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Original Research

Atmospheric dispersion of hydrogen sulfide using a modified ARPS model: a case study.

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Abstract

Exposure to disgusting smells constitutes a type of atmospheric pollution from industrial and human activities. Complaints stemming from various sources of unpleasant odors have become a serious concern in both sparsely and densely populated countries. Hydrogen sulfide is a compound characterized by its disgusting odor. In this work, a new chemical reaction was incorporated to Advanced Regional Prediction System (ARPS) model, to calculate the H_2S air concentrations. A turbulent boundary layer flow is computed using the LES code ARPS 4.5.2. A LES coupled with a Lagrangian stochastic model has been applied to the study of reactive scalar dispersion downwind of a localized source of H_2S. The study case corresponds to the H_2S emission of cellulose mill. Two bad odor event was evaluating in order to compare the result of the model with the measured concentrations. The results of this model application provides good description of the plumes for two event of bad odor records in the zone. The values resulting from the analysis of the air samples are within the concentration range estimated by the model. The model is a valid and useful tool to simulate atmospheric pollution episodes that involve non-conservative pollutants, that is, chemical species that, when in contact with the atmospheric components, react, and giving rise to the formation of secondary compounds. It is possible used the developed modeling system in cases of diagnosis and prognosis of real situations and even emergencies, with an appropriate level of precision for studies of this type.

Keywords: atmospheric odor pollution, hydrogen sulfide, ARPS, pollutant dispersion, chemical reaction.

1. INTRODUCTION

Exposure to disgusting smells constitutes a type of atmospheric pollution from industrial and human activities. These activities release volatile odoriferous molecules into the environment that degrade air quality to levels unhealthy to humans. (Ramos Rincon *et al*., 2018)

Complaints stemming from various sources of unpleasant odors have become a serious concern in both sparsely and densely populated countries. Total reduced sulfur (TRS) have gained much attention over recent decades for their involvement in malodor and health problems and for their potent role in global climate change. (Susaya *et al.*, 2011)

Various studies number of studies have described the emission of anthropogenic TRS in relation to their source processes and malodor problems (Kim *et al.,* 2006a, b). The results of these studies indicate that the main sources of TRS are: landfill areas (Kim *et al.,* 2006b; Lee *et al.*, 2006; Song *et al.,* 2007), livestock production systems (Blanes-Vidal *et al*., 2009; Schiffman *et al*., 2001), and industrial settings (Kim *et al.*, 2006a; Muezzinoglu, 2003; Nunes *et al.,* 2005; Song *et al.,* 2008). The results of previous studies generally confirm that the relative contribution of TRS, particularly H_2S, in malodor phenomenon is prominent (Kim *et al.*, 2006a; Pal *et al.*, 2009). One of the main industrial activities that generate H_2S are de cellulose mills (Ramos Rincon *et al.,* 2018).

Air quality modeling plays an important role in prediction of air pollutants in urban areas. The dispersion simulation of H_2S has been studied by Llavador Colomer, *et al* (2012), describing the experimental and modelling work being

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carried out by CEAM-UMH in the surroundings of several wastewater treatment plants (WWTPs) located in the Valencia Autonomous Community (Spain). This work permitted the estimation of H_2S emission rates at different WWTPs under different environmental and operating conditions. Our methodological approach for analyzing and describing the most relevant aspects of the olfactory impact consisted of several experimental campaigns involving intensive field measurements using passive samplers near several WWTPs, in combination with numerical simulation results from a diagnostic dispersion model.

In the same way Baawain *et al.* (2017), used the environmental protection agency (EPA) regulatory model (AERMOD) in order to assess the urban air quality in the city of Muscat, Sultanate of Oman, for the prediction of hydrogen sulfide (H_2S) emissions, a neighborhood claimed issue, from Al-Ansab sewage treatment plant.

Ribeiro Augusto *et al* (2019) analyzed the emission and dispersion of hydrogen sulfide gas (H_2S), odor indicator, produced during the anaerobic treatment of wastewaters, using WATER9 and AERMOD models for two distinct events. Results show a good performance from the model in comparison to the observations.

These researchers have been studied the local dispersion of H_2S passive emission, derivate of the wastewater treatment, applying Gaussian dispersion models; however, to know the regional impact of the H_2S emission, generated by industries, is necessary use Large Eddy Simulation.

