# Importance of dew as a remover of atmospheric cations and anions in an urban area of Santiago, Chile

*MARÍA A. RUBIO*[1*]*, PATRICIA BUSTAMANTE*[1]*, EDINSON ALDAIR GAMEZ*[1] *,*
*ERNESTO GRAMSCH L.*[2]

*1 Chemist and Biology Faculty, Universidad de Santiago de Chile, Chile. A. of Libertador Bernardo O'Higgins3 363, Santiago, Chile.*
*2. Physics Department. Universidad de Santiago de Chile. Avda. Ecuador 3493, Santiago, Chile.*

## *ABSTRACT*

In an urban commune of Santiago, Chile, a monitoring campaign for dew and $PM_{10}$ atmospheric particulate matter was implemented during 2022. The pH, conductivity, cation and anion concentrations of dew water, and the water-soluble fraction of $PM_{10}$, were analyzed. In the water-soluble fraction of PM10, the average cation concentrations were: 4.19 $\mu gm^{3}$ for ammonia; 1.40 $\mu gm^{-3}$ for calcium; 0.46 $\mu gm^{-3}$ for potassium; 0.36 $\mu gm^{-3}$ for sodium; and 0.17 $\mu gm^{-3}$ for magnesium. In a decreasing order, concentrations were: NH4 > Ca > K > Na > Mg > Zn > Ba > Cu > Mn > Al > As > V. Among anions, the nitrate ion showed concentrations within the 4.49 to 20.09 $\mu gm^{-3}$ range. The concentration of the carbonate ion ranged between 0 and 6.7 $\mu gm^{-3}$; the sulphate ion ranged from 2.65 to 6.13 $\mu gm^{-3}$; the chloride ion from 2.21 to 3.43 $\mu gm^{-3}$ M; the phosphate ion varied between 2.08 and 2.33 $\mu gm^{-3}$; the nitrite ion between 1.21 and 1.33 $\mu gm^{-3}$; and the fluoride ion between 0.14 and 0.18. Simultaneously, 60 water dew events were collected during working days, with a total volume of 6465 mL, and 20 events on weekends. This volume was similar to the total level of rainfall in Santiago during 2022 (8217mL). In the dew water, the mean pH was 7.47, and the mean concentrations were: ammonia:13300 $\mu gL^{-1}$, calcium: 12040 $\mu gL^{-1}$, potassium: 2600 $\mu gL^{-1}$, sodium 1530 µgL-1 , magnesium: 669 $\mu gL^{-1}$, zinc: 65 $\mu gL^{-1}$, manganese: 50 $\mu gL^{-1}$, and copper:19 $\mu gL^{-1}$. Among anions, mean concentration values were: chlorides: 8720 $\mu gL^{-1}$ ; sulphates: 28938 $\mu gL^{-1}$; nitrates: 32538 $\mu gL^{-1}$: nitrites: 7556 µgL-1; and carbonates: 14540 µgL-1. Simple linear correlations between cations and anions present in dew water and $PM_{10}$ showed values of 0.788 and 0.81, indicating a key removing role from the dew water in this city. In Santiago, dew water has a cleansing or removal effect as important as that of rain water.

Keywords: *Dew, dew water-soluble ions, Santiago de Chile, $PM_{10}$.*

## INTRODUCTION

Weather and topographic conditions, as well as high population density, make Santiago, Chile (South latitude 32º55' and 34º19', and West longitude 69°47' and 71°43') prone to the occurrence of high pollution episodes caused by photochemical factors and particulate matter [1]

Pollution from particulate matter such as $MP_{10}$, $MP_{2.5}$ and ultrafine particles predominates in the period of high atmospheric stability, and when the atmosphere mixed layer is at low levels, *i.e.*, during the months of Fall and Winter, and especially during nighttime [2,3,4] The current emissions inventory for Santiago [5] indicates that the main sources associated with $PM_{10}$ and $PM_{2.5}$ are transportation and residential heating. Residential sources are responsible for 33% of $PM_{10}$, and 35% of $PM_{2.5.}$ Mobile sources or transportation produce 44% of PM10, and 41% of $PM_{2.5.}$ One of the residential sources that stands out as highly polluting is the combustion of firewood, which has emission percentages around 95% for $PM_{10}$ and $PM_{2.5.}$ Santiago de Chile is considered one of the most polluted cities in America due to the presence of high levels of particulate matter ($MP_{10}$ and $PM_{2.5}$), and gases such as carbon monoxide, volatile organic hydrocarbons, and nitrogen oxides, which exceed the Chilean air quality standard [1].

Despite the regulations on atmospheric pollution control, in 2022, Santiago launched several environmental alerts and pre-

**Corresponding author: maria.rubio@usach.cl*

emergency states. Pollution has been present for years, but according to Gramsch, et al.,[2], $PM_{10}$ levels have decreased by 35.4% from 1988 to 2018. However, in 2022, it surpassed the current Chilean standard of 50 $ugm^{-3}$.

