Air Pollution Characterization and Modeling of an Industrial Intermediate City

David G. Allende[1,2*], Fernando H. Castro[1] and Salvador E. Puliafito[1,2]

[1]*Grupo de Estudios Atmosféricos y Ambientales-Facultad Regional Mendoza – Universidad Tecnológica Nacional, Rodriguez 273, (5500) Mendoza, Argentina.*
[2]*Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Argentina*
E-mail: david.allende@frm.utn.edu.ar

Abstract

Bahia Blanca is one of the most important port cities in Argentina, with a significant economic growth accompanied by air pollution caused by industrial and vehicle emissions. The ambient concentrations of gases like NO_x, CO, NH_3 and SO_2 and concentrations of particulate matter have been measured by the local environmental authority between 1997 and 2008. The pollutants were monitored near an industrial complex, providing useful information to evaluate tendencies, to estimate the compliance of regulations and to evaluate the effects of control strategies, but giving only limited indication of spatial variation in concentration and source contribution to air quality. In order to complete the information provided by the monitoring data, pollutant dispersion was simulated with the CALPUFF modeling system. All industrial emissions were included in the model using detailed inventories requested by the local environmental authority. The mobile sources emissions were calculated according to EMEP/CORINAIR methodology, including road, air, railway and ship transportation. Residential and fugitive sources were also included in the simulation. Modeling results show that NO_x, SO_2, and NH_3 concentrations were significant in the town of Ingeniero White, located 10 km SE of Bahia Blanca. CO higher concentrations however, were located downtown in Bahia Blanca since they are associated to road traffic. Simulated PM_{10} concentrations presented high spatial variability associated to the multiple sources of this pollutant. Although the urban center is strongly influenced by industries, their impact may not be significant due to the fact that all these emissions are subject to a bigger dispersion and dilution than traffic related emissions.

Introduction

The city of Bahía Blanca (38º 44' S latitude and 62º 16' W longitude) is located in the South-West of the province of Buenos Aires, Argentina on the Atlantic coast with a population of 274500 inhabitants according to the 2001 census. It is an important trans-shipping and commercial center, handling a large export trade of grains, wool, oil and fruit in the region, as well as being the petrochemical pole which concentrates 45% of the country's total petroleum processing. The combination of trade potential, availability of energy (natural gas and electricity) and human resources make the area quite interesting from an industrial and commercial perspective.

The population is densely distributed around the urban nucleus in about 100 quarters each with distinct characteristics. Over the last decade, the population growth has developed new areas with important commercial activities. This population expansion increased the traffic related emissions, and the constant growth of industrial activities has enhanced the exposure levels because of people living in close proximity to the sources. In the year 2000, after the accidental releases of chlorine and urea from the industrial complex, an Executive Technical Committee was created to monitor air quality, evaluate air pollution tendencies and compliance to local regulations. Industrial and traffic related pollutants were monitored in a chosen site next to the industrial area, in a zone with elevated concentrations of particles, nitrogen oxides, ammonia, sulfur dioxide and ozone.

Pollutant concentration measurements constitute a good indicator of the impact of anthropogenic activities [1, 2], while continuous monitoring networks are a common practice to evaluate pollution patterns. In that sense, ground levels of NO_x and ozone precursors [3-5], particulate matter [6, 7] and several traffic and industrial related pollutants [8-10] have been monitored to understand sources contribution and determine spatial distribution of concentrations.

Air quality modeling studies carried out by Abdul-Wahab [11], Wang et al. [12], Turtos Carbonell et al. [13], Ainslie and Jackson [14], Song et al. [15], among many others, show the importance of simulations to support measurements of distinct anthropogenic sources. In this respect, the spatial prediction of pollutant concentrations due to traffic activities has been simulated with many air quality applications, from simple Gaussian models [16-18], to Lagrangian models [19] and other more elaborated ones [20, 21]. Different simulation methods have been proposed to evaluate the impact of industrial stacks with acceptable performances in various situations [22-25]. Since urban centers concentrate human activities, the cities act like sources of local air pollution, and sometimes may even contribute to transboundary pollution [26]. Air pollution is clearly a typical phenomenon associated to urban centers and industrialized regions and their impact is often simulated on local, regional or global scale.

The present work is focused on two aspects: analysis of air quality monitoring data from a single station located near the petrochemical pole, and evaluation of the

CALPUFF model [27] simulating all anthropogenic pollutant sources in the urban center of Bahía Blanca.

For this paper, the raw data of the continuous measurements made in the years 2005-2006 were provided by the Executive Technical Committee authorities.

Study area and periods
Bahia Blanca

In this study we evaluated the impact of all anthropogenic sources in the air quality of the Bahía Blanca area during the monitoring campaign in the year 2005. Since we wanted to reproduce pollutant dispersion in the urban center, we set the modeling domain in the South West region of the province of Buenos Aires, containing the city of Bahía Blanca and its port sector of Ingeniero White. The domain covers an area of 1600 km^2 between 38.5º and 39.0º S latitude and 62.0º and 62.5 W longitude in a flat region with elevations up to 150 m, increasing to the NE. A view of the modeling domain is presented in Fig. 1. The horizontal mesh cells cover squares of 1 km sides to reproduce the terrain features adequately and, simultaneously, keep computation resources reasonable.
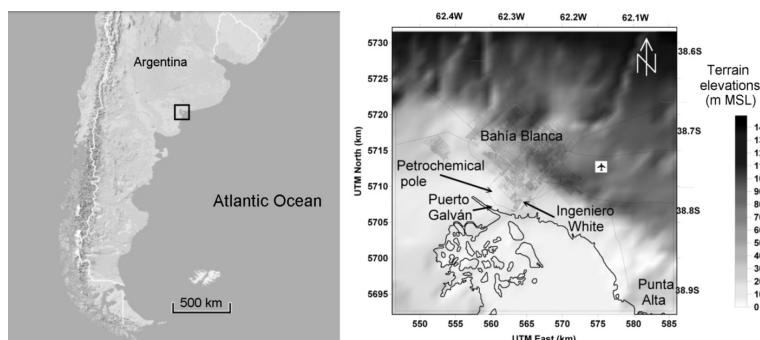

Figure 1: Map of Argentina showing location of the modeling domain in this study. To the right, a detail of the urban area of Bahia Blanca, major highways, the industrial complex, and the port area.