According with this, Aguirre (2005), has modified Advance Regional Prediction System (ARPS), coupling the equations of the Eurelian method to resolution of LES and the Lagrangian stochastic (STO) method to simulation of small scales, that permit simulate the fluid particle trajectory. Aguirre *et al.*, (2006 a,b) validated this model, through a wind tunnel experience.

This model allows coupling diffusion and chemical reaction models. Initially Aguirre *et al.* (2006 a,b) incorporated to the model the chemical reaction within nitrogen oxides, emitted by a point source, and ozone present in the atmosphere to estimate the concentration at 2.50 m. Then, Aguirre *et al* (2014a), applied the model to calculate the concentration at ground level, of solid particulates generated by multiples sources, incorporating the gas outlet velocity calculation, but without consider the chemical transformation.

However, the complete model, has not been applied to the study of gaseous particles, considering active and passive emission, multiples sources (point and diffuses), and species chemically reactive in the atmosphere. For that reason, at the present work, incorporate a chemical reaction to ARPS to simulate de transformation of H_2S, gaseous emission, in the atmosphere, considering the three active point sources and one diffuse source to estimate de air concentrations at breathing level, comparing the result with air quality measurement.

2. MATERIALS AND METHODS

The ARPS meso-scale model has been developed by the Center for Analysis and Prediction of Storms (CAPS) at the University of Oklahoma (USA). It is non-hydrostatic and compressible type and was originally used for storm monitoring since it has sub-models of heat flow and water vapor, cloud formation and precipitation. It considers the orography and land cover as well as the initial conditions of both the soil and the atmospheric boundary layer. (Aguirre *et al.*, 2014b) In this work is used de version code 4.5.2.

From the point of view of numerical resolution, the calculation is based on the finite differences method centered on an Arakawa C-grid cell and uses a curvilinear coordinate system that follows the terrain undulations. The atmospheric model takes into account the compressibility of the flow. The presence of acoustic waves due to variations in air density limits the time step of explicit numerical resolution. (Aguirre *et al*., 2014b)

For simulating atmospheric turbulence is used a global Eulerian code LES (Large Eddy Simulation) in order to obtain a description of the behavior of large scales. LES with the dynamic Smagorinsky–Germano subgrid-scale (SGS) model is used to study passive and reactive scalar dispersion in a turbulent boundary layer. Instead of resolving the scalar transport equation, fluid particles containing scalar are tracked in a Lagrangian way. The Lagrangian velocity of each fluid particle is considered to have a large-scale part (directly computed by the LES) and a small-scale part. A three-dimensional Langevin model gives the movement of fluid elements, containing scalar at a subgrid level. The stochastic model is written in terms of SGS statistics at a mesh level. Diffusion is taken into account by a particle pairing exchange model. (Aguirre *at al.,* 2006b)

The advantages of using the STO model for the monitoring of fluid particles in the simulation of the atmospheric dispersion of pollution, is the possibility of easily introducing models of diffusion and chemical reaction by contact between fluid particles carrying species that exchange between they part of their concentration. This type of contact models has been used initially for the resolution of combustion problems or in the engineering of industrial processes. (Curl, 1963; Dopazo, 1975, Pope, 1976).

Lagrangian models are efficients for short-range simulations. However, long-range simulations require the calculation of a large number of single trajectories that rapidly increases the computational cost. Nested models use Lagrangian approach near the source and interpolate the concentration field to Eulerian grid at a given distance to perform large-scale Eulerian simulation. (Leelossy *et al.,* 2014).

Coupled models of diffusion and chemical reactions have been introduced in the LES-STO simulation code to obtain a complete model (MC) that allows consider both processes for each time step. Thanks to this, the instantaneous values of

concentration levels of chemical species and their distribution space in an episode of pollution. (Aguirre *et al,* 2006a).

ARPS was adapted by Aguirre *et al.* (2014b) to be force to Boundary Layer Model, (BLM), which was specially developed to study the atmospheric circulation in low layers over the Río de La Plata estuary and its area of influence. It is three-dimensional and is formulated in primitive equations based on the three physical principles that govern atmospheric motion, that is, conservation of linear momentum, conservation of mass, and conservation of energy. (Berri, Sraibman, Tanco and Bertossa, 2010).

