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# Identifying Patterns and Sources of Anthropogenic Trace Metals in the Argentine Central Andes by using snow samples and an Atmospheric Dispersion Model

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## Environmental significance statement

This work aims to identify levels, patterns and sources of anthropogenic trace metals in the environment of the Argentine Central Andes, combining the use of analytical chemistry in snow and modeling techniques. Results revealed that local emission sources play a central role in the determined levels of trace metals. This study represents an important contribution to the knowledge and preservation of the local Andean cryosphere, considering that, to our best knowledge, it constitutes the first of its type in the Argentine Andes region. These new findings will help not only to understand the relationship among the multiple factors involved in this problem, but also could serve as a tool to decision makers to establish measures to preserve these areas.

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## ARTICLE

## Identifying Patterns and Sources of Anthropogenic Trace Metals in the Argentine Central Andes by using snow samples and an Atmospheric Dispersion Model

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This study presents the first local measurements of metals in snow from the Argentine Central Andes. Cu, Pb and Zn were selected as specific tracers of anthropogenic local emission sources in the study area. Snow samples were collected during winter (2014, 2015 and 2016) at two sites with different characteristics: Punta de Vacas and Vallecitos. The samples were analyzed by ICP-MS, and the average concentrations found were 1.4  $\mu\text{g L}^{-1}$  (Cu), 2.2  $\mu\text{g L}^{-1}$  (Pb) and 14.2  $\mu\text{g L}^{-1}$  (Zn) in the snow samples from Vallecitos, and 5.3  $\mu\text{g L}^{-1}$  (Cu), 2.6  $\mu\text{g L}^{-1}$  (Pb) and 24.0  $\mu\text{g L}^{-1}$  (Zn) in the snow samples from Punta de Vacas. These data and the snowfall amount in each sampling site were statistically analyzed. Results suggested that the levels of metals in the snow are influenced not only by the atmospheric concentrations, but also by the amount of precipitated snow. Additionally, an atmospheric dispersion model, CALPUFF, was applied in the study area to determine the origin of the studied metals and to understand the spatial distribution pattern of the concentrations found. Results showed that the metal atmospheric loads in the study area derived from local sources, especially vehicular traffic and mining. This work represents an important contribution to the knowledge and preservation of the local Andean cryosphere, and it could be used as an input to develop protection policies in the area through the combination of different and complementary tools for the evaluation of air quality.

### Introduction

Most metals are necessary for life since they have, at low concentrations, specific roles in vital functions of organisms; however, at high concentrations, they can be toxic<sup>1</sup>. Anthropogenic activities are known as the main emission sources of certain metals into the atmosphere, which contribute to increasing levels in environment<sup>2,3</sup>. As result, certain trace metals are considered anthropogenic tracers<sup>4,5</sup>, with copper, lead and zinc as the most ubiquitous<sup>6,7</sup>. Although the atmospheric pollution produced by these substances has received greater attention in urban areas, since these tend to present the highest levels of pollution, as well as concentrate most of the population exposed to health risks, these metals can also be present and cause local effects on remote ecosystems. Such is the case of the Central Andes Cryosphere, which plays a central role in the hydrological cycle and the water supplies of surrounding populations, whereby, nowadays there is an increasing awareness of the potential impacts from local pollution sources and long-range transport.

Among the variety of methodologies that exist to determine the presence of metals in the atmosphere, active sampling of particulate matter (PM) has been one of the most widely used worldwide<sup>8–10</sup>. Nevertheless, this method presents some drawbacks of its implementation in the Andean Cryosphere, considering it is a remote location, with extreme weather conditions and a very limited availability of facilities

and electrical energy for the correct installation and operation of expensive instruments.

In this context, the implementation of other methodologies could help in properly assessing the metal presence and sources in the atmosphere of the Andean Cryosphere. Snow can be considered an effective matrix for studying the load of metals in the atmosphere of snowy ecosystems because they get trapped in snow, either during its fall or in a later deposition, and they dilute in pure water, acting as a natural passive sampler. Therefore, snow composition can be unambiguously measured even at very low concentrations<sup>11,12</sup>. Additionally, snowflakes have larger specific surface and lower falling speed than liquid precipitation, which allows capturing more atmospheric pollutants during their fall<sup>13</sup>. Likewise, snow sampling procedures are simple, and its analysis is feasible by using instrumental with appropriate sensibility<sup>4,14</sup>.

The use of snow samples as an indicator of local air quality by analyzing trace metals has been reported in several regions of the world, mainly in the Northern Hemisphere. Some authors<sup>15–17</sup> reported low levels of trace metals in remote locations, where it could be deduced that the main source of these substances was atmospheric transport. Other studies<sup>13,14,18,19</sup> reported snow analysis in urban areas, where levels were higher and the contribution of local sources, especially vehicular traffic, was more relevant. These works showed that concentrations of anthropogenic metals in snow samples of urban areas were up to a hundred times higher than those found in remote areas. Additionally, it was observed that the concentration of anthropogenic metals in

Electronic Supplementary Information (ESI) available

snow samples collected from sites close to main roads increased with the average daily traffic and the time of residence of the snow<sup>6</sup>. To the best knowledge of the authors, there are few scientific reports about the use of snow as an indicator of atmospheric pollution with anthropogenic metals in South America. Cereceda-Balic et al.<sup>4</sup> found trace metals in snow samples from two areas of the Chilean Andes. The authors reported high concentrations of Cu (an average of 33  $\mu\text{g kg}^{-1}$ ) at one of the sample sites, probably deriving from the city of Santiago de Chile combined with mining activities in the area. Levels found in snow samples of the region farthest from the urban centers were comparable to background concentrations (an average of 3.6  $\mu\text{g kg}^{-1}$ ).