Meteorology

The weather in the zone is of continental type. Since the city is located right in the limit between the Pampas and Patagonia, it is warm and more humid toward the North and varies rapidly to the South becoming dryer. Average temperatures are warm, the annual mean being 15.5ºC with variations between 42 ºC and -11.8 ºC. June and July are the coldest months (mean 7.25ºC) while January is the warmest (mean 22.3ºC), according to maximum and minimum solar radiation. The average rainfall is on the threshold of 620 mm/year, March, September, October and November being the months when most of the rainfall is expected. Local air circulation is characterized by mean winds of 5.3 m/s with a 3 % of calm winds (with a speed of less than 0.5 m/s).

Predominant winds blow from the N –NNW sector. Autumn and winter tend to be the windy seasons. Fig. 2 shows the wind patterns in the zone.
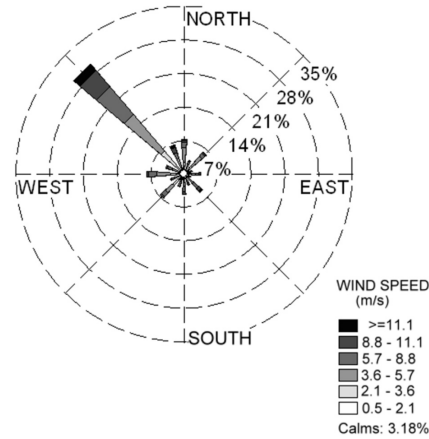

Figure 2: Wind rose from Comandate Espora station (38º 42'S, 62º 09'W) located at the local airport to the East side of the urban center, for the period 2005-2006.

Methods

CALPUFF modeling system

CALPUFF is a multilayer, multi-species non –steady-state puff dispersion model which can simulate the effects of time and space-varying meteorological conditions on pollutant transport, transformation and removal [27]. CALPUFF utilizes a Gaussian puff formulation to calculate the concentration of a pollutant at any given location downwind, and the deposition in user specified locations (''receptors'') at ground level. The model can use three dimensional meteorological fields developed by the CALMET model or, simple single station winds in a format consistent with the meteorological files used to drive the ISCST3 model [28]. Detailed algorithms for different physical processes involving pollutant dispersion and transformation and details on model applications can be found in Scire et al. [27] and US EPA [29]. Equation 1 and equation 2 show that the puff contribution at a given receptor is:

$$C = \frac{Q}{2\pi\sigma_x\sigma_y} g \exp\left[- d_a^2 / \left(2\sigma_x^2\right)\right]\exp\left[- d_c^2 / \left(2\sigma_y^2\right)\right]$$

(1)

$$g = \frac{2}{\left(2\pi\right)^{1/2}\sigma_z} \sum_{n=-\infty}^{\infty}\exp\left[- \left(H_e + 2nh\right)^2 / \left(2\sigma_z^2\right)\right]$$

(2)

Where, C is the ground-level concentration (g/m^3), Q the pollutant mass (g) in the puff, σ_x is the standard deviation (m) of the Gaussian distribution in the along-wind direction, σ_y is the standard deviation (m) of the Gaussian distribution in the cross-wind direction, σ_z is the standard deviation (m) of the Gaussian distribution in the vertical direction, d_a the distance (m) from the puff center to the receptor in the along-wind direction, d_c the distance (m) from the puff center to the receptor in the cross-wind direction, g the vertical term (m^{-1}) of the Gaussian equation, H_e the effective

height (m) above the ground of the puff center, h the mixed-layer height (m) and n is the extent of vertical plume spread inclusive of multiple reflections off the mixing lid and the ground.

The model is usually recommended by the U. S. Environmental Protection Agency (US EPA) to simulate the effects of pollutant dispersion in long range transport, typically between 50-200 km, but contains algorithms which apply to much shorter distance [30]. CALPUFF was chosen because of its ability to simulate not only atmospheric transport of several pollutants but also wet and dry deposition and pseudo first order chemical transformation of NO_x and SO_2. The model also employs gridded fields of geophysical data like terrain elevations and land use categories allowing a proper characterization of complex modeling domains like coastal areas. Also, CALPUFF provides an advantage over other Gaussian models like ISCST3 since it can process calm wind situations, avoiding unrealistic high concentration estimates [31]. Support references about the model application can be found in Bennet et al. [32], Levy et al. [33], Zhou et al. [34] and Indumati et al. [35].

Industrial sources

All industrial sources are located on a Petrochemical Pole, an Industrial Park and the port sector. The Executive Technical Committee made a gaseous emissions sources inventory in 2003, requesting sworn statements supplemented by environmental assessment studies involving stack measurements, mass balances and estimations based on emission factors characteristic of each type of industry and pollutant.