In Santiago de Chile, atmospheric pollutants should be removed by winds and rainfall associated with cold fronts from the West. However, the winds are too weak and rainfall is occasional and scarce [2]. In a normal year, rainfall in Santiago averages 300 mm and is concentrated between June and July. [6], while water dew events occur from March to September.

Dew is formed when a mass of air reaches the temperature called the “dew point” on a surface. At this temperature, water vapor starts to condense on the surfaces, producing dew [7]. In Santiago, the efficiency of dew formation is at its maximum at dawn, between 6 a.m. and 8 a.m. After dawn (sunrise), the temperature increases and dew water evaporates [8], Dew is formed by drops of water with a radius between 0.1 and 1 mm. It slowly accumulates and reaches its maximum at the end of the night. Sunlight causes it to evaporate rapidly, and pollutants dissolved in drops and adsorbed by the surface are returned to the atmosphere.

Dew formation alters the properties of the surface, which can contribute to efficiency in the capture of pollutants that are both gaseous and associated with particulate matter. The composition of dew water will be defined by the characteristics of the atmosphere during its formation and by the capture of pollutants during its time on the surface where it is deposited [9,10]. Dew is widely used by plants and small animals, and in arid zones, it contributes to the survival of these organisms. Currently, its interesting potential as an alternative source of drinking water is under study. In Chile, some studies have been carried out, among which the work by Carvajal et al. [11], however, this topic has not been a priority in Santiago de Chile. The possible uses of dew water often require the analysis of its physicochemical quality [12]. Its chemical composition shows high levels of atmospheric pollutants compared with rain water. The quantity of water incorporated into dew is the excess of water, in a column, that during the night has diffused to the surface. It is expected that pollutants in these columns that are very water-soluble or captured by humid surfaces with high efficiency are incorporated quantitatively to dew water.

Therefore, their concentration in dew water will be the value of the pollutant concentration present in the entire air column that diffused onto the surface. In addition, this could remove the thick particulate matter that is close to a drop, or that is deposited on surfaces by gravity [13]. In turn, substances incorporated to dew water can return to the atmosphere during the first hours of the morning, which would cause an increase in pollution during this period after evaporation. In some cities from India and China, the values of ammonium, magnesium, and sulfates are very high as well [14.15] determined the chemical composition of dew water, rainfall, and mist, with significant differences among them. In the Chinese city of Changchun, deposited metals have both anthropogenic and natural origins; this confirms that dew water is influenced by local sources and by transportation [16]. In this city, dew water exhibits high values of light and heavy metals, associated with the soils and environmental dust; however, source assignation is multiple, with the influence of particulate matter emitted by vehicles, carbon combustion, and the earth’s crust.

Since 1998, several studies have been conducted in Santiago. [17] These demonstrated that dew is basic and has high ion concentrations, especially of nitrites. Nitrite concentration in dew water is strongly correlated with pH, having a more favourable distribution when pH is more basic. Likewise, peroxides and heavy metals could indicate the presence of significant oxidation chemical reactions in this water. In addition, the presence of compounds derived from phenol would imply whether absorption from the gaseous phase or the transformation of compounds during deposition.

Given the significance of dew composition as an indicator of the characteristics of the atmosphere, it is of interest to find its chemical composition in terms of anion and cation concentration levels, as well as its relationship with the ions present in the labile fraction of atmospheric particulate matter. The objective of this study is not only showing the chemical characteristics of dew water but also contributing to the knowledge about the role of dew as a pollutant removal and/ or source.

The values of the soluble ions present in the atmospheric particulate matter, $PM_{10}$, and the ions removed by dew water in a completely urban area are compared. Additionally, the variation of some types could be related to the most used heating sources in Santiago. This could be important data about source control. The degree of concentration of some ions will also inform us about the quality of the water deposited on exposed surfaces such as house roofs, vegetation, and vehicle bodywork, which would help people to take precautions to prevent deterioration.

**Figure 1.** Santiago of Chile and “Estación Central.”

## EXPERIMENT

### Sampling location

Santiago de Chile has a total surface of 15,403 km$^2$. It is divided into 6 zones: Chacabuco, Cordillera, Maipo, Melipilla, Talagante, and Central Santiago. The urban surface of Santiago is 834 km$^2$, and is located at the centre of the region, as shown in Figure 1.

The samples of $PM_{10}$ were collected from April 18 to August 05, 2022, in the Usach weather station, at the Physics Department of Universidad de Santiago, which is located in the commune of "Estación Central ", 33.45_S, 70.68_W, 528 m. above sea level. $PM_{10}$ sampling was conducted for 48 hours.

