

REGIONAL DISPERSION OF SO₂ IN CENTRAL CHILE: EVOLUTION OF IMPACTS

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ABSTRACT

Chile is one of the leading copper (Cu) exporting countries worldwide. One of the largest copper smelters (Caletones) located 80 km south of Santiago, was responsible for 0.4% of the sulfur emissions released by anthropogenic sources in 2000. The valley of Santiago and neighboring valleys have unique ecosystems and agricultural activities that include a major fraction of the country's wineries. Hence a risk assessment was conducted by applying air quality dispersion modeling tools to a summertime episode that was characterized by a heat wave with record setting high temperatures in central Chile.

The Comprehensive Air Quality Model with Extensions (CAMx) was applied to a nested domain (regional: 240x160 km², urban: 120x80 km²) that includes the greater metro area of Santiago, Chile, and the largest stationary sources at a regional level. Two emission scenarios were developed, for 1997 and 2000, respectively, that included the reductions in emissions effected by the existing regulations in the country. The results show that there is an overestimation of the urban SO₂ emissions for Santiago in 1997, and that there are significant regional reductions in average sulfur dioxide and particulate sulfate impacts, that reach up to 10 ppb and 0.4 µg/m³, respectively, that are conservative lower bounds for the benefits (expressed as annual impacts) that can be ascribed to the emission reductions prompted by local regulations. Despite the significant emission reductions effected, there are still significant zones with summertime average SO₂ concentrations that exceed critical loads according to the European annual standard of 30 ppb. From a mass balance standpoint, more than 90% of the emitted SO₂ and generated sulfate are transported out of the region, leading to a long range transport of pollution in South America. More research needs to be conducted in order to simulate wintertime concentrations, which are likely to be higher than the values estimated for summertime, to better define the regions at more risk.

INTRODUCTION

The air quality in the city of Santiago is one of the worst in Latin America. The most dominant pollutant is particulate matter (PM₁₀, PM_{2.5}) and a number of episodes resulting in a high concentration of PM₁₀ have been recorded in the last fifteen years, with 24 h averages of PM₁₀ and PM_{2.5} as high as 400 and 300 µg/m³, respectively, during fall and winter episodes [1]. Subsidence conditions prevail most of the year, with mild winters with few precipitation and warm, dry spring and summer seasons. Under these conditions photochemical activity is relevant, and the top 8-h ozone values reached 205 and 210 µg/m³ in 2000 and 2001, respectively, within the greater metro area [2]. This poor air quality is primarily caused by the combination of the topographical location of Santiago, the emission densities in the city and adverse meteorological conditions which exist especially in the fall and winter seasons [3,4,5]. It has been shown [6] that in the autumn and winter season the dispersion capacity of

the Santiago basin is only 20-25% of the corresponding summertime values, resulting in a strong seasonality in the meteorological factors that govern air quality levels.

EMISSION INVENTORY SCENARIOS

One of the key inputs in urban scale air quality simulations is to have available emission file inputs with spatial and temporal resolution capable of describing the complex dynamics of air pollution on the urban scale. We have developed an in-house EDB tool name SAIE, Spanish acronym for “Emission Inventory Development and Updating”, based on Fox Pro, that processes the raw information in the original format provided by public ministries [1,7]. The outcome of the data processing consists in annual, aggregated emissions for the city and also detailed spatial and temporally varying source strengths for generating emission input files for air quality models. Currently there are two chemical mechanisms available for speciation: the Carbon Bond Mechanism IV [8] (for the UAM-IV [9] and CAMx [10] models) and the Regional Acid Deposition Model version 2 (RADM2) mechanism [11] required by the CADM model [12].

Large stationary sources in Chile are subject to emission reduction plans that seek reductions in SO₂ ambient impacts until ambient air quality standards are met; these standards for SO₂ are the same ones as in the USA. This information is publicly available through the Internet [2]. Table 1 below shows a summary of the emission scenarios for Santiago, Chile, and the regional sources that surround the city’s basin.

Source	1997	2000
Santiago, point	22	2
Santiago, area	5	5
Santiago, mobile	2	2
Caletones	740	466
Ventanas	84	28
Chagres	16	8
Totals	869	511

Table 1. Urban and Regional emission scenarios for 1997 and 2000 (kton SO₂/year).