The Bahía Blanca Petrochemical Pole comprises a gasoline and hydrocarbons fractioning plant and a polyethylene production plant with high NO_x and SO_2 emissions, several oil refineries with SO_2 emitting stacks, an ammonia and fertilizer industry involving ammonia emissions in the urea granulation equipment, and a vinyl chloride monomer (VCM), polyvinyl chloride (PVC) monomer, PVC resins and Caustic Soda manufacturing facility, emitting CO and particulate matter.

The port sector includes a number of cereal concentration plants involving large amounts of particulate matter emissions from loading, unloading and transport operations. An important power plant, gas fired and partly heavy–oil fired, is located to the East side of the port area and produces the main contribution of SO_2 emissions in the zone. Fig. 3 shows the location of all industrial sources.
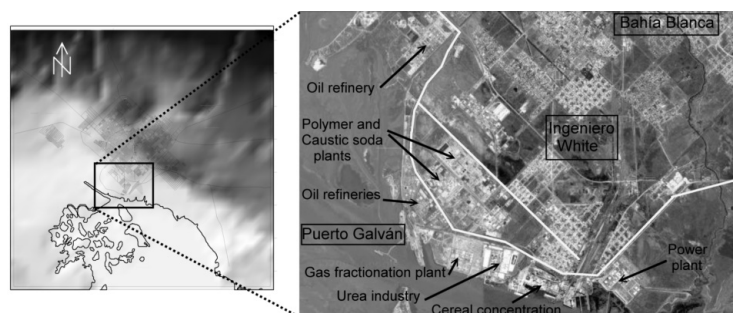

Figure 3: The Bahia Blanca urban center and a detail of the Petrochemical pole and industrial complex (Source: Google Earth).

Transportation emissions
Road transport
The COPERT III model was used to estimate road transport emissions. The model can compute hot, cold, start and evaporative emissions combining activity parameters such as annual vehicle kilometers traveled, average trip distances and average velocities with emission factors for each vehicle category and pollutant [36]. COPERT III was selected because of the similarities between the Argentinean and the European fleets [37].

The vehicle fleet was arranged into 4 vehicle classes and 28 technology categories depending on fuel type, vehicle size, fuel delivery system and exhaust control system (Table 1). Of these categories, 19 belong to light duty vehicles and passenger cars, 6 to heavy duty vehicles and 3 to urban buses. Information from the National Vehicle Registration Directory (DNRPA) and the Automobile Manufacturers Association (ADEFA) was used to determine the fleet composition. The exhaust control system of each vehicle was established comparing the year of compliance through with the legal emission limits for new vehicles. In this respect, Argentina follows the European standards but with several years of delay, for instance, the EURO 3 standard from year 2000 has only been enforced in 2007 [38].

Table 1: Bahia Blanca fleet distribution by fuel.

Vehicle class	Number of vehicles	Fleet distribution by fuel(%)		
		Gasoline	CNG	Diesel
Passenger	56.151	76	14	10
Light duty	12.718	50	14	36
Heavy duty	3.684	0	0	100
Buses	600	0	0	100

COPERT III emissions rates were used for all vehicles except for the ones fueled with compressed natural gas (CNG). The use of this fuel has greatly increased in Argentina since 1995, especially due to its low market cost. Emission factors of vehicles fueled with CNG were derived from the results of two local studies [39, 40]. To derive emission rates, the model considers different average velocities for different types of driving conditions. In this work, we considered three driving conditions associated each to a specific road hierarchy:
  (a) Highways: roads characterized as main intra county, suburban areas or inter-regional highways connecting main town poles in the metropolitan area, with a high traffic imposition, no traffic lights and high average speed (70-100 km/h).

(b) Primary roads: roads that are main streets connecting important urban district areas, with a high vehicle density, with most intersections regulated by traffic lights, and a low average speed (20-30 km/h).

(c) Secondary roads: roads that are mainly residential streets with a low vehicle density, very few or no traffic lights regulating intersections, although, in some cases, with the presence of speed limiters and a low–medium average speed (25-35 km/h).

Average velocities on each road hierarchy were estimated from information collected on a set of vehicles equipped with a global positioning satellite (GPS) unit.

Assumptions on the annual average kilometers traveled (VKT) by a single vehicle were made to obtain the annual vehicle activity. Since vehicle activity information is scarce in Bahia Blanca, the values of VKT for different vehicle categories were taken from the Mobile Emission Inventory compiled by the local environmental agency [41]. These values are similar to the ones used in a recent study of mobile sources emissions in Buenos Aires [37].

The distance traveled on each road hierarchy by vehicles of each class was estimated and used as a spatial distribution proxy. There are other simpler approaches to distribute traffic emissions [42] but the different assignments of traffic activity and fleet composition in different road hierarchies can significantly improve the spatial disaggregation of emissions [43]. The amount of kilometers traveled on each road hierarchy for each vehicle class was determined by flow measurements and knowledge of traffic characteristics. For instance, heavy duty vehicles were supposed to circulate mainly on highways because its traffic is associated with the many industries located outside the city.

The total amount of emissions estimated for highways, primary roads and secondary roads was distributed in the road network proportionally to the segments length.

Railway transport

The railway in Bahía Blanca is mainly oriented to cargo transportation, passenger transport being only a secondary activity. Railway emissions were estimated applying the simplest CORINAIR methodology [44]. Specific fuel consumption factors, the amount of train operations and bulk emission factors were used in the estimation. Then, the total amount of emissions was evenly distributed along the railway network.

Ship transport

Bahía Blanca is one of the main ports of Argentina. Most of all its operations are related to the presence of industries in the city. Emissions were estimated with the simplest CORINAIR methodology for maritime activities [44]. The number of operations and the port waiting time were considered to obtain fuel consumption of cargo ships. A bulk emission factor was then used for the estimation, and an approach path to the port was assumed in order to spatially distribute the emissions from the ships.