**Figure 2.** Relief of Santiago, Chile Basin. (National environment Center, Chile).

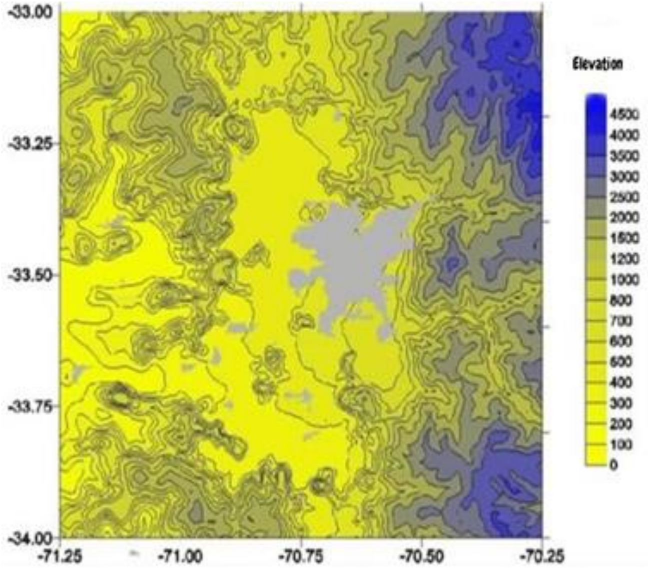
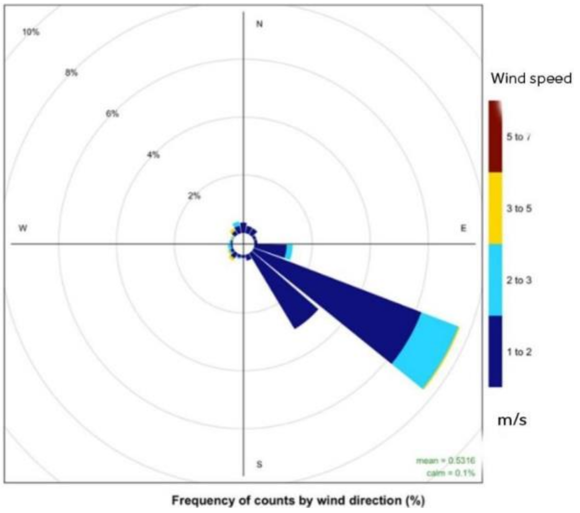


**Figure 3.** Wind rose measured at the O'Higgins Park weather station during the months of April to August 2022.



Dew water was collected at the campus of the Universidad de Santiago de Chile, which is located in the commune of Central Station in Santiago. Samplers were located on the roof of the Chemistry Faculty at an average height of 5 meters, and kept away from pollutant sources. Dew water collection was conducted between March and September 2022. Weather data recorded from April to August show a wind speed range between 0 and 3.5 ms$^{-1}$, with a constant 2 ms$^{-1}$ during sampling time. These speeds are low and prevent the adequate dispersion of pollutants.

The wind pattern in Santiago de Chile has a valley-mountain behavior with speeds that are generally low. The predominant wind in the city occurs during the afternoon (11-19 hrs.) in a south-east direction, as shown in the wind roses of Figure 3. It can be seen that during the afternoon, the wind direction is the same for all stations and has little dispersion. During these hours, the speed is also higher than during the night or early morning. There is also a very clear difference between day and night winds.

$PM_{10}$ samples were collected through a gravimetric method using a Harvard impactor; Teflon filters of 37 mm in diameter with 0.2 µm pore size were used. Teflon filters were conditioned before and after the sampling of a chamber with controlled humidity and temperature. Relative humidity varied between 20% and 45% in a controlled environment, while temperature oscillated between 15°C and 30°C. Each filter was weighed before and after sampling using a ± 0.01mg high precision analytical scale.

Dew water was collected manually on clean Teflon film (1m$^2$ x 0.4 mm) supported on insulating foam folded in the middle at a 90º angle, and arranged with a funnel and a polyethylene bottle. Samples were collected from 19:00 hours until 08:00 hours the following morning from April through August 2016, 2017, 2018, 2019, and 2022. Immediately after collection, samples were taken to the laboratory, where their acidity, conductivity, and volume were measured. The samples were then filtered and kept refrigerated at 5ºC until analysis.

Chemical analyses pH and conductivity were measured using a Hanna 213 pH meter. The identification and quantification of the metallic elements of interest in the labile fraction of PM10 and in dew water was conducted through inductively coupled plasma optical emission spectrometry ICP (Perkin Elmer, Optima 2000) using Certipur Merck, and multi elements IV and VII for their quantification. The analysis of anions such as chloride, sulphate, nitrate, nitrite, and phosphate was performed with Ionic Chromatography (Dionex Aquion, Dionex Integrion, and Thermo L.D. were 1.0 ppb). Ammonium was measured through UV spectrophotometry by the complex, indophenol blue method (Limit detection of 0.04ppm). For quantification, grade 1 calibration standards and certified samples, TMDA-51.3 and TMDA-53.3 (Environmental Canada), were used. Element concentration calculation in total $PM_{10}$ was conducted through X- ray fluorescence (XRF, Thermo Fisher Scientific XL3t

950) with an RX analyzer equipped with internal calibration and quantification patterns; namely, 44812.4826 Test, All Geo analysis Certificates. Filters were analyzed in 4 points, thereby achieving reading repetitiveness. No variation was observed in the readings due to sample homogeneity. Likewise, reading variations attributed to thickness (matrix effect) were not found, as the thickness of the solid material was of micrometer order.