METEOROLOGY

Another key input for air quality model simulations is the dynamical state of the atmosphere, in the form of three dimensional fields of wind speed, temperature, photolysis rates, cloud cover, vertical turbulent diffusivities and so on, that are required to properly simulate the different processes that operate upon the pollutants released in the atmosphere. In order to describe the meteorology on the complex terrain basin of Santiago, the Fifth Generation Penn State/NCAR Mesoscale Modeling System (MM5, Version 3.0 [13]) was run. The simulation domain covers South America with successively nested domains down to the metropolitan area of Santiago de Chile. Figure 1 displays the selected domains for the meteorological model. The coarse domain (D01) with 54 km grid size covers main parts of South America. The successive nested domains D02, D03 and D04 are embedded in each other, with the

regional and urban domains defined for subsets of the domains D03 and D04, respectively. Further details are given in reference [14].

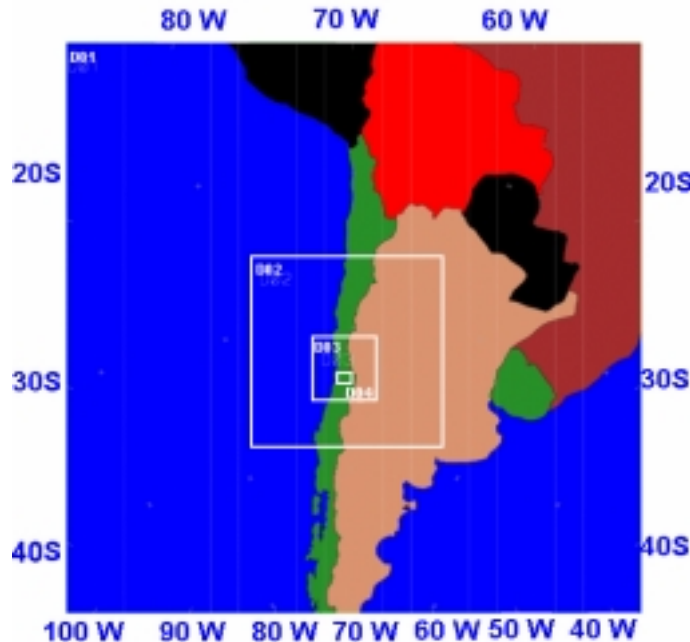


Figure 1. Model domain configuration for MM5 simulations.

SIMULATION RESULTS

We have chosen a summertime episode that led to high ozone impacts in the valley: January 15-22, 1998 (Thursday to Thursday). The Comprehensive Air Quality Model with Extensions (CAMx, version 4.03) was run in a nested configuration; a coarse, regional domain spanning 160 km E-W and 240 km S-N, with 4x4 km cells was constructed from domain D03 MM5 output. The urban domain spans 120 km E-W and 60 km S-N with 2x2 km cells was constructed from domain D04 MM5 output, and completely encloses the greater Santiago metro area, as shown below in figure 2. The surface meteorology observed at network stations was used to improved the meteorological fields near to the ground, as discussed in [14]. The stations in the air quality network measure hourly averages of SO₂, and this information will be used to assess the quality of the simulations on the urban scale. Let us discuss the regional scale results first.

Figure 3 shows the average SO₂ impacts modeled for the regional scale domain, for the 1997 and 2000 emission scenarios and for their difference, respectively. The maximum impacts in both scenarios happen at the same grid point, corresponding to the location of the Caletones copper smelter; likewise, that is also the grid cell with the highest decrease in impacts. There are significant impacts near the Ventanas copper smelter, near the NW corner of the domain. Notice also the difference patterns in the plumes coming from those two large copper smelters. Ventanas is located at the coast (40 m ASL), hence the wind is dominated by the persistent summertime high pressure in subtropical South America, leading to predominant S-SW winds [3]. By contrast, Caletones is located at 2,400 m ASL, and so it is subject to northerly winds that show up in central Chile above 2,000 m ASL as a consequence of the

wind flow impinging against the Andes, with top altitudes between 5,000 and 6,000 m ASL along central Chile [3,4,5]. This summertime pattern seems quite stable and prevents the plume from reaching Santiago.