Emission grid

After the total amount of mobile sources emissions was estimated, the results were spatially distributed using GIS tools. In practice, this means that the total emissions were allocated in a regular grid with a spatial resolution of 0.25 km^2 covering the area under study. The emission map was obtained by adding the emission values relative to every road segment, railway and marine path to each cell of the regular grid. Fig. 4 shows the spatial distribution of CO emissions due to transportation.
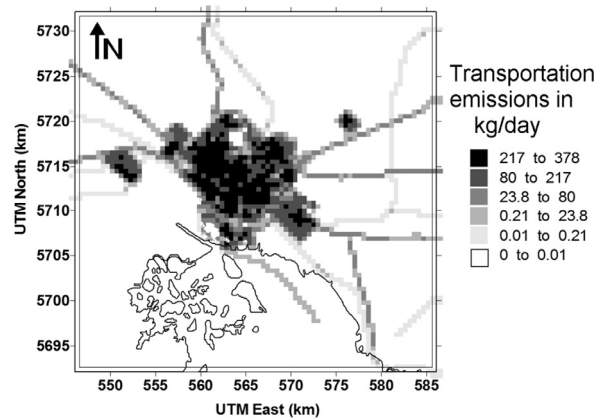
Figure 4: Grid system showing the intensity of the CO emissions due to transportation in kg/day for the area under study. Road, railway, ships and airport activities are included. The same procedure was used for all pollutants.

Residential and commercial sources

Emissions from residential and commercial sources (Table 2) were estimated using data of natural gas consumption in the city. Natural gas distribution is about 135000000 m^3 /year, which is used mainly for heating; it generates 970000 kg of pollutant gases, for the most part consisting of hydrocarbons and carbon monoxide. The numerous and wide distributed residential and commercial sources were treated as area sources, distributed according to land use maps of the urban center.

Table 2: Pollutant emissions from residential and commercial sources [41].

Pollutant	CO	NO$_2$	SO$_2$	PM10	HC
Emission factor	2500 mg/kg	1324 mg/m^3	0.56 mg/m^3	107.31 mg/m^3	0.5%
Kg/year	240 980	202 500	75.6	14 490	511 650

Windblown dust emissions
Since natural semi arid lands are believed to be main suppliers of atmospheric dust, and strong winds are a key factor governing dust emissions, we decided to include in the model the particulate matter injected to the atmosphere by wind erosion. The assessment of the windblown dust emissions for the selected region was incorporated into the CALPUFF model as a discontinuous process. We assumed a threshold wind of 6.8 m s^{-1}, located in the range of literature data, i.e. 6-13 m s^{-1}. Also, land use data were used to divide the modeling domain into potentially erodible and unerodible surfaces. The emissions were quantified using the EPA equations [45] for basic wind erosion, and we used area sources to simulate dust sources. When all variables in the erosion model were quantified, an emission rate was calculated for each area in the land use grid network. Since we adopted literature data for most of the variables involved, a great uncertainty in dust emissions rate is expected.

CALPUFF runs and model settings
The modeling domain was arranged as a 40 x 40 grid with 1 km resolution. Terrain features were incorporated using the United States Geological Survey (USGS) global 3 arc-sec data. The major part of the pollutant sources is located in the center of the domain. The land cover used was Global Land Cover Characterization (GLCC) data, obtained by 1-km resolution Advanced Very High Resolution Radiometer (AVHRR) from April 1992 through March 1993. Meteorological data was obtained from the local airport station Comandante Espora (38º 42'S, 62º 09'W, 75 m MSL) located 12 km East of the urban center over a one year period. CALPUFF was run in a mode that enabled ISC3-type meteorological data as input. Hourly calculation of mixing heights was carried out by the local weather forecast service, using sounding data from the airport and surface information from both airport and CTE's meteorological stations.

We modeled seven species: NO_x, SO_2, PM_{10}, NH_3, CO, SO_4^{2-} and NO_3^-, and the MESOPUFF II chemical mechanism [27, 46] was chosen to simulate SO_2 and NO_x conversions. During daytime periods, when gas phase free radical chemistry is active, CALPUFF uses ozone concentration and solar radiation intensity as surrogates for the OH concentration. The model requires ammonia background concentration for the HNO_3/NH_4NO_3 equilibrium calculation. Monthly background ammonia and ozone concentrations were set in the model, according to the monitoring data. We used monthly averages, listed in Table 3. At night, NO_x and SO_2 oxidation rates resulting from heterogeneous reactions are generally much lower. For nighttime oxidation rates, we used the model's default values of 0.2% and 2.0% for SO_2 and NO_x respectively.

Table 3: Background ozone and ammonia concentrations for CALPUFF internal computation of chemical transformation rates.

Month	Average O_3 concentration (ppb)	Average NH_3 concentration (ppb)
January	34	5
February	20	14
March	14	7
April	13	7
May	13	7
June	12	7
July	13.6	3
August	14	2
September	16	5
October	17	9
November	15	9
December	12	15

We included the plume rise in our model, stack tip down-wash and vertical wind shear above the stack top options for all industrial stacks. Dry deposition of gas species of SO_2, NO_x and HNO_3 was calculated using the model default values of diffusivity, reactivity, resistance and solubility. PM_{10} dry deposition was also included with the default data of size distribution. As to wet deposition, scavenging coefficients for liquid precipitations were set at 3×10^{-5}, 1×10^{-4}, 1×10^{-4} and 1×10^{-4} s^{-1} for SO_2, $SO_4{}^{2-}$- NO_3^- and PM_{10} respectively.