The ARPS model forced by BLM was validated by Aguirre *et al.* (2014b) and Orcellet *et al.* (2016), through the measured obtained by three local weather stations.

The calculation of gas exit velocity, was incorporated to APRS model, by Aguirre *et al.* (2014a), applied the Beournoulli theorem, considering the exhaust gas temperature, wind speed at chimney level.

2.1 Study case

Social complaints about bad odors associated with reduced total sulfur (TRS) compounds from the pulp mill located in Fray Bentos, Eastern Republic of Uruguay (ROU), are recurring in the coastal areas of the Uruguay River in the neighboring city of Gualeguaychú, Argentina.

This industry produces cellulose pulp, the basic process of which is the removal of lignin, through the chemical method called Kraft. It consists of debarking the pieces of wood and then reducing them to chips. Such chips are transported through belts to reactors, called digesters, where they are cooked with sodium hydroxide, sodium sulfide and calcium carbonate (white liquor), at 200°C and high pressure to reduce the pieces to a pulp, dissolving large part of the lignin that binds the wood fibers, thus releasing those fibers. (Cheremisinoff and Rosenfeld 2010).

After cooking, the sulfuric gases are separated to be treated (they are generally incinerated), and the rest of the mixture is filtered by different mechanisms to remove the pieces that have not degraded during cooking. (Cheremisinoff and Rosenfeld 2010).

The cooked product is processed in washing filters. The pulp is rinsed with water to wash away the cooking liquids and recover the used chemical compounds. The paste is filtered and thickened by removing water, where the fibers and residual liquor are separated. The obtained pulp is classified, cleaned, thickened and stored. (Cheremisinoff and Rosenfeld 2010).

The mixture of dissolved wood and chemicals, called black liquor, is usually removed from the washing machine with about 14 to 17% solids. Then it is concentrated through evaporation up to a level of 65% in solids of which between 3 and 5% are composed of sulfur species. (Harper, 1989)

After this process, the black liquor is sprayed into the recovery boiler, which is similar to a conventional boiler, where the wastewater evaporates and the organic material is burned. The inorganic fraction is recovered as sodium compounds. Most of the sulfur is reduced to form sodium sulfide (Na_2S), and the residual sodium is in the form of sodium carbonate (Na_2CO_3).

During the different stages of this process, TRS compound emissions are generated, among which methyl mercaptan (CH_3SH), dimethyl sulfide ($(CH_3)_2S$), dimethyl disulfide ($(CH_3)_2S_2$), and hydrogen sulfide (H_2S) stand out. (Liang, 2008)

These four TRS compounds have the peculiarity of giving off very characteristic odors that are unpleasant for humans, so they are generally called odorous gases. The characteristic odors associated with each of the mentioned TRS compounds are described in Table 1.

Table 1: components of the TRS and description of the characteristic odors. (Arellano García, 2009)

Compound	Odor Description
Hydrogen Sulfide	Rotten egg
Methyl Mercaptan	Onion, garlic
Dimethyl Sulfide	Rotten vegetables
Dimethyl Disulfide	Putrefaction process

H_2S generally represents the highest proportion of gaseous TRS emissions from the Kraft process (40.33%) and is not directly generated in cooking due to its alkaline conditions. This compound is formed in the consecutive process where the black liquor and the washing waters are stored and the pH decreases below 10 and even to lower values and the sodium sulfide present in the liquor dissociates and becomes H_2S. (Liang, 2008)

This substance characterized by having an unpleasant odor (similar to "rotten egg"), generates discomfort in the population in concentrations greater than 0.7 μg m^{-3}. (Ecometrix, 2006, Arellano-García, 2009)

Likewise, in concentrations of this substance, above the detection threshold, different health effects may be manifested, these being proportional to the increase in concentration, causing from slight eye irritation to death. (Beauchamp *et al.* 1984)

Orcellet et al, (2016) carried out an initial study on the dispersion of these TRS compounds in the Uruguay River region, which concluded that the odor episodes registered in the area coincided, in most of the cases studied, with the simulate plume.