However, it is well known that the representativeness of the information provided by these samples is somehow limited due to the low spatial and temporal resolution, which must be considered to ensure the validity of the data obtained and the conclusions drawn from them<sup>20</sup>. In this context, the use of a dispersion model based on an emission inventory as a complement of the analytical determination in snow samples would contribute in obtaining greater spatial and temporal representativeness. By using this type of models, a relationship between the anthropogenic activities that produce emissions and the levels of anthropogenic metals in the environment can be established.

This study aims to delve into the current scenario of air quality in the Central Andes using metals as tracers of anthropogenic impact, combining an atmospheric dispersion model and metal determinations in samples of fresh snow from the study area, in order to evaluate the spatial distribution patterns of metals in the region. The combination of both tools constitutes the first study of its type in the Argentine Andes region; thus, this work represents an important contribution to the knowledge and preservation of the local Andean cryosphere. Furthermore, results exhibited a negative correlation between the levels of anthropogenic metals in snow and the amount of snowy precipitation, which had been underestimated in its use as an environmental indicator until now. Finally, it is worth highlighting the ability of the dispersion model to reflect the levels of trace metals found in the snow, which makes it an useful tool for the proper design of monitoring networks, considering the time and cost that sampling campaigns take, and the conclusions that are intended to be made from the analysis of the obtained data.

## Methods

### Study Area and Emission Sources of Anthropogenic Metals

The Andes Mountain Range is located in the western part of South America. This work is focused on the Argentine side of the Central Andes (Fig. 1).

The orography of the Andes Mountains modulates the climate of the region. It influences significantly the moisture transport from the Amazon basin, the convective processes

and the precipitation patterns through the mechanical forcing of winds and topographic blocking of the western frontal system with a high humidity load from the Pacific Ocean<sup>21</sup>. In the study area, snowfalls of great volume and marked seasonality are produced by these systems, in conjunction with low temperatures<sup>22</sup>. The snow accumulated during the winter melts when spring arrives. This process is the main source of water for the numerous rivers that flow through the region<sup>23</sup>. Regarding this, although the climatic phenomenon "El Niño Southern Oscillation" (ENSO) influences precipitation over the entire coast of South America, the impact on Andean mountains is most direct between 28°S and 35°S, where the area of interest is located. The amount of winter precipitation in this area is significantly correlated to the Southern Oscillation Index (SOI), with higher values during "El Niño" years, which means that there is a great inter-annual variation in the amount of snow registered in the zone in relation to this phenomenon<sup>24</sup>.

The main economic developments in the region are agriculture, mining and other industrial activities<sup>25</sup>. On the western slope of the mountain range, within the study area, there are two copper mines. In the industrial area of Mendoza, there are several facilities where different types of activities are performed<sup>25,26</sup>, including cement and glass production plants, as well as power plants. In addition, it is important to consider other anthropogenic activities developed in the urban center of Mendoza that might also contribute to the metal emission in the study area, considering that the region has a population of 1 million inhabitants.

These activities are waste dumping and management, including incineration of clinical waste and the open burning of municipal solid waste<sup>27</sup>. Another relevant source of Cu, Pb and Zn considered in the studied location is vehicular traffic<sup>28</sup> at the urban level, and that related to the National Route n°7 (RN 7) (Fig.1, emissions are distributed all over the road network). RN 7 is the main overland connection between Argentina and Chile (1244 km long), and it is used to transport goods and people to, or from, Brazil, Paraguay and Uruguay to Chile; thus, it has high traffic, around 2000 vehicles per day, of trucks, buses and cars<sup>29</sup>.

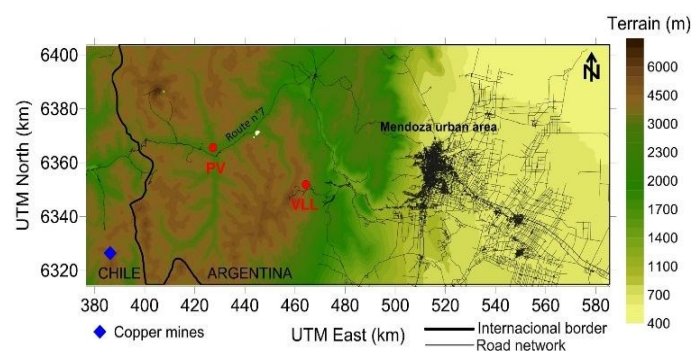


Fig. 1. Study Area. Points represent the two sampling points, Punta de Vacas (PV) and Vallecitos (VLL). The diamond represents the location of the copper mines in Chile.

More details about emissions sources can be found in the "Supplementary Material" section.

For the snow sampling, two points were selected on the Argentine slope of the Central Andes (Fig.1). Punta de Vacas (PV, -32.83°, -69.77°; 2,800 m.a.s.l.) and Vallecitos (VLL, -32.91°, -69.42°; 2,990 m.a.s.l.). Punta de Vacas is a small rural village located in the main part of the mountain range. This site is crossed by RN 7 and it has no permanent population. The distance from Punta de Vacas to the nearest mining development is 55 km far, and 88 km to the Mendoza urban center. Vallecitos is also a small rural village with no permanent population, located in the frontal mountain range. It was historically a ski center, but nowadays it is barely visited since it was closed. This site is located 90 km far from the nearest mining development and 50 km far from the urban center of Mendoza.

### Snow Sampling and Sample Analysis

The reagents used in the sampling and analysis procedures were sub-boiled nitric acid, obtained by distillation from nitric acid 65% w/w analysis grade (Merck, Darmstadt, Germany) in the laboratory by using an acid cleaning system PFA/PTFE ECO M (Maassen GmbH, Germany), and ultrapure water (18 MΩcm).