Monitoring data and measurement techniques
Concentration patterns of NO_x, CO, PM_{10}, NH_3 and SO_2
Air quality monitoring site in the city of Bahía Blanca was established in a point very near the industrial complex in order to improve control over stack emissions. The sampling station is composed of 6 instruments to measure airborne concentrations of NO_x, SO_2, CO, NH_3, O_3 and PM_{10}. The concentrations were measured continuously during the period, though there were several data gaps due to equipment maintenance and calibration.

CO was measured with a Thermo 48C model that utilizes a gas filter correlation to determine low ambient concentrations. Ambient NO, NO_2, NO_x and NH_3 concentrations were measured using a Thermo 17 C Chemiluminescence Analyzer. Pulsed Fluorescence gas analyzer Thermo 43C was used to measure SO_2 concentrations. The PM values were determined with Rupprecht & Patashnick TEOM 1400a Ambient Particulate Monitor. Ozone concentrations were monitored with a Thermo 49C analyzer.

Results and discussion
Emissions

Fig. 5 shows the contribution of each source type to the total emissions of CO, SO_2, NO_x, PM_{10} and NH_3 from Bahia Blanca in 2005. The total emissions of CO, NO_x, SO_2, PM_{10} and NH_3 were 23863, 8698, 3750, 588 and 1435 tons respectively. We do not report secondary pollutants since their concentration is not measured by the Executive Committee.

Transport sources emitted the largest part of CO and NO_x, about 96 and 42% of total emissions. The contribution of SO_2 emissions from oil refineries was close to 91% of the total. The highest emission of PM_{10}, about 46%, and NH_3, almost 99%, arose from the urea and fertilizer producer.
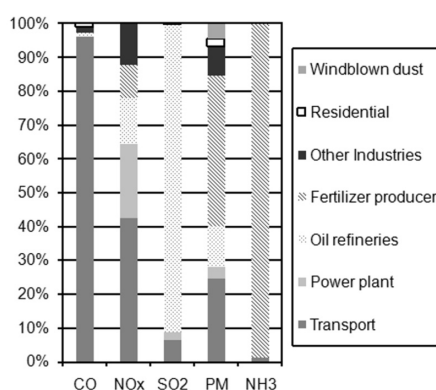
Figure 5: Emissions distribution for all pollutant modeled. Notice that industrial activities are the main contributor for all pollutants, except for transportation that is the most important CO emitter.

Air quality impact

Fig. 6 to 10 show average 24-h concentrations for all pollutants. Our model shows that the petrochemical pole concentrates all of the pollutant concentrations, excepting CO, with a spatial distribution focused on the streets network, and PM_{10} that is influenced by all sources, including fugitive dust from soils. In general, the concentration distribution in this study area is moderately affected by meteorological conditions following surface winds during the entire period of simulation. The daily averages of pollutant concentrations for the grid network are 89.1 $\mu g/m^3$ for CO, 17.3 $\mu g/m^3$ for NO_x, 2.8 $\mu g/m^3$ for NH_3, 8.5 $\mu g/m^3$ for SO_2 and 175.4 $\mu g/m^3$ for PM_{10}. The urban averages are 299.8 $\mu g/m^3$ for CO, 55.8 $\mu g/m^3$ for NO_x, 3.6 $\mu g/m^3$ for NH_3, 43.1 $\mu g/m^3$ for SO_2 and 270.0 $\mu g/m^3$ for PM_{10}. In general, the industry related pollutant concentrations decrease radially from the sources. The highest grid concentrations are 419.7 $\mu g/m^3$ for CO, 305.4 $\mu g/m^3$ for NO_x, 205.3 $\mu g/m^3$ for NH_3, 369.1 $\mu g/m^3$ for SO_2 and 693. $\mu g/m^3$ for PM_{10}, located in the area between the Petrochemical pole and the Industrial complex, except for the CO, that is located in the center of the city of Bahia Blanca. The most polluted area is the town of Ingeniero White.
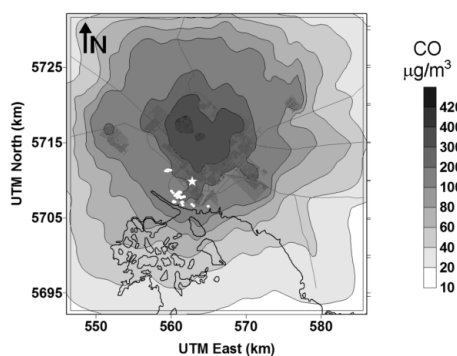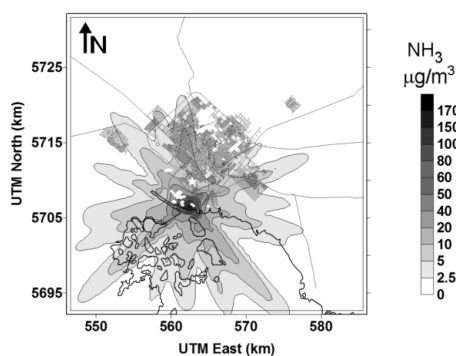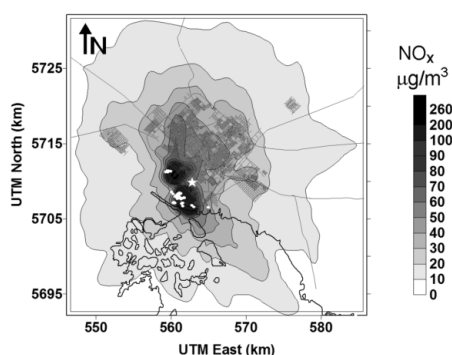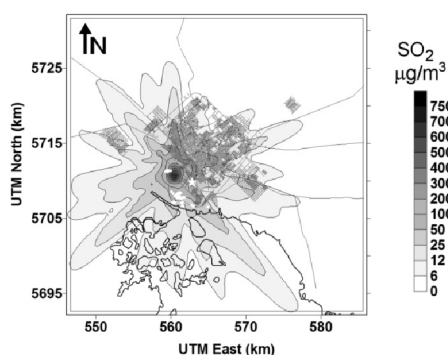
Figure 6