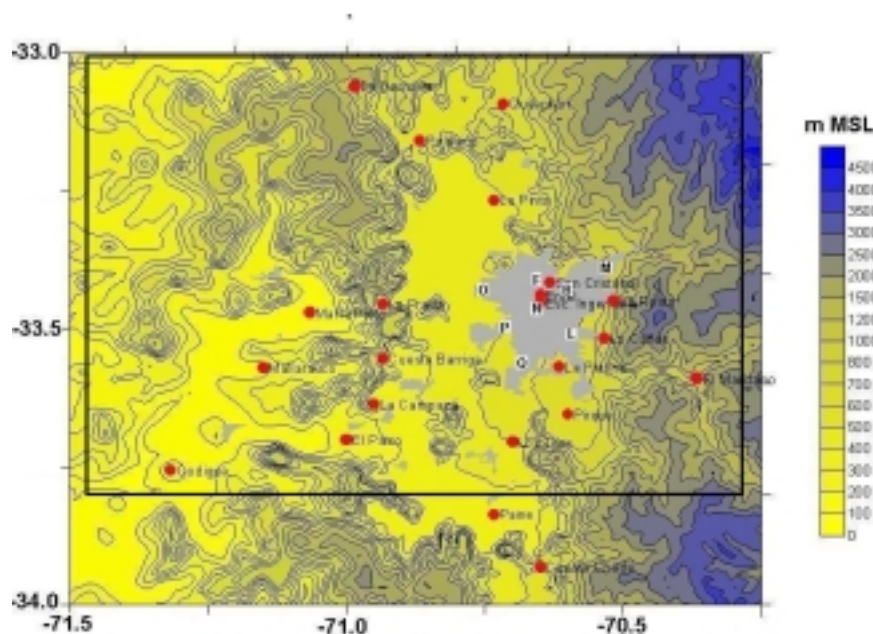


Figure 2. The CAMx nested, urban modeling domain; letters denote air quality monitoring stations; red dots stand for surface meteorological stations.

In addition, the current, 2000 emission scenario shows that there are significant parts of the domain subject to more than 30 ppb of SO_2 (the European critical level); this summertime average estimate is a conservative lower bound of the annual average that we would expect had we conducted an annual simulation of impacts.

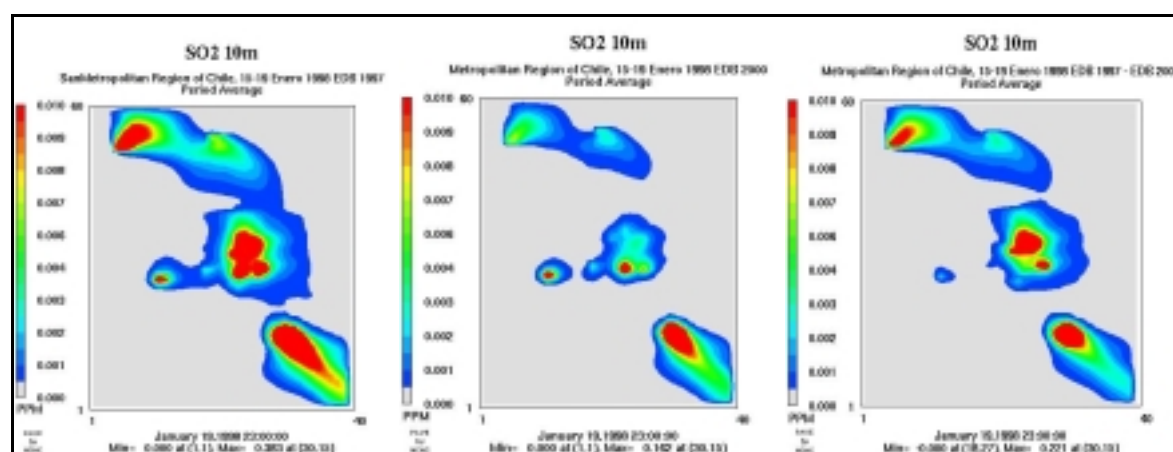


Figure 3. Average impacts of SO_2 for the 1997 and 2000 scenarios and the difference, for the regional scale domain.