The sampling material (new PET bottles and plastic shovels) was rinsed with tap water, then with sub-boiled HNO<sub>3</sub>, and it was immersed in a 0.5% HNO<sub>3</sub> bath for 24 hours. Finally, the sampling elements were rinsed with ultrapure water. The internal standards (Chem-lab, Belgium) used were Sc to correct the Cu signal, Y to correct the Zn signal and Ho to correct the Pb signal. The calibration curve was prepared in 2% v/v sub-boiled HNO<sub>3</sub> solution, in the calibration range from 0.1 to 75 μg L<sup>-1</sup>, from the ICP multi-element standard XXI (Merck, Darmstadt, Germany) and suitable dilutions with ultrapure water.

In order to consider equivalent periods of dry deposition on the surface of the accumulated snow, the samples were collected in the same sample points in the month of June of each year, within the week after a snowfall. The sampling campaigns were carried out during three consecutive winters (2014, 2015 and 2016). Snow samples were collected in new PET bottles from the top of the snowpack, in an area of 1 m<sup>2</sup> and 10 cm thick layer, where the snow had not been disturbed, using a clean plastic shovel and disposable dust-free nitrile gloves. Sample weighed around 400-500 g, and they were kept always frozen (-10°C), during transport and storage, until they could be processed in the laboratory. Samples were collected by duplicate or triplicate, as the case permitted (Tables S16 and S17 of the supplementary material present details about the number of samples in each campaign, together with analysis results). In the laboratory, samples melted at room temperature and were acidified with sub-boiled HNO<sub>3</sub> until reaching a concentration of 2% v/v. Subsequently, the solution obtained was analyzed in duplicate directly by inductively coupled plasma mass spectrometry (ICP-MS) according to ISO 17294-2(30), in an Agilent Technologies

7500 Series device. Samples were analyzed without any previous treatment of the samples to avoid contamination, taking into account that, in the conditions of the samples (average value of pH = 5.2), the studied metals are predominantly dissolved<sup>12,19</sup>.

For the quantification of metals, internal standards with multi-parametric calibration curve were used. The internal standards were added to both, blanks and samples, prior to nebulization in the device. This procedure allows the accurate quantification of the trace metals using an external calibration considering the signal ratio of metal: internal standard. Thus, it was possible to compensate small variations on the signal intensity throughout the analysis due to the instability of the ionization source and the impurities accumulation on the sample introduction interface<sup>31</sup>.

For quality control of the data, the uncertainties in the measurements were calculated according to the method proposed by Magnusson<sup>32</sup>, and they resulted in 11% for Cu, 25% for Zn and 9% for Pb, all with a 95% confidence, applying a coverage factor  $k = 2$ , using reference material ("ICP multi-element standard X CertiPUR® for surface water testing"; traceable to standard reference materials from NIST. Merck, Darmstadt, Germany.)

The analytical blank used was a 2% v/v sub-boiled HNO<sub>3</sub> solution using sub-boiled acid and ultrapure water. Based on the analysis of four independent blanks, the detection limits of the analytical method were obtained, being 0.08 μg L<sup>-1</sup> Cu, 0.08 μg L<sup>-1</sup> Zn and 0.05 μg L<sup>-1</sup> Pb.

Concentrations of other metals, in addition to those studied in this case (Cu, Zn and Pb), were also determined by ICP-MS. These results were included in the Supplementary material section, along with additional data related to the QA/QC.

### Statistical Analysis

The data analysis was carried out in two steps: Pearson analysis and Welch's ANOVA test. There are reports that show that the concentration of trace metals in the snow is not only conditioned by their atmospheric levels, but it is also influenced by the volume of precipitation<sup>33,34</sup>. To evaluate the relationship between (I) the mean value of metal concentration for each year  $C_{ijk}$ , where  $i$  is the metal,  $j$  is the year and  $k$  is the site), and (II) the corresponding value of fallen snow in the 30 days prior to sampling on each site ( $S_{jk}$ ), a Pearson's product-moment correlation was run.  $S_{jk}$  values were taken from GIOVANNI System<sup>35</sup>. Based on the achieved results of the Pearson analysis, Welch's ANOVA test was carried out to evaluate whether there were statistically significant differences between the two sampling areas. A null hypothesis ( $H_0$ ) was proposed stating that there were no differences between the two sites. The null hypothesis was tested considering a significance level  $\alpha = 0.05$  and verifying the validity of the assumptions needed for data analysis using this test. The statistical analyses were carried out using the IBM SPSS Statistical Software.

## WRF/CALMET/CALPUFF Modeling System

The atmospheric dispersion of selected metals was simulated using the WRF/CALMET/CALPUFF modeling system<sup>36–38</sup> based on a high-resolution emissions inventory elaborated by the authors for the metals determined in the snow samples (Cu, Pb and Zn). The CALPUFF (California Puff) model has a superior ability to estimate dispersion in complex environments. The Guide on Air Quality Models of the United States Environmental Protection Agency<sup>39</sup> recommends its use for applications where the terrain contains variations and where land cover is not uniform, as in this case, where mountains have an important role in the atmospheric dispersion. In addition, CALPUFF, unlike Gaussian models such as ISC3, can process calm conditions, avoiding estimates of very high, unrealistic, concentrations<sup>40</sup>. Rood<sup>41</sup> compared CALPUFF performance with steady-state models and concluded that CALPUFF exhibited smaller variances and higher correlations with measured values in real samples. MacIntosh et al.<sup>42</sup> evaluated the use of CALPUFF to simulate metal dispersion in complex terrain and found that it is a reliable model for the prediction of concentrations in this type of cases.