Figure 7

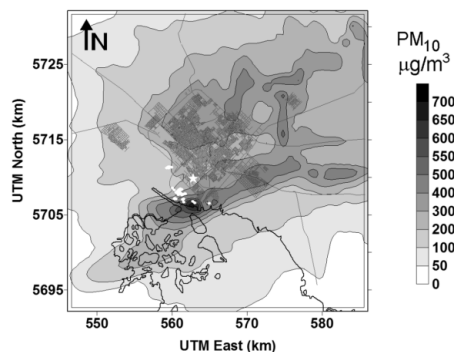**Figure 8**

Figure 9

Figure 10

Figure 6 to 10: Isoconcentration plots simulated with CALPUFF for (a) CO (b) NH_3 (c) NO_x (d) SO_2 and (e) PM_{10}. The scales are in $\mu g/m^3$. The white triangles represent industrial stacks and the white star locates the monitoring point.

Simulated concentrations over the total period at one site located downtown were averaged in order to estimate the contribution of every source to local air quality. Fig. 11 shows that mobile sources are responsible for the main air quality problems in the urban center, the most important source of CO, NO_x and PM_{10} concentrations, and the second contributor of NH_3 and SO_2. This seems to be reasonable considering the intensity of the traffic in the chosen site. The influence of the industrial complex is also very important since simulation results showed high concentrations for all

pollutants coming from these sources as well. In this respect, it can be observed that about 38% of NO_x, 25% of CO and 35% of PM_{10} are industry related. As expected, most of the NH_3 and SO_2 transported to the metropolitan area are originated in the petrochemical pole.

Residential sources are only significant for CO, NO_x and PM_{10} at this urban site.

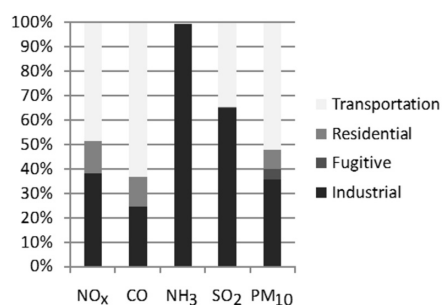Finally, soil dust generates a small contribution (about 5%) in PM_{10} concentrations.

Figure 11: Estimated source contribution at one site located downtown for each modeled pollutant.

Model performance evaluation

We compared the 24 h concentrations obtained with CALPUFF to the measured ones in the monitoring station. Fig. 12 to 16 show the comparisons between the modeling results and the observations, near the industrial complex. Fig. 17 to 21 show the correct match of the frequency distribution between calculated and measured concentrations. In general, the concentrations calculated with CALPUFF follow the measured trend. Extreme concentrations are not correctly simulated by the model and in the case of PM_{10} there is a systematic underestimation. These conclusions can be confirmed by observing the frequency distributions, where simulated concentrations of NO_x, NH_3 and SO_2 follow the pattern of measured ones. In the case of PM_{10} the simulated distribution is displaced to lower values probably because of the absence of some sources in the model (e.g. re-suspension of road dust). The CO frequency distributions show both a bimodal behavior, probably produced by the influence of two different sources. As suggested by the analysis of source contribution previously presented, it appears that traffic related CO and industrial CO affect local air quality at the measuring point. This is more evident in the simulated distribution where the gap between modes is larger.
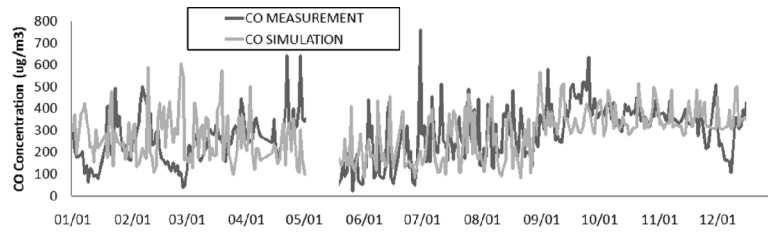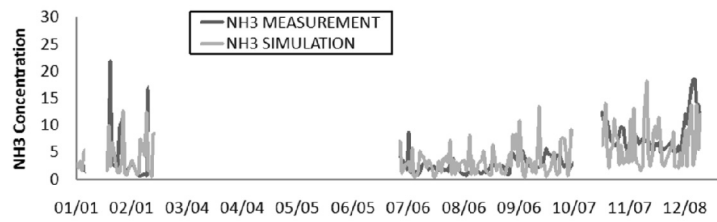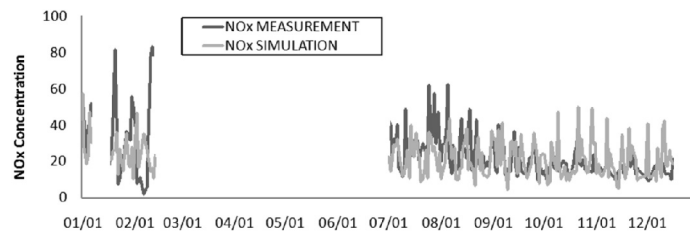
Figure 12