Figure 4 displays the same kind of comparison as figure 3, but for the particulate sulfate concentrations. It can be seen that the largest impacts are again near the Caletones smelter, but now the major changes happen within the Santiago area. An explanation for this behavior is that for Santiago we have a full inventory, including biogenic and anthropogenic VOC emissions, compounds that enhance photochemical activity, thus increasing the rate of oxidation of SO₂ to sulfate in the gas phase—recall that the summer is the dry season in central Chile. We do not have such a detailed inventory for the COV and NO_x emissions near the copper smelters, hence our estimates are likely biased downwards, constituting conservative estimates for sulfate impacts. The same can be said for Santiago's summertime impacts, because the ozone is consistently being underestimated by the model across the city (results not shown), an outcome that we ascribe to under and over estimations of COV and NO_x emissions, respectively, coming from mobile sources.

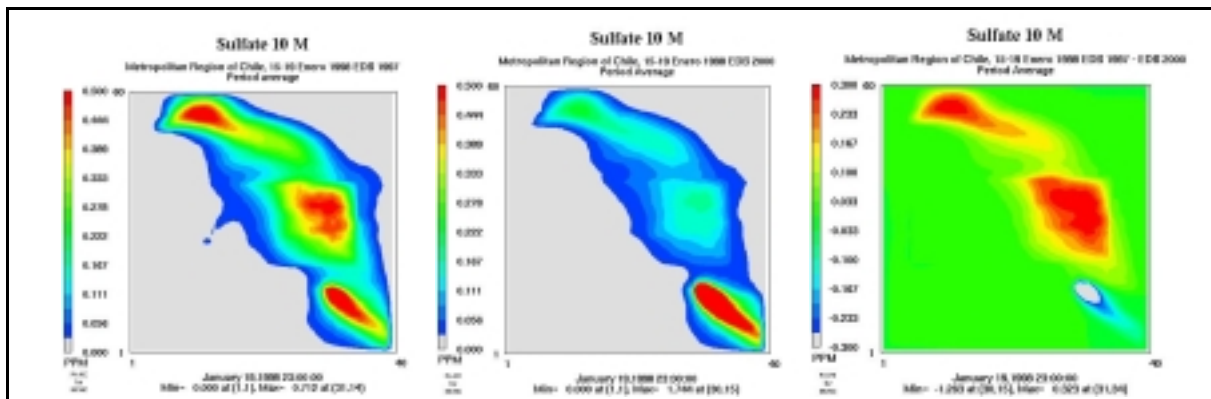


Figure 4. Same as for figure 3, but for particulate sulfate.

Turning now our attention to the urban scale simulations, we can expect that the nesting configuration improves the boundary conditions—for SO₂ and sulfate—that are inputs to the inner domain, because the most relevant sources and processes are being considered in the coarser grid. In addition, the emission inventory is known in more detail in this smaller domain, so we would expect that synergic effects such as photochemical production of OH radicals (that in turn oxidize SO₂ to sulfate in the gas phase) would be better captured at this urban scale than at the regional scale, where we lack complete emission inventories.

Figure 5 shows the urban scale results for the SO₂ impacts, using the same layout as in the two previous figures. From this figure we can conclude that most of the SO₂ impacts within the city are caused by the urban emissions, with the exception of a small contribution from Chagres, a copper smelter located north of Santiago—see figures 3 and 5 for comparisons. There are differences up to 10 ppb when comparing impacts from the two scenarios analyzed here. It also seems clear that the Caletones smelter does not contribute in a significant way to pollution levels within the city, at least on this summertime episode.

In order to assess the quality of the predictions of SO₂ produced by the model within the city, we have plotted time series of hourly observations and predictions of the model using the two emission scenarios under study. Figure 6 below displays comparisons for the following stations: B and F (downtown), L and M (eastern) and O and P (west and south, respectively).