The system consists of a meteorological diagnostic model in three dimensions called CALMET, and a transport, dispersion, deposition, and chemical transformation model called CALPUFF. CALMET is a meteorological model that produces wind and temperature hourly fields in a three-dimensional gridded modeling domain, necessary to run CALPUFF. Likewise, it associates variable fields in two dimensions, such as mixing layer height, surface characteristics, and dispersion properties. CALPUFF is a Gaussian puff dispersion, multilayer, non-stationary and multi-component state model, which can simulate the effects of the variable weather conditions in transport, transformation and removal of pollutants. CALPUFF performs considering terrain elevations, as well as land use features. Detailed algorithms for the different physical processes involved in the dispersion and transport of pollutants, as well as details on applications of the model, can be found in the literature<sup>38,39</sup>. This model has been previously applied in the study area to assess the transport and atmospheric levels of other compounds with good results<sup>37</sup>.

The objective of the modeling in this work was to generate fields of atmospheric levels of the studied metals to contrast this information with the values of concentrations determined in the analyzed snow samples. Thus, to establish the ability of the model to predict the spatial distribution considering that the snow reflects the composition and magnitude of the surrounding atmosphere<sup>11</sup>. From the outputs of the model, it was possible to describe the distribution of metals (Pb, Cu and Zn) in the atmosphere of the study area, as well as to evaluate the contribution of the different emission sources to the simulated atmospheric levels at each measurement point.

The modeling domain was organized in a grid of 210 × 90 km<sup>2</sup>, with a basic horizontal grid cell of 1 km × 1 km, for a 30-days period (June 2015). This month was selected because it belongs to the austral winter season when there are snowfalls in the studied areas, which are seasonal. While it is known that meteorological conditions of each period are

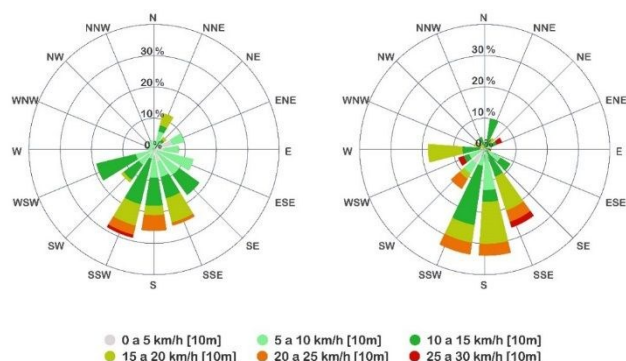
different and, because of this, the resulting dispersion would also be different, the case was considered as descriptive of the situation in the area. For its operation, the model required the following inputs:

**Topography, land use and land cover:** Terrain features were incorporated using data from the Shuttle Radar Topography Mission (SRTM), available in a 1-arcsecond resolution (approximately 30 m) courtesy of the U.S. Geological Survey<sup>43</sup>. The SRTM data were processed on the domain of interest to obtain terrain elevations with a 500 m resolution. Vegetation maps of the Global Land Cover 2000 Project (GLC 2000) for South America with a 1 km resolution and data generated by the Department of Geography of the University of Maryland (UMD Global Land Cover) were used for land use and land cover features<sup>44</sup>.

**Meteorological data:** The CALMET module requires meteorological fields on surface and height as inputs. Since there are no permanent meteorological data sources with the desired resolution, every 1 hour for both surface and height, which were representative of the area and for long periods of time in the vicinity of the study area, data were generated with a meteorological model to initialize CALMET with fields such as “initial conditions”. The Weather Research and Forecasting (WRF) model<sup>45</sup> was used to obtain 3D fields covering the modeling domain and period of time<sup>46</sup>. The procedure involves the use of outputs from the regional WRF model as the initial estimate for CALMET. For this purpose, an off-line preprocessor called CALWRF (version 1.4) was used, which initializes CALMET replacing the required hourly parameter values of the planetary boundary layer (PBL) and the surface layer of the atmosphere with those derived from WRF. The WRF model has been previously used and validated in the study area<sup>47–49</sup>. Table S14 of the Supplementary Material section shows the configuration and parameters used in the implementation of the WRF model. Fig. 2 presents the wind rose obtained in the meteorological simulations (left), summarizing the average winds for the modeling period. The same figure (right) presents average values of wind speed and direction from the same period but taken from two meteorological stations belonging to the Argentine National Meteorological Service (SMN).

**Emissions data:** The modeled species were Cu, Pb and Zn. The possible emission sources within the area of interest were surveyed and, based on this, an own emission inventory was elaborated following the guidelines of the European Environment Agency<sup>50</sup>, which is detailed in Section S1 of the Supplementary Material section. The annual emissions data by source are shown in Table 1. Since the selected pollutants are not part of the default CALPUFF library, they were included as particulate matter (PM), considering that because of their physicochemical characteristics and their emission sources, these metals are released into the atmosphere associated with other particles, as part of PM<sup>42,51–54</sup>. Metals of interest (Cu, Zn and Pb) were modeled as PM of three different aerodynamic diameters: PM<sub>10</sub> (10 μm or less); PM<sub>2.5</sub> (2.5 μm or less) and PM<sub>1</sub> (1 μm or less). For each emitting source, a characteristic size distribution was considered to divide the total emission of

each metal estimated in the emission inventory in the PM diameters above-mentioned (More details in Section S2 of the Supplementary Material). To be included in the model, the total annual emissions were adequate for the time scale and the type of source (area, point or line).



**Fig. 2.** Wind rose constructed from simulated data in the modeled period (left) and from meteorological stations, average for the same period (right), in the study area

**Table 1.** Atmospheric emissions calculated for the selected metals in the study area. Emissions are presented in  $\text{kg yr}^{-1}$ , together with the corresponding percentage of the total emission of each metal.