Figure 13

Figure 14

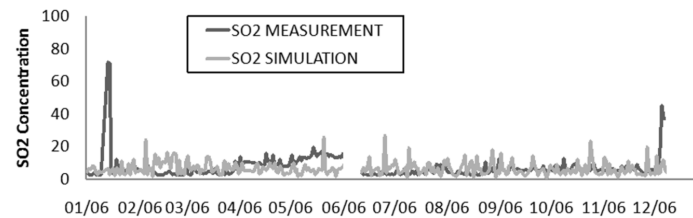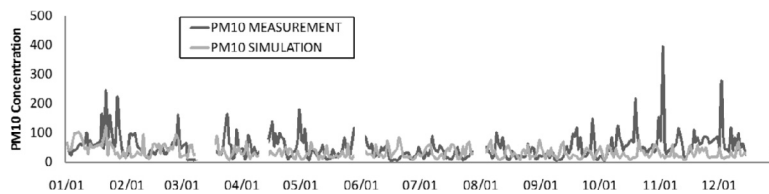**Figure 15**

Figure 16

Figure 12 to 16: Daily variation of pollutant concentration ($\mu g/m^3$) at the monitoring point. We included a curve with simulated values using CALPUFF. Notice several gaps in the measured data due to equipment maintenance.
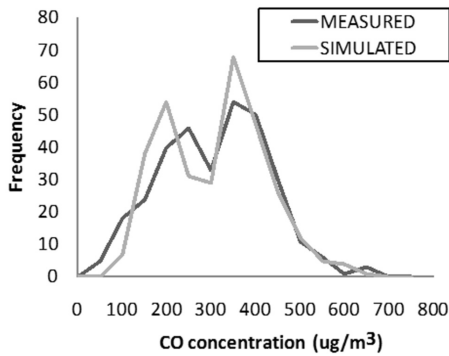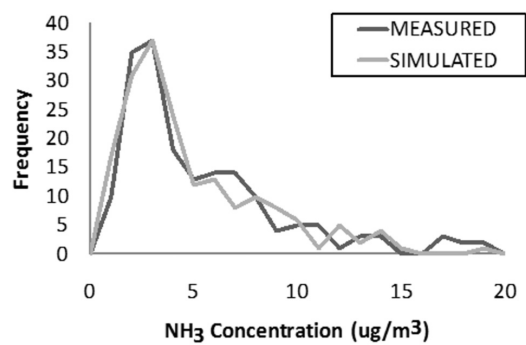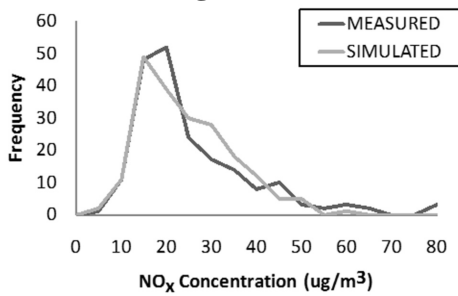
Figure 17

Figure 18

Figure 19
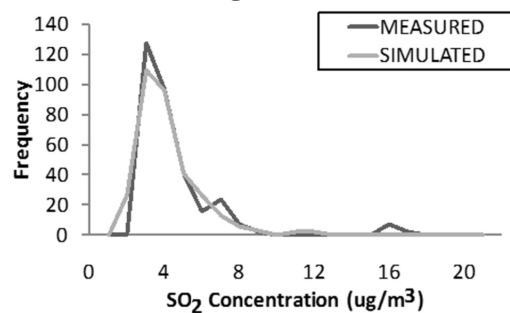
Figure 20
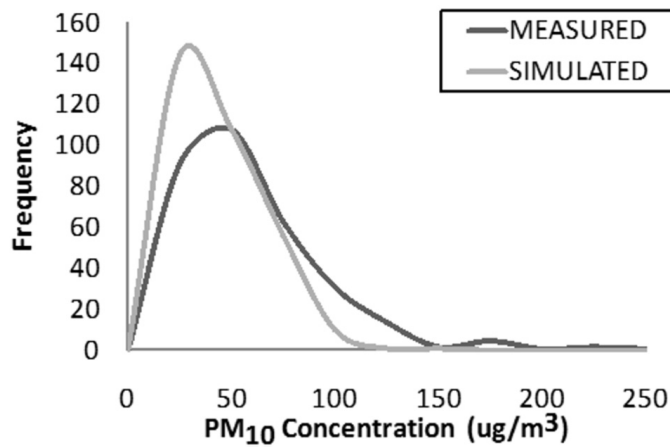
Figure 21

Figure 17 to 21: Frequency plots for (a) CO (b) NH_3 (c) NO_x (d) SO_2 and (e) PM_{10}.

A consistent procedure should be applied in order to evaluate the model performance. In this study, we used the information content in the difference between the observed and model-predicted values. In this respect, we applied the Willmott [47] and Seigneur et al. [48] proposed statistical performance measures. The evaluation statistics are shown in Table 4. For each pair of modeled and measured values, a signed difference ($P_i - O_i$) was calculated. We computed the mean bias error (MBE), to

provide an indication of bias along the receptor's measurements, the root mean square error (RMSE) to show a general indication of the variance. Also included are the mean absolute error (MAE), and the mean fractional bias (MFB), both indicators of the model performance summarizing the mean difference, and Willmott's index of agreement (d) being the value of 1.0 for the perfect fit.

Table 4: Statistical measures of model performance for the four pollutants simulated, being N, the number of sampling times.