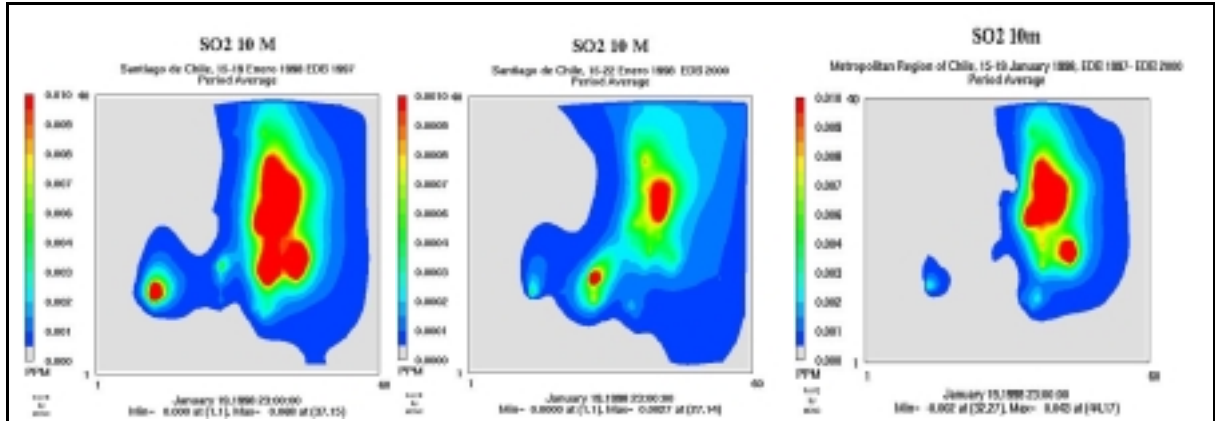


Figure 5. Average impacts of SO_2 for the 1997 and 2000 scenarios and the difference, for the urban scale domain.

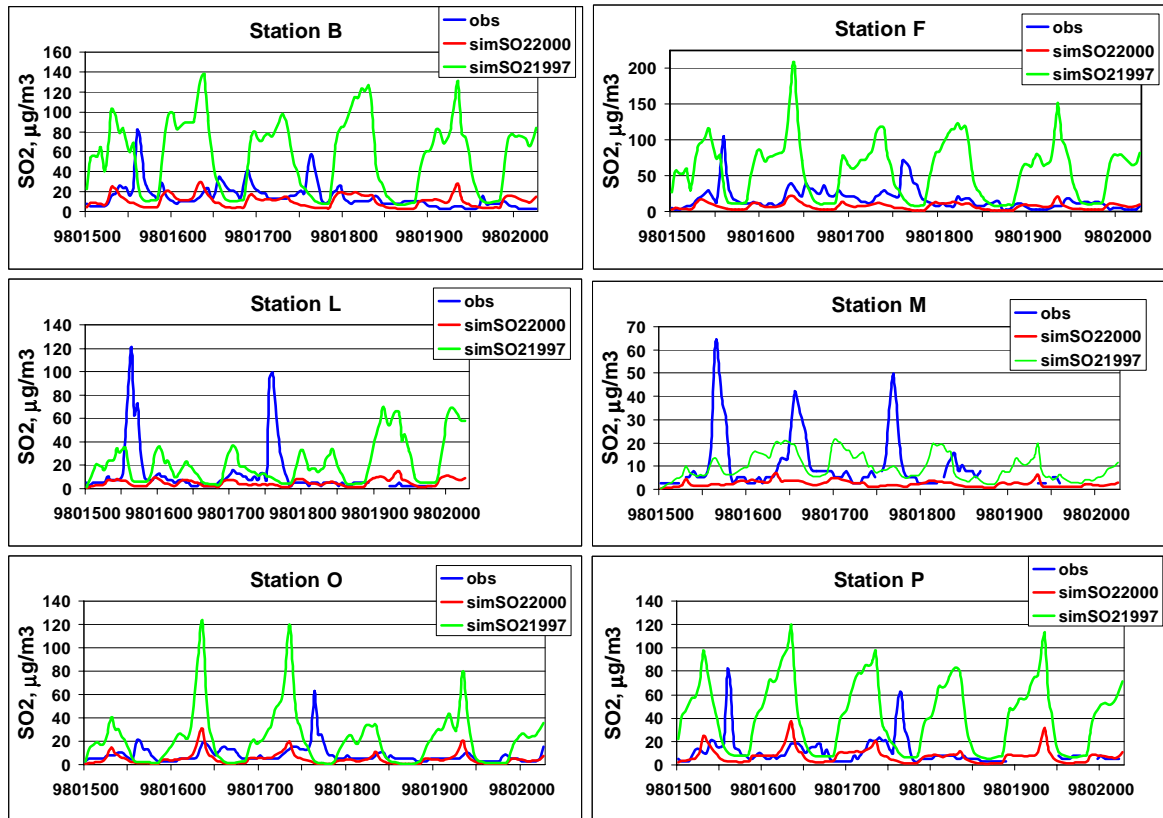


Figure 6. Comparison of observed and simulated impacts of SO_2 for the 1997 and 2000 scenarios, for several monitoring stations within the greater Santiago metro area.