$PM_{10}$ filters were subject to aqueous extraction. Filters were introduced into 15ml falcon tubes, to which 15 ml of MilliQ grade ultrapure water were added and sonicated at 35 kHz for 15 minutes. The resulting solution was filtered using hydrophilic filters with a 0.22 µm pore diameter. Subsequently, samples were refrigerated until their chemical analysis.

## RESULTS AND DISCUSSION

### $PM_{10}$ mass concentrations

In Santiago, Chile, $PM_{10}$ concentrations have decreased continuously since 1998, but the trend has slowed down since 2010. The $PM_{10}$ yearly average of the 9 stations from the SINCA Air Pollution Network inside the city of Santiago is continuously monitored. [5] This network is used by the authority to monitor several air pollutants and meteorological variables. $PM_{10}$ is measured using TEOM monitors (Rupprecht & Patachnick, Albany, NY USA, and Thermo Fisher Scientific, Waltham, MA USA). From 2007 (70.3µg $m^{-3}$) to 2010 (63.0µg $m^{-3}$) there was a slight decrease in $PM_{10}$; however, this trend did not continue, and $PM_{10}$ has levelled out since 2010.

During these years, significant measures have been implemented to reduce air pollution from public transport, which include the restructuring of the public transport system, the renewal of the vehicle fleet, and the shortening of circulation routes. These measures were moderately unpopular, leading to a slight increase of private vehicles, with around 6% more cars in 2009 compared to 2003 [18]. This result agrees partly with the report of the Public Policies Society of Chile, which notes that "the annual evolution of PM10 between 1997 and 2010 shows a decreasing but moderate trend, indicating that air quality has improved steadily over the past 15 years, with an improvement in 2010 2017). [17].

When comparing the PM10 concentrations of the last 6 years, from 2017 to 2022, during the same period of study in the "Parque O'Higgins" weather station, close to the Usach weather station, concentration values reached 74.00 µg$m^{-3}$ in 2017, and 78.55 µg$m^{-3}$ in 2020. A decrease in PM10 was observed in 2020 compared to 2017-2019; however, this trend did not continue and PM10 increased in 2021 (81.61 µg$m^{-3}$) and 2022 (86.41 µg$m^{-3}$). Table 1 shows the monthly average of PM10 in µg$m^{-3}$ for the "Parque O'Higgins" weather station, measured from April to August in the 2017-2022 period.

**Figure 4.** Lineal correlation Anions values in dew and soluble fraction of $PM_{10}$

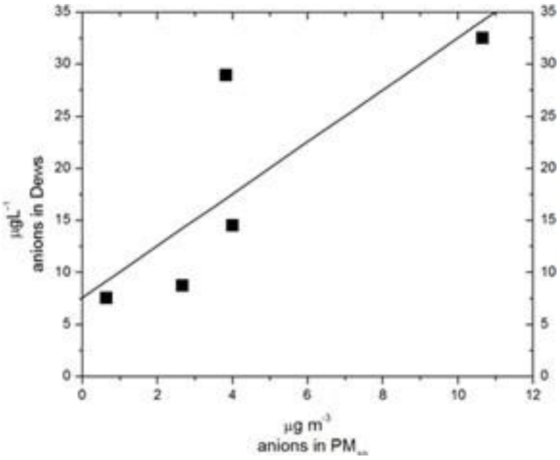


**Table 1.** Monthly $PM_{10}$ average in the Parque O'Higgins weather station. (*mma.gob.cl.*2022).

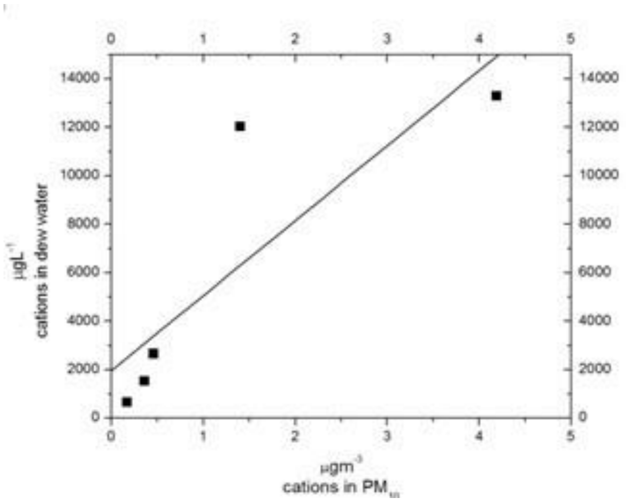
| year | $PM_{10}$ maximun | $PM_{10}$ minimum | Average value |
|---|---|---|---|
| 2017 | 174 | 10 | 74 |
| 2018 | 175 | 8 | 81 |
| 2019 | 211 | 16 | 97 |
| 2020 | 151 | 15 | 79 |
| 2021 | 173 | 15 | 82 |
| 2022 | 186 | 11 | 86 |

**Table 2.** Average concentration (µg/$m^3$) and standard deviation of the metallic elements and ammonia present in the soluble fraction of $PM_{10}$

| | $NH_4^+$ | Ca | K | Na | Mg | Zn | Ba | Cu | Mn | Al | As | V |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Mean values | 4.19 | 1.40 | 0.46 | 0.36 | 0.17 | 0.04 | 0.03 | 0.03 | 0.02 | 0.02 | 0.01 | 0.01 |
| Standard Deviation | 2.45 | 0.35 | 0.22 | 0.35 | 0.16 | 0.03 | 0.01 | 0.01 | 0.01 | 0.01 | 0.005 | 0.005 |