This model is specific to simulate the transport and dispersion of pollutants in that area, since its geographical characteristics require the adaptation of a model on a regional scale that allows the details of atmospheric circulation to be accurately represented in low layers. However, this work only involved the study of physical phenomena of atmospheric transport and diffusion, without considering the chemical

reactions that mediate the transformation of TRS compounds once emitted. (Orcellet, et al. 2016)

The study area was defined considering the location of the main possible Argentine receivers, which are: Gualeguaychú city (27 km), General Belgrano Village (24 km), Ñandubaysal Beach (12.5 km) and finally the International Bridge (2 km). (Fig. 1)

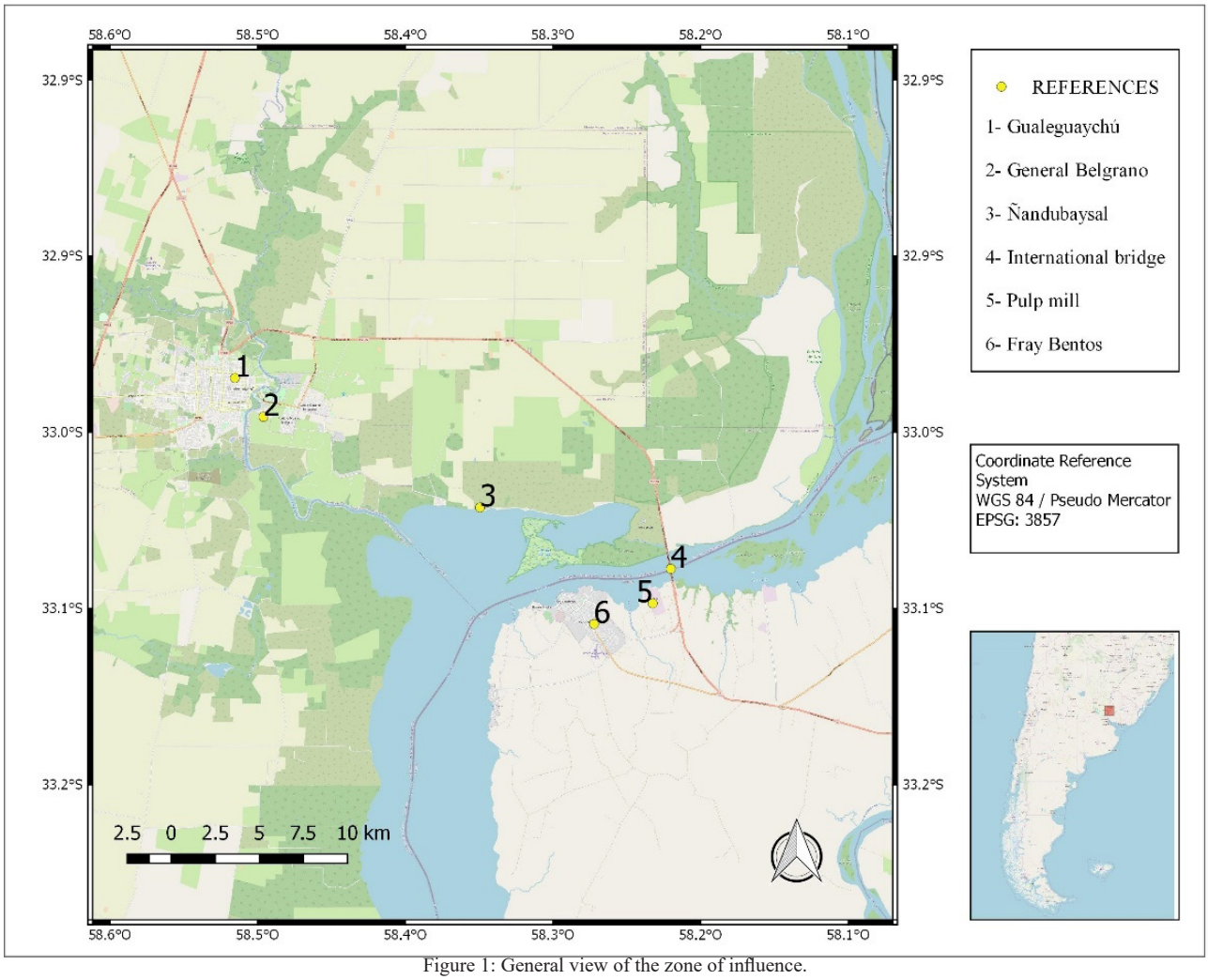

Figure 1: General view of the zone of influence.