First, we see that the simulations performed with the 2000 emissions tend to slightly underestimate the impacts at all monitoring stations, as expected beforehand for an episode in January 1998. Second, the simulated values are much larger if we choose the 1997 emission scenario, leading to a gross overestimation of impacts; this effect is mostly due to local source reductions. Notice also that there are spikes in the ambient monitored data at several stations during the period simulated. Because the timing of those spikes does not coincide with high

traffic activity levels, we presume they are due to plume fumigation processes. A closer look at the actual monitored emissions in the large SO₂ sources showed that those sources present periods in which their controls shut down, and their emissions increase by a factor of 4 to 6 in a few hours, before returning to controlled operation. Therefore, the spikes that we see in the ambient data are ascribed to transient sources that tend to behave as uncontrolled sources. Recall that the introduction of compressed natural gas from Argentina started early in 1997 with industry, then with residential and commercial uses. This fuel switch effected the large reductions in SO₂ emissions that appear on Table 1. Given the results in figure 6, it seems that the 1997 emission estimates for stationary sources are overstated. We will return to this point in the discussion section.

Figure 7 shows the evolution of particulate sulfate impacts, at the urban scale, between the two scenarios studied.

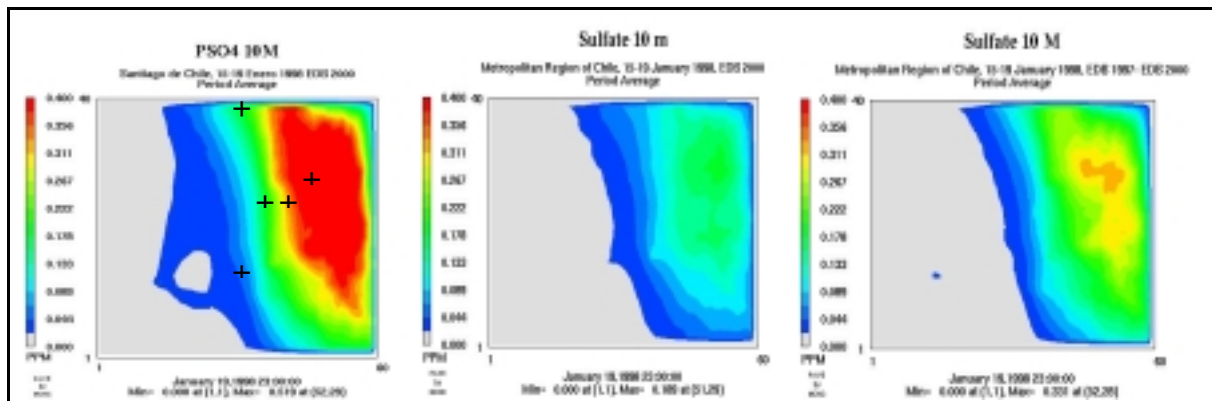


Figure 7. Average impacts of particulate phase sulfate (PSO₄) for the 1997 and 2000 scenarios and the difference, for the urban scale domain.

We do not have systematic data for comparing the sulfate simulated data, only a brief campaign conducted in winter 1998 (July 15th till August 22nd) by Artaxo et al. [15] — the sites are denoted by ‘+’ signs on the leftmost panel of figure 7. In that campaign it was found a rather uniform particulate sulfur content in the aerosol sampled at those five sites, two of which correspond to north and west background sites away from the city. That uniform sulfate concentration across Santiago’s basin seem to be supported by the simulations in figure 7, for both scenarios analyzed. The average levels measured on that campaign are of about 1.8 µg/m³ of sulfur, thus equivalent to 5.4 µg/m³ of particulate sulfate. This values are higher than the ones simulated for summertime conditions because of the poorer dispersion conditions in wintertime and the aforementioned underestimation of photochemical processing in the summertime simulations. Hence there is consistency between simulations and measurements for this species too.

MASS BALANCE

For each simulation conducted, we computed the mass balance for the simulation period, taking into account the emission inputs, the boundary outflow, the deposition and chemistry processes, and so on. Table 2 presents the results for the sulfur dioxide mass balance for the 1997 and 2000 emission scenarios. The most distinctive feature is that more than 90% of the

emissions are transported out of the region, leading to a long range transport of pollution in South America.