Low $PM_{10}$ levels could be related to the COVID-19 pandemic, as during most of the pandemic, there were lockdowns, quarantines, the halt of some industries, and low vehicle cir-

**Figure 5.** Lineal Correlation cations values in dew and soluble fraction of $PM_{10}$



culation, according to a report by the Ministry of Environment. According to Montes (2021), winter 2020 in Santiago recorded the best air quality of the last 30 years. However, this promising scenario of 2021 and 2022 started to slowly fade as communes moved forward in the "Step by Step Plan" ("Plan Paso a Paso") launched by the Ministry of Health, and communes finished their lockdowns. This brought back the environmental alerts and pre emergency states and therefore led to increases in $PM_{10}$ levels.

### Soluble chemical species in $PM_{10}$

Table 2 shows the concentrations of metallic elements (cations) and ammonia present in the soluble fraction of $PM_{10}$ from 2022. Average concentration values of the quantified metallic elements and ammonia and their standard deviation are displayed. The values are expressed in $\mu gm^{-3}$. Table 2 shows that $NH_4^+$ has the highest concentration in the soluble fraction of $PM_{10}$, with a mean value of 4.19 $\mu gm^{-3}$, followed by Ca with a mean value of 1.4 $\mu gm^{-3}$, K with a mean value of 0.46 $\mu gm^{-3}$, Na with a mean value of 0.36 19 $\mu gm^{-3}$, and Mg with a mean value of 0.17 $\mu gm^{-3}$; these elements being the most soluble compared to the other elements under study. The concentrations are the following in decreasing order: $NH_4^+$> Ca> K> Na> Mg> Zn> Ba> Cu> Mn> Al> As> V. It is noteworthy that metallic elements like Ca, which have high content in the labile fraction and clearly represent the composition of particles from the soil, reveal a significant natural contribution of anthropogenic emissions; in turn, K is related to an anthropogenic origin as it derives mainly from biomass combustion. Lastly, the main contribution of PM10 concentration originates from ammonia, which should mostly come from emissions of ammonia into the atmosphere. The less soluble elements are Zn, Ba, Cu, Mn, Al, As, and V.

The metallic elements Ni, Pb, and Fe were not quantifiable, as they are under the detection limit of the technique used. Studies conducted in Santiago on the soluble fraction of $PM_{10}$ during 2006, 2008, 2009, and 2010 [18] found that the $NH_4^+$ cation was the most labile compared to the other cations under study. The

**Table 3.** Mean concentration ($\mu gm^{-3}$) and standard deviation of the anion species present in the soluble fraction of $PM_{10}$.

| | $NO_3^{-1}$ | $CO_3^{-2}$ | $SO_4^{-2}$ | $Cl^-$ | $HPO_4^{-2}$ | $NO_2^-$ | $F^-$ |
|---|---|---|---|---|---|---|---|
| Mean values | 10.65 | 4.0 | 3.82 | 2.66 | 0.77 | 0.64 | 0.15 |
| Standard Deviation | 4.4 | 1.8 | 0.97 | 0.28 | 0.08 | 0.05 | 0.01 |

**Table 4.** Standardized concentrations of soluble ions present in $PM_{10}$ expressed in $\mu Eqm^{-3}$.

| ion | $\mu Eq\ m^{-3}$ | ion | $\mu Eqm^{-3}$ |
|---|---|---|---|
| $NO_3^{-1}$ | 0.17 | $NH_4$ | 0.23 |
| $SO_4^{-2}$ | 0.08 | Ca | 0.07 |
| $Cl^{-1}$ | 0.08 | K | 0.012 |
| $HPO_4^{-2}$ | 0.05 | Na | 0.02 |
| $NO_2^{-1}$ | 0.03 | Mg | 0.01 |
| $CO_3^{-2}$ | 0.10 | --- | --- |
| **Total amount** | **0.43** | **Total amount** | **0.35** |

**Table 5.** Water volume, pH, conductivity and number of dew events and rains for Santiago in 2022.

| Event | Total volume mL | Mean volume mL | pH | Conductivity $Scm^{-1}$ | Number of events |
|---|---|---|---|---|---|
| Dew- weekdays | 6465 | 110 | 7.47 | 354 | 60 |
| Dew-weekends | 956 | 106 | 7.29 | 706 | 9 |
| Rain | 8217 | 547 | 6.22 | 31 | 15 |

**Table 6.** Weighed mean values of metallic elements and ammonium present in dew water. Values expressed in µgL-1 and µEqL$^{-1}$

| | $NH_4^+$ | Ca | K | Na | Mg | Zn | Mn | Cu | Total amount |
|---|---|---|---|---|---|---|---|---|---|
| µgL$^{-1}$ | 13300 | 12040 | 2600 | 1530 | 669 | 65 | 50 | 19 | |
| µEqL$^{-1}$ | 643 | 602 | 66 | 66 | 55 | 2 | 6 | 6 | 1432 |