Of the point sources of the pulp mill, the following stand out: recovery boiler, lime kiln and concentrated non-condensable gases boiler (CNCG) + diluted non-condensable gases bypass (DNCG), CNCG boiler and DNCG bypass. The characteristics of each of them are detailed in table 2.

Table 2: physical characteristics of emissions and physical properties of the output gases

Source	Chimney Height (m)	Chimney Diameter (m)	Output Speed (m s^{-1})	Output Temperature (°C)	Wet Volume (m^3 s^{-1})
Recovery Boiler	120	4.6	22	160	340
Lime Kiln	120	2.5	14	220	68
CNCG boiler + DNCG bypass	120	1.5		50	
DNCG boiler	120	1.2		300	
CNCG bypass	120	0.3		300	

The coordinates of the main chimney are: 58°15'36''W and 33°07'00''S. Several individual chimneys corresponding to different point sources mentioned in the previous paragraph are located inside a large concrete structure.

In addition, since various studies have shown that the liquid effluent treatment systems of pulp mills are an important source of H_2S emission, generated from the anaerobic decomposition of sulfates and sulphites. This study incorporates diffuse emission source. (Rava, 2008), (Hoa *et. al.*, 1996).

In this case, the surface considered to carry out the simulation is estimated at 70.650 m^2, since the complete system of liquid effluents is considered as a single diffuse source. Emissions in this case are considered at ground level, with zero output speed and ambient temperature.

The table 3 shows the annual average TRS emission rates, in mg s^{-1}, considered to perform the simulations.

Table 4 presents the two modeled events, in which the Environmental Monitoring Plan (EMP) of the city of Gualeguaychú, registered episodes of contamination by unpleasant odors, which are on October 12 and November 30, 2009. Likewise, for each event the concentrations of H_2S measured at the time of the verification are detailed.

2.2 Model data

The meteorological data were the product of the BLM, executed daily by the National Meteorological Service (NMS), forced on a regional scale from the daily operational forecasts of the Eta / NMS model, to generate 24-hour forecasts. In this study, the outputs used were wind speed and direction values, organized in a spatial grid of resolution of 1 kilometer for each hour throughout a day.

ARPS incorporate as initial conditions, surface data (vegetation type, normalized vegetation index and roughness), soil type, surface temperature and digital elevation model.

The surface data were obtained from the Landsat 5 satellite image, obtained from the National Institute for Space Research (INPE) of Brazil, for November 19, 2009, as it is the closest to the study period. The visible and near infrared spectrum bands have a spatial resolution of 30 meters, while the thermal infrared band has a spatial resolution of 120 meters. The spatial resolution was taken to 1 km and the information of relevance for the specific study area and the requirements of the model was obtained. At the end of this process, the files are obtained in the valid format to run the subroutines of the model and generate the input data. The terrain elevation model (DEM) of the study area was obtained from the U.S. database Geological Survey.

With the bands of the energy spectrum corresponding to the near infrared, red and green, a classification is made through the cluster analysis which allows differentiate types of coverage through the patterns of reflectance. From the classified image, land cover data such as the type of vegetation in rural areas, urban areas and areas covered by water were obtained, bringing the spatial resolution to 1 km, in order to match with the BLM data.

These vegetation types were taken into categories according to the Olson World Ecosystem Classes typology (Olson *et al.* 1985) and from the correspondence proposed by the authors, the ground roughness parameter map was obtained.

To obtain the Normalized Vegetation Index (NDVI), the data from the Moderate Resolution Imaging Spectroradiometer (MODIS) sensor mounted on the TERRA satellite, were used. These were purchased from the Land Processes Distributed Active Archive Center (LP DAAC) database of the USGS / Earth Resources Observation and Science (EROS) Center, Sioux Falls, South Dakota (http://lpdaac.usgs.gov/get_data). The values of energy emitted by the elements of the earth's surface obtained from the LANDSAT 5 satellite image in the thermal infrared band were taken to temperature values following the methodology proposed by Jiménez Muñoz *et al (*2010).