Emission source	Cu	Pb	Zn
	Emission (percentage)	Emission (percentage)	Emission (percentage)
Energy industries	11.1 (0.5%)	10.4 (0.2%)	164 (9.7%)
Fugitive emissions from oil	22.6 (1.0%)	22.6 (0.3%)	22.6 (1.3%)
Refining/storage			
Cement production	47.6 (2.1%)	72.1 (1.1%)	312 (18%)
Glass production	0	1218 (18.2%)	0
Lead-acid batteries production	0	315 (4.7%)	0
Road transport	858 (38%)	185 (2.8%)	1197 (70%)
Clinical waste incineration	115 (5.0%)	72.5 (1.1%)	0
Copper production	1215 (54%)	4774 (71.5%)	0
Open burning of waste	1.8 (0.1%)	7.5 (0.1%)	3.2 (0.2%)
TOTAL ( $\text{kg}\cdot\text{year}^{-1}$ )	2271	6677	1699

## Results and discussion

### Metals in Snow

Table 2 presents the data of metal concentration found in the analyzed snow samples collected from the Central Andes on the Argentine slope (More details can be consulted in Tables S16 and S17 of the Supplementary material). Comparing the data obtained in both sampling sites, it is worth

to highlight that mean concentrations of Cu and Zn were 280% and 69% lower in Vallecitos than in Punta de Vacas. This result may be related to the proximity of each sampling site to the emission sources since Punta de Vacas is crossed by RN 7, while Vallecitos is located 10 km from RN 7. Punta de Vacas is also nearest to the copper mining development in Chile. In the case of Pb, the difference is not that noticeable, being 18% higher in Punta de Vacas than in Vallecitos.

The metal concentrations range was compared with reports of similar studies from around the world, which also used comparable sampling and analytical methodologies (Table 2). The concentrations found were comparable with those published by Cereceda-Balic et al.<sup>4</sup> which were obtained from two sampling sites also located in the Central Andes, on the Chilean slope (Cerro Colorado and Nevados de Chillán, 36 km NE and 500 km S of Santiago, respectively). The reported values for Cu in Cerro Colorado were conditioned by its proximity to Santiago, which presents severe episodes of atmospheric pollution during winter, and its proximity to a copper mine in Chile (40 km far), worsened by the orographic barrier represented by the Andes mountain range, which does not allow a proper dispersion of the atmospheric emissions<sup>4</sup>.

A feature to highlight in our case, as in the Chilean determinations, is that the concentrations in the studied sites corresponded, in order of magnitude, with urban sites rather than remote areas. This suggests an influence of local sources, both vehicles and mining activities.

The concentrations of metals in Punta de Vacas showed higher variability (higher values of SD) in all cases, which is a feature of locations nearest to emission sources, where variations in emission patterns can be captured by the surroundings. On the other hand, Vallecitos presented a smaller variability in the metal concentration values, suggesting that they may be attributable to atmospheric transport with less influence of local emission sources, like traffic or mining activities.

Although the literature reports the use of metal concentrations of snow samples as an indicator of the surrounding air quality; it is important to note that these concentrations are conditioned by the snowfall amount<sup>12</sup>, in addition to limitations regarding spatial and temporal resolution. Therefore, comparisons of metal concentrations in snow samples must be carried out cautiously and complemented with the information provided by other tools, such as those used in the following sections.

### Statistical Analysis of Data

An exploratory analysis was carried out by using Pearson's product-moment correlation. This tool showed a linear relationship with all variables normally distributed, as assessed by Shapiro-Wilk's test ( $p > 0.05$ ), and there were no outliers. A strong negative correlation was found between metal concentrations and values of fallen snow in each studied site (see Table 3), and in most cases, there is an acceptable statistical significance for these correlations ( $p = 0.072$  for Cu,  $p = 0.25$  for Zn and  $p = 0.005$  for Pb). This output indicated that

there was dependence between  $C_{ijk}$  and  $S_{jk}$ , which could be due to a set of situations explained as follows: at the beginning of the snowfall, metals were present in the atmosphere at certain concentration together with the particulate matter in

suspension. As the precipitation event progressed, a wet deposition occurred, that scavenged the particulate matter (and metals) from the atmosphere, and thus, it decreased the concentration of particles (in this case, metals) in the air<sup>55</sup>.

**Table 2.** Metal (Cu, Zn and Pb) concentrations in snow samples ( $\mu\text{g L}^{-1}$ ) determined in this study and comparison with reports from around the world.

	Metal concentration in snow ( $\mu\text{g L}^{-1}$ )			Type of studied area	REFERENCE
	Cu	Pb	Zn		
Vallecitos (Argentina)	1.4 (1.1 - 1.9/0.3)	2.2 (1.5 - 3.7/0.8)	14.2 (3.7 - 27.1/7.7)	Semi-remote	This study
Punta de Vacas (Argentina)	5.3 (0.8 - 12.9/4.4)	2.6 (0.7 - 4.7/1.4)	24.0 (4.1 - 58.0/18.2)	Semi-remote	This study
Cerro Colorado (Chile)	33.3 (4.97 - 386.7)	19.5 (2.4 - 74.9)	29.6 (10.1 - 114.5)	Semi-remote	(4)
Nevados de Chillán (Chile)	3.6 (1.1 - 17.8)	9.2 (1.9 - 13.6)	14.9 (13.2 - 16.6)	Semi-remote	(4)
Dolomites (Italy)	0.7 (0.01-29.1/1.9)	1.8 (0.02-33.7/2.9)	3.5 (0.002-63.1/6.2)	Semi-remote	(7)
French Alps	0.3 (0.08-29.1)	0.9 (0.02-33.7)	1.7 (0.02-63.1)	Semi-remote	(15)
Tibbitt to Contwoyto Road (Canada)	0.124 (<LD-0.227)	0.142 (0.073 - 0.229)	0.012(<LD - 0.02)	Remote	(16)
Mt. Everest (Tibet)	0.343	0.005	2.03	Remote	(17)
Poznań (Poland)	2.03 (<LD - 13.7)	4.93 (0.42 - 34.1)	13.2 (<LD - 31.0)	Urban	(56)
Ostrava (Czech Republic)	1.18 (0.45 - 5.42)	2.97 (0.72 - 24.3)	11.9 (2.96 - 169)	Urban	(11)