**Table 7.** Weighed mean values of anions present in dew water. Values expressed in µg L$^{-1}$ and µEqL$^{-1}$.

| | $Cl^{-1}$ | $SO_4^{-2}$ | $NO_3^{-1}$ | $NO_2^{-1}$ | $CO_3^{-2}$ | Total amount |
|---|---|---|---|---|---|---|
| µgL$^{-1}$ | 8728 | 28938 | 32538 | 7556 | 14540 | |
| µEqL$^{-1}$ | 246 | 362 | 525 | 164 | 720 | 2017 |

high standard deviation in the $NH_4^+$ cation would be related to sample size. Table 3 shows the mean concentration values of soluble anions measured in $PM_{10}$, and their standard deviation expressed in µgm$^{-3}$.

Table 3 shows that the nitrate ion is the most abundant, with concentrations in the 4.49-20.09 µgm$^{-3}$ range. The carbonate ion is the second most abundant component, ranging from 0 to 6.7 µgm$^{-3}$. The sulphate ion comes third in quantity, in the 2.65-6.13 µgm$^{-3}$ range, followed by the chloride ion, with concentrations ranging from 2.21 to 3.43 µgm$^{-3}$. The phosphate ion exhibited concentrations varying from 2.08 to 2.33 µgm$^{-3}$; the concentration of the nitrite ion oscillated between 1.21 and 1.33 µgm$^{-3}$, and finally, the fluoride ion was found to be in a lower concentration, within the 0.14 to 0.18 µgm$^{-3}$ range.

Similar studies were conducted on the soluble fraction of $PM_{10}$ in different cities around the world. For example, in Delhi, India [19], the solubility trend was the following: Ca > $SO_4^{-2}$ > Cl − > $Na^+$ > $NO_3^-$ > $NH_4^+$ > $NO_2$− > K+ > $Mg^+{}_2$ > $PO_4^{-2}$ > F−. In Ulsan, South Korea [20] , the metal elements Na and Ca and the chloride and nitrate ions were dominant in the soluble fraction of PM10. In Mangalore, India [21], the metallic element Na was found to have the maximum concentration, followed by the chloride anion, the metallic elements Ca and K, and finally the fluoride anion. Studies in Nanjing, China [22,23] reported the metallic elements Al, Ca, Fe, Mg, and Na as the most abundant, as well as the chloride and nitrate anions, calcium, and sulphates in the 2016-2017 period. In the Delta region, China, 24 the sulfate and nitrate anions and the ammonium cation were the dominant fraction of soluble ions. In San Francisco de Campeche, México [24], results showed high levels of the metallic element Na, and the chloride and sulfate anions. Finally, in La Guajira, Colombia [25] the sulfate and chloride anions, the ammonium cation, and the metallic elements Na, Ca, and Mg were the most soluble. Our results are similar to the results of these cities, as most studies report the same solubility order of the ions under study.

According to Rubio et al. [17], the solubility results, in addition to providing data on lability in the respiratory system, may provide some evidence about the possible chemical states of the species, *i.e.*, the types of salts present in particulate matter. Water-soluble Zn is often found in the form of zinc sulfate, while in the residual fraction, it commonly presents as zinc oxide, and is frequently associated with Fe and Mn, carbonates, or aluminates[...]. Likewise, water-soluble Cu is usually found as copper sulphate, while the residual fraction is linked to sulphides and silicates. Urban pollution episodes are characterized, in general, by large amounts of inorganic and organic secondary components. Among the inorganic components, ammonium nitrate is the most abundant and originates mostly from the transformation in the atmosphere of exhaust gases, (NOx into nitrates) from industry and vehicles [26]. According to Doria, C., & Fagundo [25], sulphate and nitrate inorganic ions can be neutralized by $NH_4^+$, formed by gaseous $NH_3$ emitted by the food and agriculture industries. These ions usually exist in the form of $(NH_4)_2SO_4$, $NH_4HSO_4$ and $NH_4NO_3$.

The comparison of the levels of chemical species present in other atmospheres can be similar or totally opposite. The results indicate that the concentration levels of the elements in Santiago are similar to those of other cities; however, it should be noted that suspended dust is a key polluting source in PM10 pollution.

The ionic balance in Table 4 shows that anion and cation concentrations, expressed in µEqm$^{-3}$, are similar but with a slight predominance of anion species over cation species. This could indicate the absence of a cation of the sum of undetected cations. It seems that the soluble fraction corresponds mostly to ammonium nitrate.