2.3 Chemical reaction

The reaction between the H_2S and OH species has been sufficiently studied (Baulch et al., 1982; Grosjean et al., 1984; Seinfeld, 1986), the products thereof are known as well as the residence times in the atmosphere. However, these reactions are based on estimated OH concentrations of the order of 1.0 * 10 ^{6} molecules per cm^3, (4.06 * 10 $^{-8}$ ppm) considering averaged daily mean global in the boundary layer. (Atkinson, 2000).

For the study of this case, the model for the simulation of the chemical reaction represented in Eq. (1) was adapted:

$$H_2S + OH \rightarrow H_2O + SH^- \quad (1)$$

Where: H_2S: hydrogen sulfide molecule; OH: oxydryl radicals; H_20: water molecule; SH^-: sulfhydryl group.

It represents the direct reaction of H_2S emitted from the source, when it comes into contact with the OH radicals present in the atmosphere. In this case, the inverse reaction is not considered, since what we propose to obtain is the direct variation of the H_2S concentration.

The variations in the concentration levels of the H_2S, OH, SH- species within each fluid particle *p* are simulated using the system of Eq. (2);

$$\begin{cases} \frac{d[H_2S]}{dt} = -k[H_2S][OH] \\ \frac{d[OH\ ]}{dt} = -k[H_2S][OH] \\ \frac{d[H_2O + SH^-]}{dt} = k[H_2S][OH] \end{cases} \quad (2)$$

Where: k: is the direct reaction constant and is equal to 1.30*10^2 (ppm^{-1}, s^{-1}) (Baulch et al. (1982). The atmospheric concentration of the OH radical is estimated at 4.06 * 10 $^{-8}$ ppm.

Table 3: annual average emission rate (g s^{-1}) under normal operating conditions for point and diffuse sources. (Orcellet et al, 2016)

Point and diffuse sources.	TRS mg s^{-1}
Recovery boiler	4730
Lime kiln	490
DNCG gas boiler CNCG gas boiler	430
Wastewater treatment	60
Total	5650

Table 4: date, time, and location and H_2S measured concentration to the modeled events.

Date	Time	Place	Lat - Lon	H_2S concentration µg m^{-3}
Oct 12 2009	09:00 - 10:00	International Bridge	33° 5’56.71”S, 58°14’54.73”O	1.37
Nov 30 2009	16:00 - 17:00	International Bridge	33° 5’56.71”S, 58°14’54.73”O	2.27

Table 5: annual average emission rate of H_2S (mg s^{-1}) under normal operating conditions for point and diffuse sources.

Point and diffuse sources.	H_2S mg s $^{-1}$	Nº particles
Recovery boiler	1907.61	8.29
Lime kiln	197.61	0.85
DNCG gas boiler CNCG gas boiler	173.49	0.75
Wastewater treatment	24.19	0.1
Total	2302.89	10

2.3.1 Hydrogen sulfide emissions

The H_2S emission at the chimney mouth is obtained by multiplying the value of the total TRS emission (5710 mg s^{-1}) (Table 3) by the proportion that this substance represents (40.33%), which results in 2302.89 mg s^{-1} of H_2S. (Table 5).

To estimate the concentration in the chimney mouth, the emission value is divided by the volume of the calculation cell, 4.5 * 10^5 m^3, resulting in 5.11 * 10^{-3} mg m^{-3}, (3.91 * 10^{-3} ppm).

Simulations performed with the ARPS model require long times to run for short periods for this, the time step considering was of 0.5 seconds, to decrease the instabilities of the model and guarantee the reaction time between species. The number of fluid particles emitted was established in 10 per second (5 per of time step), so that the weight of each fluid particle is estimated in 230 mg. The distribution is presented in the table 6.

The number of fluid particles distributed in each calculation cell is used to estimate the H_2S concentration, applying Eq. (3):

$$C = (n\ wp) / V \quad (3)$$

Where: C: is the H_2S concentration; n: is the number of particles in each cell resulting from the model; wp: is the weight of each particle in µg; V: the volume of each cell in m^3.

3. RESULTS

In this work, a new chemical reaction was incorporated to ARPS model, to calculate the H_2S concentrations of two events, in order to compare the results obtained by the measurement realized in the places, and the original ARPS version. The plume shows at the figures, represents the hourly average at a height of 1.50 m (average respiration level - immission).