This temporal variability of the atmosphere composition was evidenced in the chemical composition of the snow<sup>11</sup>. If the instantaneous value of the concentration of metals in the fresh snow reaching the ground is determined, it could be noticed that at the beginning of the event, these levels would be relatively high, since they correspond to an atmosphere highly loaded with metals and particulate matter. As the snowing event progressed, the atmospheric concentration of metals decreased due to the efficient scavenging, which implied that the metal concentration in the snow decreased along with the snowing event<sup>57,58</sup>. If the total mass of snow deposited during an event is considered, the greater the amount of precipitation, the greater the total mass of snow deposition would be. However, the temporal gradient and the instantaneous value of metal concentrations would decrease with greater snow amounts. Additionally, when the snowfalls become very intense the road traffic is suspended in the mountain area of the RN7 by the National Authorities. This produces a decrease in the emissions of one of the main metal emission sources close to Punta de Vacas. The results achieved showed that the variation of metal concentrations due to the

amount of precipitated snow is higher in Punta de Vacas, which is nearest RN 7, than in Vallecitos.

Based on the achieved results, both variables were aggregated ( $C_{ijk}$  and  $S_{jk}$ ) in one ( $P_{ijk}$ ), defined as the product  $C_{ijk} \times S_{jk}$  (see Fig. 3). This type of variable association was used in a study of pollutants in snow to obtain a general representation of processes that influence the spatial variability of the concentrations obtained, when these depend on more than one factor, allowing some cause-effect relations to be established<sup>6</sup>. From this new variable, the null hypothesis ( $H_0$ : no differences between the two sites) was tested considering a significance level  $\alpha = 0.05$ . There were no outliers and the data were normally distributed for each group, as assessed by boxplot and the Shapiro-Wilk test ( $p < 0.05$ ). However, homogeneity of variances was violated, as assessed by Levene's Test of Homogeneity of Variance ( $p < 0.01$ ). For this reason, a Welch's ANOVA test (instead of a one-factor ANOVA test) was run, showing statistically significant differences for  $P_{ijk}$  between different sites (PV and VLL): Welch's  $F_{Cu}(1, 3.01) = 18.00$ ,  $p < 0.005$ ; Welch's  $F_{Pb}(1, 6.09) = 36.00$ ,  $p < 0.001$  and Welch's  $F_{Zn}(1, 6.05) = 23.00$ ,  $p < 0.003$ . It was found that Punta de Vacas displayed greater values of  $P_{ijk}$  for those analyzed metals.



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**Table 3.** Correlation coefficient (*r*) calculated for the average concentration *C<sub>ijk</sub>* and fallen snow in the 30 days prior to sampling *S<sub>jk</sub>* (*i* = metal, *j* = year, *k* = site)

Year	Vallecitos			Punta de Vacas				
	fallen snow <i>S<sub>jk</sub></i> * ( $\text{kg m}^{-2} \text{s}^{-1}$ )	Cu ( $\mu\text{g L}^{-1}$ )	Pb ( $\mu\text{g L}^{-1}$ )	Zn ( $\mu\text{g L}^{-1}$ )	fallen snow <i>S<sub>jk</sub></i> * ( $\text{kg m}^{-2} \text{s}^{-1}$ )	Cu ( $\mu\text{g L}^{-1}$ )	Pb ( $\mu\text{g L}^{-1}$ )	Zn ( $\mu\text{g L}^{-1}$ )
2014	7.3E-07	1.6	3.0	20.0	4.3E-05	10.3	4.1	45.0
2015	5.9E-06	1.5	2.2	17.1	9.6E-05	1.4	1.4	9.4
2016	9.3E-06	1.3	1.6	8.4	6.9E-05	6.1	3.1	25.0
<i>r</i>		-0.9935	-0.9988	-0.9221		-0.9997	-0.9997	-0.9967

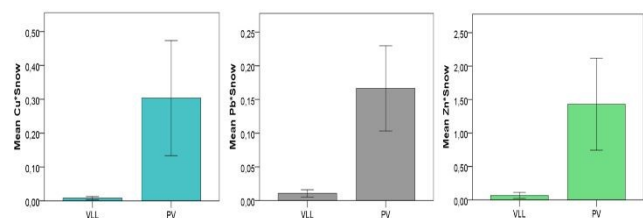
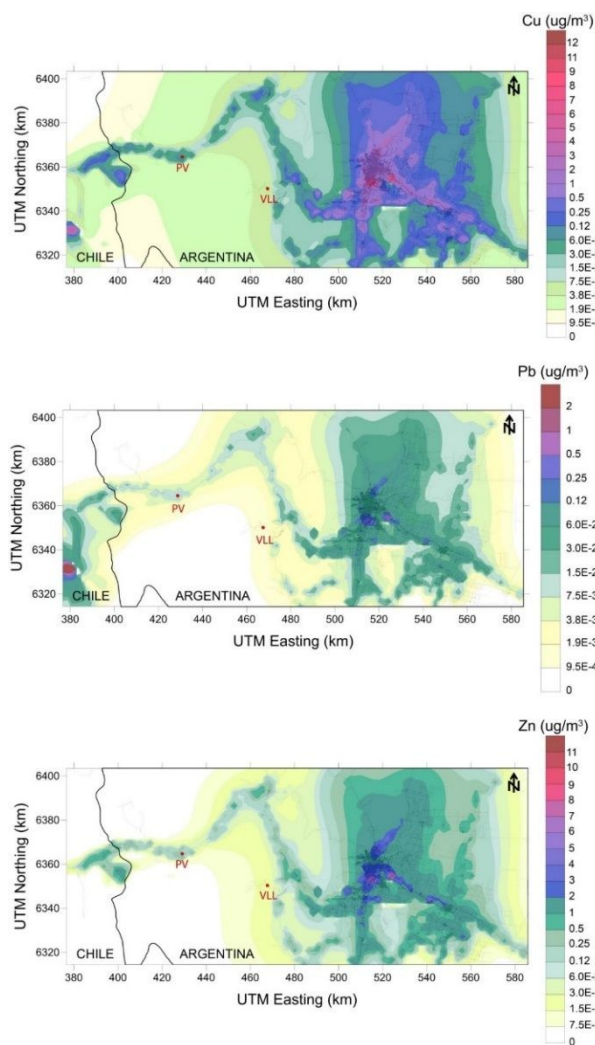