Mass Balance Components (mass/time)	1997 Emissions Scenario		2000 Emissions Scenario	
	gmol/h	%	gmol/h	%
Total emissions:	1.51E+06	100.00	9.09E+05	100.00
Boundary net outflow:	1.31E+06	86.22	7.94E+05	87.34
Top net outflow:	9.73E+04	6.42	5.72E+04	6.29
Deposition sink:	1.91E+04	1.26	8.05E+03	0.89
Chemistry loss:	1.79E+04	1.18	1.90E+04	2.09
Nest change:	4.29E+04	2.84	1.46E+04	1.61
Accumulation:	3.15E+04	2.08	1.63E+04	1.79

Table 2. Mass balance for the sulfur dioxide on the regional scale domain.

For the particulate sulfate mass balance, we have to consider that this is a secondary pollutant, generated by the oxidation of sulfur dioxide to particulate sulfate. Table 3 displays the results for the mass balance of this secondary species. More than 90% of the sulfate generated within the domain is transported outside the domain, that is, it reaches long range features. Notice also the lower fraction that is deposited, compared with sulfur dioxide, that is explained by the lower values of sulfate deposition values, as compared with sulfur dioxide values.

Mass Balance Components (mass/time)	1997 Emissions Scenario		2000 Emissions Scenario	
	g/h	%	g/h	%
Chemistry generation:	2.07E+06	100	1.92E+06	100
Boundary outflow:	1.87E+06	90.43	1.77E+06	92.20
Top outflow:	1.71E+05	8.28	1.31E+05	6.84
Deposition:	9.72E+02	0.05	5.75E+02	0.03
Accumulation:	2.58E+04	1.25	1.79E+04	0.93

Table 3. Mass balance for the particulate sulfate on the regional scale domain.

CONCLUSIONS

A regional scale assessment of oxidized sulfur impacts for central Chile has been conducted by applying an air quality model with meteorological summertime conditions (January 1998) and with official emission inventories for the city.

The Comprehensive Air Quality Model with Extensions (CAMx) has produced spatial and temporal patterns that describe the most likely locations of the potential ecosystem impacts on vegetation and agricultural activities in the region. The estimates are only valid for summertime conditions, yet they provide conservative lower bounds of what the annual values would be.

The results of the comparisons of the simulated and observed SO₂ impacts within the city led us to conclude that the emission estimates for January 1998 are closer to the emission scenario for 2000. By contrast, the point source emissions for 1997 seem to be overstated. To check this, we compared the average observed concentrations in 1997 and 2000, 19.9 and 12.5 µg/m³, respectively leading to a ratio of 1.6 for that period. This ratio is much lower than

the ratio of simulated concentrations for the 1997 and 2000 databases, which is $36/7=5.2$ for the summertime simulation. Hence point sources are overestimated and they need to be reassessed.

A conclusion that we achieve is that the 1997 emission scenario for point sources within Santiago was developed as though all sources kept their old fuels —no compressed natural gas at all— until the end of that year, something that clearly is neither supported by the data nor by the existing information of natural gas consumption in the city in 1997. In addition, for the purposes of modeling it is paramount to obtain the actual emission values of the largest sources, because they indeed show intermittence in the emission values. This produces the spikes observed in the ambient monitored data in January 1998, and the evidence collected afterwards (spikes decreasing in frequency and magnitude for the following years) indicates that most major sources have improved their emission controls and drastically reduced emissions. Hence the 2000 emission inventory is more adequate for the purposes of modeling SO₂ impacts within Santiago greater metro area.

Regarding the large stationary sources (copper smelters), each one has been subject to planned reductions and mandatory mass balances to release the amount of SO₂ emitted at each facility, on a monthly basis. Hence the conclusions regarding the magnitude of the reductions in SO₂ and particulate sulfate effected by the regulations upon those large sources are supported by the data. Nonetheless, it would be interesting to collect further information on ambient monitoring near those sources to verify the model predictions. In addition, a regional network of stations measuring air quality and deposition fluxes, away from the influence of major sources and run by an independent institution, would be a valuable tool to assess regional air pollution in central Chile.

In order to better define the zones at risk (besides the city of Santiago, with its 5.7 million population), it is necessary to simulate wintertime conditions of poor dispersion in the region. This is a challenging task because the meteorological representation is far more complex and needs an accurate portray of the low winds, complex circulations and intense thermal inversions that happen in those circumstances.

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