## Chemical species in dew water measured in 2022

As mentioned above, dew is a phenomenon present during at least 6 months per year in Santiago. In 2022, dew water samples were collected from March 22 to September 7. However, in days with high PM pollution that led to environmental alerts and pre-emergency states in Santiago, no condensation occurred and dew water was absent. The absence of dew on days of environmental alerts and pre-emergency states in this city indicates that dew water is an effective and crucial remover of $PM_{10}$ in Santiago. During 2022, 9 weekends and 15 rain events

**Table 8.** pH values, conductivity, and annual average cations and anions concentrations in dew water. Years: 1995-2006 and 2010, 2013, 2016, 2017, 2018, 2019 y 2022.

| | **1995-2006** | **2010** | **2013** | **2016** | **2017** | **2018** | **2019** | **2022** |
|---|---|---|---|---|---|---|---|---|
| pH | 6.4 | 7.3 | 7.3 | 7.6 | 7.4 | 7.3 | 7.4 | 7.4 |
| EC (µS cm$^{-1}$) | | | 561 | 247 | 212 | 348 | 399 | 354 |
| $Cl^-$ (mEqL$^{-1}$) | 0.125 | 0.381 | | | 0.4 | 0.22 | 0.19 | 0.246 |
| $SO_4^{2-}$(mEqL$^{-1}$) | 0.363 | 0.385 | 0.16 | 0.666 | 0.16 | 0.106 | 0.13 | 0.362 |
| $NO_3^-$ (mEqL$^{-1}$) | 0.115 | 0.619 | 0.487 | 0.455 | 0.15 | 0.248 | 0.22 | 0.525 |
| $NO_2^-$ (mEqL$^{-1}$) | 0.179 | 0.103 | 0.163 | 0.008 | 0.04 | 0.188 | 0.26 | 0.164 |
| $HPO_4$(mEqL$^{-1}$) | | | | | 0.003 | 0.005 | 0.01 | 0.12 |
| **Total** | **0.782** | **1.488** | **0.81** | **1.129** | **0.753** | **0.767** | **0.81** | **1.417** |
| $Ca^{2+}$ (mEqL$^{-1}$) | 0.411 | 0.809 | 0.306 | 0.628 | 0.365 | 0.408 | 0.532 | 0.602 |
| $Na^+$ (mEqL$^{-1}$) | 0.071 | 0.256 | 0.093 | 0.161 | 0.121 | | 0.112 | 0.066 |
| $Mg^{2+}$(mEqL$^{-1}$) | 0.048 | 0.059 | 0.023 | 0.063 | 0.079 | 0.035 | 0.062 | 0.055 |
| $K^+$ (mEqL$^{-1}$) | 0.057 | 0.052 | 0.03 | 0.197 | 0.099 | 0.117 | 0.072 | 0.066 |
| $NH_4^+$(mEqL$^{-1}$) | 0.417 | 0.179 | 0.18 | 0.107 | 0.263 | 0.129 | 0.089 | 0.643 |
| **Total** | **1.004** | **1.355** | **0.632** | **1.156** | **0.927** | **0.689** | **0.867** | **1.432** |
| $Fe^{3+}$(mEqL$^{-1}$) | | | | | 0.0001 | 0.0005 | 0.0004 | 0.0029 |
| $Cu^{2+}$(mEqL$^{-1}$) | | | | | 0.0006 | 0.0005 | 0.0004 | 0.006 |
| $Mn^{2+}$(mEqL$^{-1}$) | | | | | 0.0012 | 0.005 | 0.0078 | 0.006 |
| $Zn^+$(mEqL$^{-1}$) | | | | | 0.00141 | 0.004 | 0.0009 | 0.002 |

were sampled. Table 5 presents the values of deposited water, pH, dew conductivity, and rainfall for 2022. The quantification results of cation and anion present in dew water, in Table 6 and Table 7 indicate high levels of ammonium, calcium, potassium, nitrates, and sulphates.

As observed in Tables 6 and 7, the micro equivalents of anions and cations are not in full balance. In dew water, carbonate values are high and increase the equivalents of anions over cations. This can be explained by the fact that, in the analysis of metallic cations, they should be under the detection limit of the techniques used. In these measurements, contributions of marine origin are not expected, as Santiago presents scarce variation in the cycle of winds from the coast.

The origin of the chemical species is essentially related to sources from the earth's crust and mobile sources that burn fossil fuels and/or wood. Currently, in Santiago, the combustion of wood is prohibited, and therefore the earth's crust and/or fossil fuel combustion are possible sources. In this way, there is no appropriate marker to elucidate this source. However, the high values of the ammonium ion, which is associated with biological sources, should be noted.

**Removal by dew water**

The following figures attempt to show that the removal of dew water adjusts positively to the purpose of this study. In Santiago, rainfall is very scarce and dew water is an important removal factor. Dew water is measured through one m$^2$. All the urban surface of Santiago could be extrapolated and this calculation would yield a significant source of cations and anions that reach all the surfaces exposed to atmospheric air. The urban surface of Santiago is 834 km$^2$.

The following Figure 3 and Figure 4, show the simple linear correlations between the soluble anions and cations of $PM_{10}$ and the dew water collected during 2022. Figure 3 shows a good correlation ($R_2$=0.78) between cations soluble in $PM_{10}$ and cations present in dew water. This confirms the removing role of dew water in urban Santiago. Likewise, Figure 4 presents the correlation between $PM_{10}$ anions and dew water anions, with $R_2$=0.82

Finally, if we compare the chemical composition of dew water collected in 1995-2006, 2010, 2013, 2016, 2017, and 2019, as shown in Table 8, no linear increasing or decreasing trends are observed, due to the absence of an identified polluting source. It could only be noted that the potassium ion and the sodium ion show a slight downward trend in annual mean values.