Fig 3. Comparison of the mean values of the variable *P<sub>ijk</sub>*, in [ $\mu\text{g.L}^{-1}$ ]. ( $\text{g.m}^{-2}.\text{s}^{-1}$ ), obtained in Vallecitos (VLL) and Punta de Vacas (PV), for Cu (left), Pb (center) and Zn (right). The error bars corresponding to a 95% confidence level are presented.

**Atmospheric Dispersion Model: Spatial Patterns and Source ApPOINTment**

The maps of metal concentrations generated from the simulations carried out with the CALPUFF model (Fig. 4) showed a strong horizontal gradient, where the highest concentrations occurred around the emission sources. The mountainous terrain features towards the west did not allow the dispersion of pollutants emitted in urban center and inroads by vehicular traffic, generating a kind of canyon, where the substances were trapped. At the lower left side of Cu and Pb maps, it was possible to observe the relevance of the copper mines activities on the Chilean side. Most noticeably, the mountain range exerts a physical barrier that did not allow a high flow of metals to the east in this area.

The implementation of the model allowed an analysis about the relative contribution of the different sources to the air quality in the study area, which was of special relevance when evaluating whether the levels of pollutants present in the



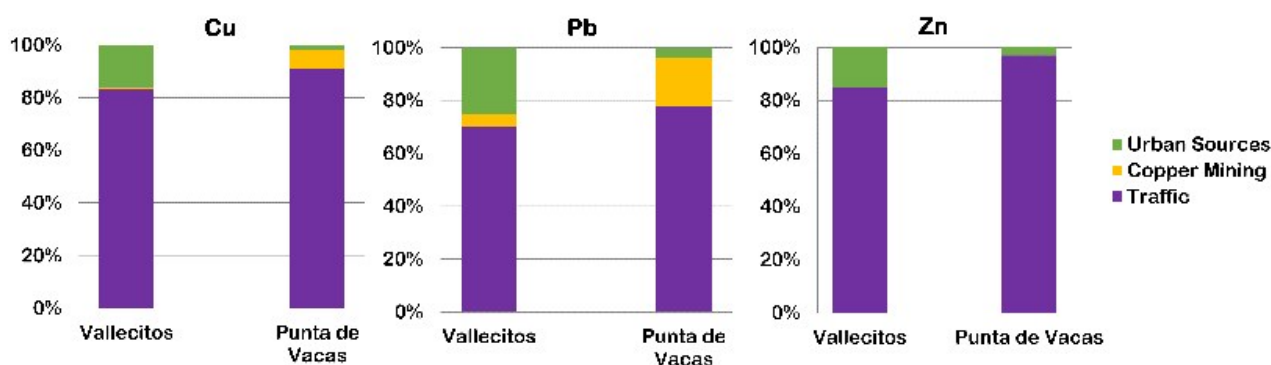
atmosphere were due to local emissions or were transported from the urban center. Fig. 5 shows the rate contribution of

Fig 4. Atmospheric concentrations of metals estimated with CALPUFF ( $\mu\text{g m}^{-3}$ ). 30-days average

each source to the atmospheric concentrations of simulated metals in the studied sites. The emission sources were grouped into four main categories considering magnitude of the emissions and distance from the sampling points: urban sources, including industries and urban solid waste disposal sites; copper mining, which comprises the two mines located on the western slope of the mountain range; and finally, vehicular traffic that is subdivided into two categories: urban traffic and traffic of RN 7, which represents the traffic in the mountain area. The contributions were evaluated from individual runs of the CALPUFF model for each category source under the same meteorological conditions, on the same domain, for the same period. For both sites, traffic in RN 7 was presented as the source that contributes the most to the emission of all metals (70% - 80%, 60% - 65%, 62% - 87%, for Cu, Pb and Zn, in Vallecitos - Punta de Vacas respectively). However, the source contribution to total atmospheric levels in each site presents some differences. The contribution of urban sources to total concentrations was higher in Vallecitos for the three metals (16% - 2%, 25% - 4%, 15% - 3%, for Cu, Pb and Zn, in Vallecitos - Punta de Vacas respectively), because this point was nearest to the urban center of Mendoza and it was not as exposed to vehicular emissions as it was the case of Punta de Vacas. In addition, the prevailing wind direction in the area (Fig.2) favored the transport of substances generated in the city to the northwest, away from the mountain range. With respect to mining activities, it was observed that this source was more relevant (1% - 7%, 5% - 18%, for Cu and Pb in Vallecitos - Punta de Vacas respectively, this activity does not emit Zn) in Punta de Vacas, mainly due to the proximity of this

site and the mine activity. It should be noted that although the results showed in Fig. 5 agreed with the calculated emissions (Table 1), this analysis highlights the effect exerted by the topography. Although the emissions from mining are significantly greater than the rest for the cases of Cu and Pb, the atmospheric dispersion is limited by the fact that mines are located east of a major topographical obstacle (Fig.1). This did not allow the metals emitted there to be transported to the other side of the terrain elevation.

