levels increased from 160 to ~2300 ppm in only 3 months.

Discussion

Several of the impacts from the PCCVE and CVE tephra on wild and domestic herbivores in the region cannot be attributed solely to inanition, rumen blockage, eye problems, or increased mechanical tooth wear (Wilson *et al.* 2013; Easdale *et al.* 2014). Certainly, the analyses of surface waters and of tephra via leachate experiments regarding the PCCVE and CVE eruptions led to the conclusions that water consumption was not threatening to humans and animals (Hufner and Osuna 2011; DGA 2012; Wilson *et al.* 2013; Anon. 2015*d*, 2015*e*). However, extrapolating these results to claim that there were thus no toxic elements involved are unwarranted, particularly in the light of the documented toxic impact caused by F in PCCVE tephra (Flueck 2014) and the high F concentrations in CVE tephra. Furthermore, the reference used by Easdale *et al.* (2014) about other analogous eruptions in Patagonia as having shown that sheep deaths resulted from physical rather than chemical properties of the Hudson tephra (Rubin *et al.* 1994) needs qualification. Early tephra analyses following the Hudson volcano eruption (1991 in Chile) revealed high fluoride levels, yet fluorosis was not identified. Instead, the thousands of sheep deaths were attributed to physical – not chemical – properties of tephra (Rubin *et al.* 1994). However, considering that the study

by Rubin *et al.* (1994) was conducted only 1 month after the eruption, not even mild chronic fluorosis could have been observed, as chronic fluorosis usually develops gradually and insidiously, and overt signs do not appear until sometime after initial exposure. Severe dental fluorosis as documented for the PCCVE (Flueck and Smith-Flueck 2013*a*, 2013*b*; Flueck 2013, 2014), and skeletal fluorosis require longer-term exposure (Shupe *et al.* 1979; Livesey and Payne 2011). Thus, the absence of research subsequent to the conclusions by Rubin *et al.* (1994) explains the absence of documented fluorotic cases from those tephra with documented high levels of F (GVP 1991). Similarly, based on early claims that the PCCVE caused problems among animals unrelated to toxic elements (Wilson *et al.* 2013), this remains the prevailing interpretation today, and the well substantiated toxic effects of F from the PCCV have gone largely unrecognised in Argentina. We are aware of only one analysis conducted on F levels in forage plants and animal tissues from the PCCVE event: in Chile, forage F levels were more than 3-fold higher than accepted levels, whereas levels in tephra and blood from livestock were also elevated (Araya, cited in Flueck and Smith-Flueck 2013*a*). Instructively, an earlier eruption of the nearby Lonquimay volcano (1988, 200 km north of PCCVE), caused fluorosis in livestock within 3 months (Araya *et al.* 1990) and elevated forage F levels for 2 years of monitoring after the eruption, such that high forage levels alone were concluded to be dangerous for animals at least 2 years after cessation of the eruption (Araya *et al.* 1993). The effects from the high F concentration in CVE tephra will only be revealed

Fig. 5.   Numerous periparturient cattle died in early spring even though the winter of 2015 had been very mild. This cow could barely stand up and make a few steps.

in the future and it will be difficult to distinguish from the continuing and overlapping effects from the PCCVE event. For instance, some ranches have experienced major losses of periparturient cattle (in October 2015) even though the winter had been very mild (Fig. 5) and this is most likely caused by the PCCVE rather than the exposure of a few months to CVE tephra. These dead animals had a mean fluoride level in bone of 2159 ppm (max. 4517 ppm, SE 418.8 ppm, $n = 11$, W. T. Flueck, unpubl.)

The expression of strong toxic effects from excess F apparently resides in the peculiar digestive system of ruminants, which makes them particularly susceptible to F-containing tephra deposits. Ruminants indeed present a complex physiochemical environment for processing any compound. Rumination involves regurgitation of rumen content for repeated mastication to diminish the size of particles. This process likely results in pulverisation of tephra as evidenced by rapid tooth wear, and thereby increases the surface : volume ratio, with the resulting effect of liberating more F. Moreover, this mastication process occurs in a chemical medium dominated by saliva, which is highly alkaline (pH of 8.2–8.5; Aschenbach *et al.* 2011). Rumination is a major component of this type of digestion, as evidenced by 20–25 chews before swallowing (Prinz and Lucas 1997), and the copious production of saliva to replace what is swallowed each time. Cattle have been measured to produce 100–200 L/day or more of saliva (Silanikove and Tadmor 1989). The greatly increased F solubility in alkaline media (e.g. Markert *et al.* 1997) likely makes this a crucial step in the mass balance of F in ruminants. Upon swallowing, the mixture enters the rumen, which essentially represents a water-based extraction system with nearly neutral pH, but with the presence of various solutes.

Finally, the suspension passes to the abomasum for final digestion at a pH of 1–2. Again, it is well documented that fluoride solubility is greatly increased in acidic conditions as compared with neutral pH. Clearly, the initial analyses done after the PCCVE and CVE eruptions on surface water and on water-based leachates of tephra did not provide any indications of future F intoxication among ruminants. Therefore, it is clear that the susceptibility of ruminants resides in their food processing: (1) intensive mastication and tephra size reduction (with concomitant excessive tooth wear), (2) thorough mixing of tephra with alkaline saliva during repeated rumination cycles, (3) water-soluble extraction in the rumen, and (4) extraction in the acidic abomasum (Flueck and Smith-Flueck 2013*a*).

For the large region affected by these recent volcanic eruptions, these impacts from fluorosis may be further exacerbated by regional iodine (e.g. Matamoros *et al.* 2003) and selenium deficiencies (Flueck *et al.* 2014). Iodine deficiency may increase the incidence of dental fluorosis and severity of damages, whereas selenium deficiency causes secondary iodine deficiency among other things (Flueck *et al.* 2012).

The lack of understanding of the importance of the toxicity of F in tephra resulting from these recent volcanic eruptions may explain the lack of additional studies among wild and domestic animals and their habitats. Such additional investigations would be beneficial for future management decisions. For example, there is no information yet about the impact on the protected native camelid (*Lama guanicoe*) coexisting in areas with demonstrated overt fluorosis in deer and livestock. Also, even though the root uptake of F by plants can contaminate forage plants and thus present another route of intoxication for herbivores, there have been no studies on the F contents of forage plants.

Acknowledgements

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