Pollutant	N	MBE	RMSE	MAE	d	MFB
CO	322	-0.11	143.7	111.6	0.89	0.02
SO_2	327	-1.27	9.38	5.32	0.96	-0.07
NH_3	180	-0.55	4.59	3.16	0.97	-0.09
NO_x	200	-2.02	15.92	10.89	0.97	-0.04
PM_{10}	320	-19.08	1.01	35.11	0.79	-0.282

From the frequency plots alone, it seems that modeled data predict well the measured values for all pollutants, and slightly underestimate the measured 24-h average concentrations. Concentrations simulated with CALPUFF are more variable than measured ones. For example, in Fig. 12, the same tendencies can be identified for CO concentrations but the model seems to have more variance, as indicated by the elevated values of RMSE. Willmott's index of agreement for all pollutants is very high, all near to 1.0. For all cases, MFB was very close to 0.0, except for PM_{10}. A qualitative inspection on the differences as they appear along the measurements indicated no pattern of bias in any of the cases.

Values for mean bias error (MBE) and mean absolute error (MAE) range from -0.11 to -19.08 and 3.16 and 111.6 respectively. Those indicate that the model agreed with the observational data to an acceptable degree. Although the model is unable to reproduce the concentration peaks exactly, the values of the statistical measures suggest that the dispersion simulation approaches the concentrations patterns on an acceptable level.

Conclusions

In this study, the CALPUFF modeling system was used to simulate pollutant dispersion in the urban area of Bahia Blanca in order to provide a general idea of the pollutant pathway for all emissions, both temporally and spatially. We performed a detailed emissions inventory, including real emissions rates from all industrial sources and estimations from mobile, residential and fugitive sources. The concentration mapping represents a major improvement for the area under study, especially in non urban areas, where monitoring is not present.

Modeling results show that the most polluted region is the town of Ingeniero White, located to the SE of the metropolitan area, and very close to the Petrochemical

Pole. The fair agreement between concentrations measured by the Executive Technical Committee over the year 2005 and the simulated ones with CALPUFF validates the proposed emissions and dispersion models. The simulated concentrations of NO_x, SO_2 and NH_3 generally follow the measured values patterns. On the other hand, CO and mainly PM_{10} simulated concentrations seem to underestimate the monitored values. Possible limitations of the methodology employed are the use of annual averages from the residential and industrial emission inventory. However, since SO_2 and NH_3simulations correlate well with monitoring data, it appears that averaged input values for industrial stacks are reasonable assumptions. About the residential sources, a conservative approach was taken since we used default emission factors due to specific information lacking. Nevertheless, these sources do not strongly impact the results; at the most, a contribution of 12% for CO was calculated by the model from this sector. In contrast, PM_{10} concentrations are influenced by several sources. Limited data were available in the region and several assumptions were made in the estimation of fugitive dust from geological sources. However, the urban center seems to be poorly affected by particulate matter coming from soil erosion. Resuspension of road dust, not quantified in this study, may be a great contributor of particulate matter. Although it appears to be advisable to incorporate dust resuspension to improve the model, its estimation is based on the silt content of the roads. The lack of this information and the difficult extrapolation of the empirical formulations used can deteriorate the reliability of these calculations.

The location of a continuous monitoring station in the town of Ingeniero White represents a powerful control policy, considering the pollutant impact in the area. Another important point is the significant pollution estimated in other areas, especially in the central and most populous urban center. Here, high concentration values were calculated by the model, with average daily values of 299.8 $\mu g/m^3$, 55.8 $\mu g/m^3$, 3.6 $\mu g/m^3$, 43.1 $\mu g/m^3$ and 270.0 $\mu g/m^3$ for CO, NO_x, NH_3, SO_2 and PM_{10} respectively.

Although the site is strongly influenced by industries, their impact may not be significant due to the fact that all point source emissions are subject to a bigger dispersion and dilution than transportation emissions. In general, the industry related pollutant concentrations decrease radially from the sources, almost symmetrically. The transportation sector appears to be the largest contributor for worsening the air quality in the Bahia Blanca urban center and management activities should be focused on traffic emissions reduction.

A major source of uncertainty in the modeling is the emission of mobile sources because of the intrinsic variability of its emissions. Other sources of uncertainty are related to the default of parameters in the estimation of residential and fugitive emissions.

In order to fully evaluate urban air quality conditions, detailed emissions inventory and the use of adequate dispersion models are very valuable tools. For the general accuracy of predictions, the results presented here, show that the modeling assumptions taken have the potential to be used in urban air quality simulations.

Acknowledgements

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About the Authors

David Gabriel Allende
Graduated with a degree in Chemical Engineering at Universidad Tecnológica Nacional in 2001 and he is in the 3rd year of his Ph.D. studies at the Engineering Faculty of Universidad Nacional de Cuyo in Mendoza. David's thesis topic involves the evaluation of multimedia environmental problems, through the optimization of several models to characterize urban pollution and aerosol transport problems.

Fernando Horacio Castro
Received an engineering degree at Universidad Nacional de Cuyo in 2003 and a master's degree in environmental management in 2005. He is starting his Ph.D. studies at Universidad Nacional de Cuyo in Mendoza. His research interests are aerosol measurements and modeling and the influence of aerosols in regional meteorology.

Salvador Enrique Puliafito
Received a Bachelor degree in electronics and electricity (1983) from the University of Mendoza, Argentina, and Ph.D. in engineering (1989) from the University of Braunschweig, Germany, in the area of atmospheric physics. He has participated in research projects on topics related to the determination of stratospheric ozone and tropospheric water vapor at institutes in Germany, Switzerland, and the United States, including four ATLAS missions on board NASA space shuttle. Dr Puliafito is an independent researcher of CONICET at Universidad Tecnologica Nacional, specializing in environmental issues, in particular in monitoring and modeling of air quality. His current area of work relates to the influence of urbanization processes on global climate change.