Table 8, Chemical composition of cations and anions, pH, EC of collected dew in 1995-2006, 2010, 2013, 2016, 2017, 2018, 2019, and 2022.

## CONCLUSION

A decrease was observed in $PM_{10}$ in 2020 compared to the 2017-2019 period; however, this trend did not continue and $PM_{10}$ increased in 2021 (81.61 µgm$^{-3}$) and 2022 (86.41 µgm$^{-3}$).

Santiago is still a city with high levels of $PM_{10}$.

Rainfall is scarce in Santiago, and therefore dew water would be an important removal factor for pollutants associated with $PM_{10}$. Dew water is measured in m$^2$. If the entire surface of the urban area of Santiago was extrapolated, the calculation would reveal a significant source of cations and anions that reach all the surfaces exposed to atmospheric air. As shown by the simple linear correlations between anions and cations soluble in $PM_{10}$ and dew water collected during 2022, the removing role of the soluble anions and cations of dew water in urban Santiago is confirmed.

## ACKNOWLEDGEMENTS

We are grateful for ANID FONDEQUIP EQY200021 (Universidad del Desarrollo). This work was supported by DICYT USACH Chile under grant N° 022341RC, and VIPO Usach.

## REFERENCES

1. *https://sinca.mma.gob.cl*
2. Gramsch E., Oyola P., Reyes F., Rojas F., Henríquez A., Choong-Min Kang. *Journal of the Air & Waste Management Association*. 71, 6, 721–736. (2021)
3. Langner J., Gidhagen L., Bergström R., Gramsch E., Oyola, P., Reyes, F. Segersson D. and Aguilera C. Aerosol Air Qual. Res. 20: 1111-1126. (2020).
4. Jorquera H, Villalobos A.M, Schauer J. *Atmospheric Pollution Research*, 12 (4) 5059. (2021)
5. *www.sinia.cl*
6. *www.meteochile.cl*
7. Trosseille J., Mongruel A., Royon L., Beysen D. *International Journal of Heat Mass Transfer*.172, 121160. ( 2021)
8. Rubio, M.A., Alvarado, L., Villena, G., Pizarro, J.,F., Lissi, E. The science of the Total Environment. 313, 115-125. (2003)
9. Narhe, R.D. González-Vinas, Beysens. *Appl surface Science* 4930-4933. (2010)
10. Beysens D., Muselli M., Carvajal D. *Atmosphere.* 13,1- 35. (2021)
11. Carvajal D., Mizonzio J-G., Casanga E., Muñoz A., Montecinos S., y Beysens . *J of Water supply. Aqua*. 67,4 (2018).
12. Beysens D., Muselli M., Carvajal D. *Atmosphere* 13, 1- 35. (2021)
13. Xu, M., Zhu, H., Tang, J., Lin, Y. *Adv Meteorol.* 104, 048. (2015).
14. Salam et al., Air Qual. *Atmos Health.* 1. (2017).
15. Xu Yingying , Yunze Zhao, Yan Yi. *Atmospheric Pollution Research* 14, (2023)
16. Shohel M., Simol, H. A., Reid E., Reid J.S., Salam A. *Qual. Atmos. Health, Air* 10: 981-990. (2017)
17. Rubio, M.A., Bustamante, P., Vásquez YJ. *Chil. Chem. Soc.*, 64, N°2. (2019).
18. Moreno F., Gramsch E., Oyola P. and Rubio M.A. *J. Air Waste Manage.* 60, 1410-1421. (2010).
19. Jangirh, R., Ahlawat, S., Arya, R., & Mondal, A. *Environmental Science and Pollution Research.* 29, 17899-17918. (2022).
20. Van Do, T., Vuong, Q., & Deuk, S. *Atmospheric Research,* 247,105145. (2021).
21. Kalaiarasan, G., Mohan, R., & Sethunath, N. *Journal of Environmental Management.*217, 815-824. (2018).
22. Ronkko, T., Jalava, P., Happo, M., & Kasurinen, S. *Science of the Total Environment*. 639, 290-1310. (2018).
23. Liu, X., Zhang, Y.-L., Peng, Y., Xu, L., Zhu, C., Cao, F., Zhai, X., Haque, M. M., Yang, C., Chang, Y., Huang, T., Xu, Z., Bao, M., Zhang, W., Fan, M., and Lee, X Atmos. *Chem. Phys*., 19, 11213–11233. (2019).
24. Fang, D., Huang, W., & Antkiewicz, D. *Environmental Science and Pollution Research*. 26, 12435-12445. (2019).
25. Doria, C., & Fagundo, *J. Revista Colombiana de Química,* vol. 45, núm. 2, 431. 19-29. (2016).
26. Rubio, M.A., Karen Sánchez, Pablo Richter, Jorge Pey, Ernesto Gramsch. *Atmosfera.* 31(4) 373-387. 2018. (2018).