The atmospheric levels obtained with the CALPUFF model were qualitatively compared with the metal concentrations determined in snow samples considering that the different nature of both variables did not allow a direct quantitative comparison. The content of pollutants in the snow is considered to come from the atmosphere and it has been captured by precipitation scavenging and by subsequent dry deposition. In this sense, the spatial patterns of both variables are expected to be similar. Fig. 6 shows this comparison. The model could predict the geographical distribution of metals in the studied area since the calculated concentrations were higher in Punta de Vacas than in Vallecitos in all cases. When the air values predicted by the model for each metal were analyzed, it was noted that they show a greater gradient than the concentrations found in the snow. This may be due to some physicochemical characteristics of these substances, such as the scavenging efficiency and the solubility, which would affect the removal and deposition<sup>33</sup>, producing a modulation in the amounts of metals captured by the snow. Finally, ability of the dispersion model to reflect the levels of trace metals found in the snow could be useful in the proper design of monitoring network, considering the time and cost that sampling campaigns take, and the conclusions that are intended to be made from the analysis of the obtained data.



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Fig 5. Percentage contribution of each source to the total simulated atmospheric levels of metals in the studied sites

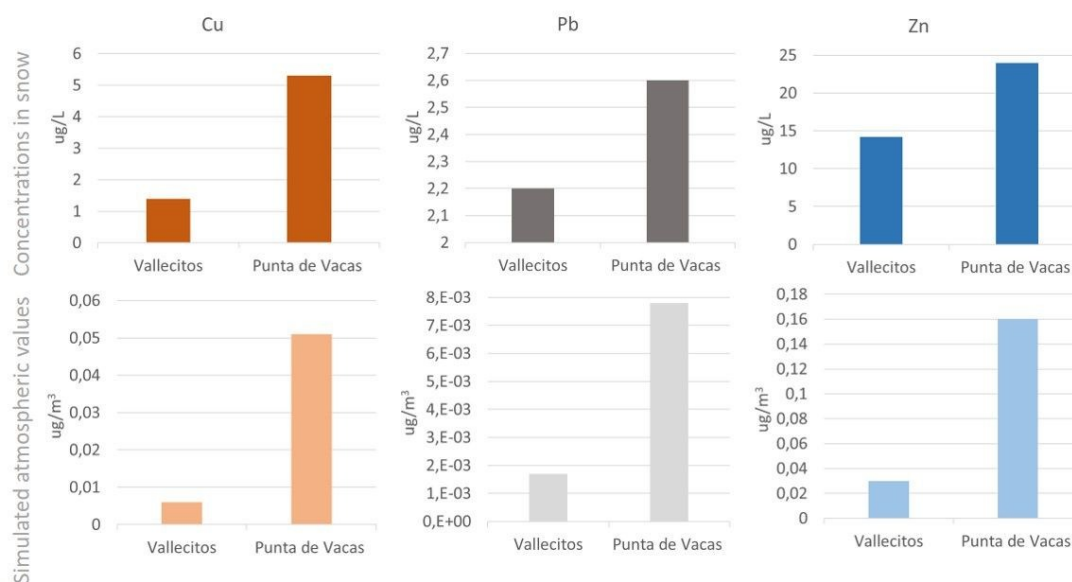


Fig 6. Comparison between metal concentrations found in the snow (first row) and simulated atmospheric levels (second row), for each sampling site.

## Conclusions

The present work describes a combined method to evaluate the air quality of the Central Andes. The use of metal determination in snow constituted the first study of its type in this Argentine region and evaluated snow as an indicator of the atmospheric concentrations of these substances, considering its ability to capture air pollutants. However, these concentrations were affected by other factors, such as meteorological conditions, and they also had limitations regarding the spatial and temporal resolution. Furthermore, the statements about the sources of the found levels were only conjectural and they require more evidence to be accepted as valid. To offset these drawbacks, the presented methodology proposes to complement these measurements with the implementation of an atmospheric dispersion model that provides greater spatial and temporal resolution and allows the performance of certain analyses regarding sources appointment and distribution patterns in relation to meteorological conditions and terrain features.

The results obtained in the measurements are consistent with the determinations obtained in the Chilean Slopes of the study area. Likewise, the source attribution mentioned in that work is like that presented here. When comparing the levels

found in the snow samples of this study with data from remote and urban sites in other parts of the world, it was found that, in this case, the order of magnitude corresponds to urban sites, evidencing the influence of local sources. The metal concentrations measured in this work were greater than those determined in places of comparable anthropic presence, such as the Italian Dolomites or the French Alps.

Although the metal concentrations in the snow did not show a clear spatial trend on their own, a strong negative correlation was found between this data and the amount of snow precipitated at the different points, indicating an important influence of meteorology on the values found. When these variables were associated by the product between both, a statistically significant difference was observed between the sampled sites, resulting Punta de Vacas the more affected area, and therefore, establishing the existence of a spatial pattern.

Furthermore, the implementation of the model, as well as the levels found in the snow, that have an order of magnitude that does not correspond to background sites affected only by atmospheric transport, but with highly exposed urban locations, suggest that metals in the Andean cryosphere are largely derived from local sources (vehicular traffic and mining), leaving atmospheric transport of metals from nearby urban areas in the background. Another aspect that could be

evaluated from the modeling is that dispersion and deposition are not only influenced by the sources, but also by the complex topography of the study area, that clearly defines the affected areas. This creates a challenge from the modeling point of view and leaves the door open to continue this line of research. It should be noted that the concentration gradient detected in the measurements of metals in the snow is also observed in the simulations, which indicates that the modeling system used is appropriate to predict the impact of anthropogenic emissions in the Central Andes and also it could be useful in the proper design of monitoring networks.

### Conflicts of interest

The named authors declare that they have no conflict of interest, financial or otherwise related with this investigation and the content presented in this manuscript.

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