For the event on October 12, 2009 the concentration, from 9:00 a.m. to 10:00 a.m in the place where the EMP registered the complaint (International Bridge), calculated by the model is in the range of 1.5 to 2 µg m^{-3} (Fig. 2), that is, it exceeds the odor detection threshold established for this substance (0.7 µg m^{-3}). Likewise, the concentration estimated by the model is very close to that obtained from the analyzed sample, equal to 1.37 µg m^{-3}.

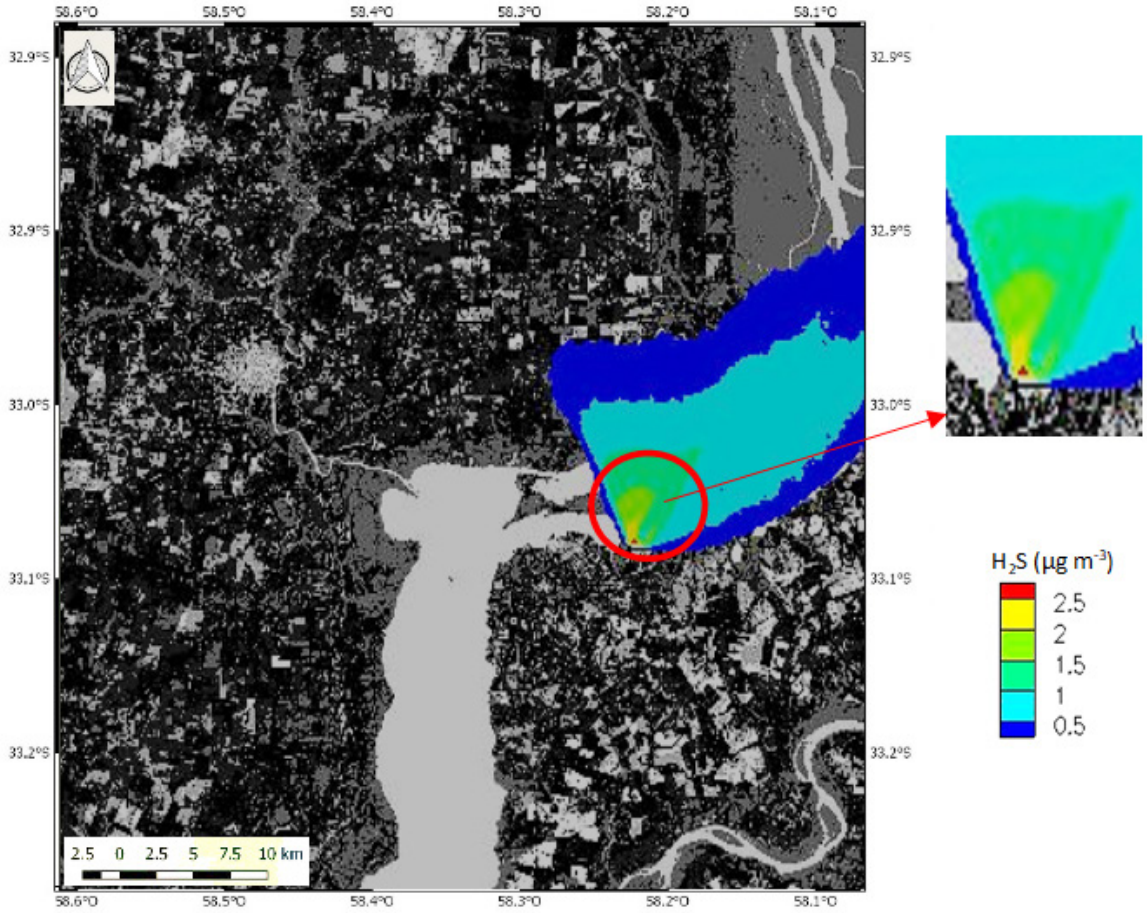

Figure 2: H_2S concentration in µg m^{-3} calculated on October 12, 2009 from 9:00 a.m. to 10:00 a.m., by the ARPS with chemical reaction.

The results of the modeling carried out for November 30, 2009, from 4:00 p.m. to 5:00 p.m. show that the concentration calculated by the ARPS model, (Fig. 3). In the area where the complaint was registered, is of the order of 2 µg m $^{-3}$, which exceeds the value of the odor detection threshold established for H_2S and coincides with the result of the analyzed air sample (2.27 µg m $^{-3}$).

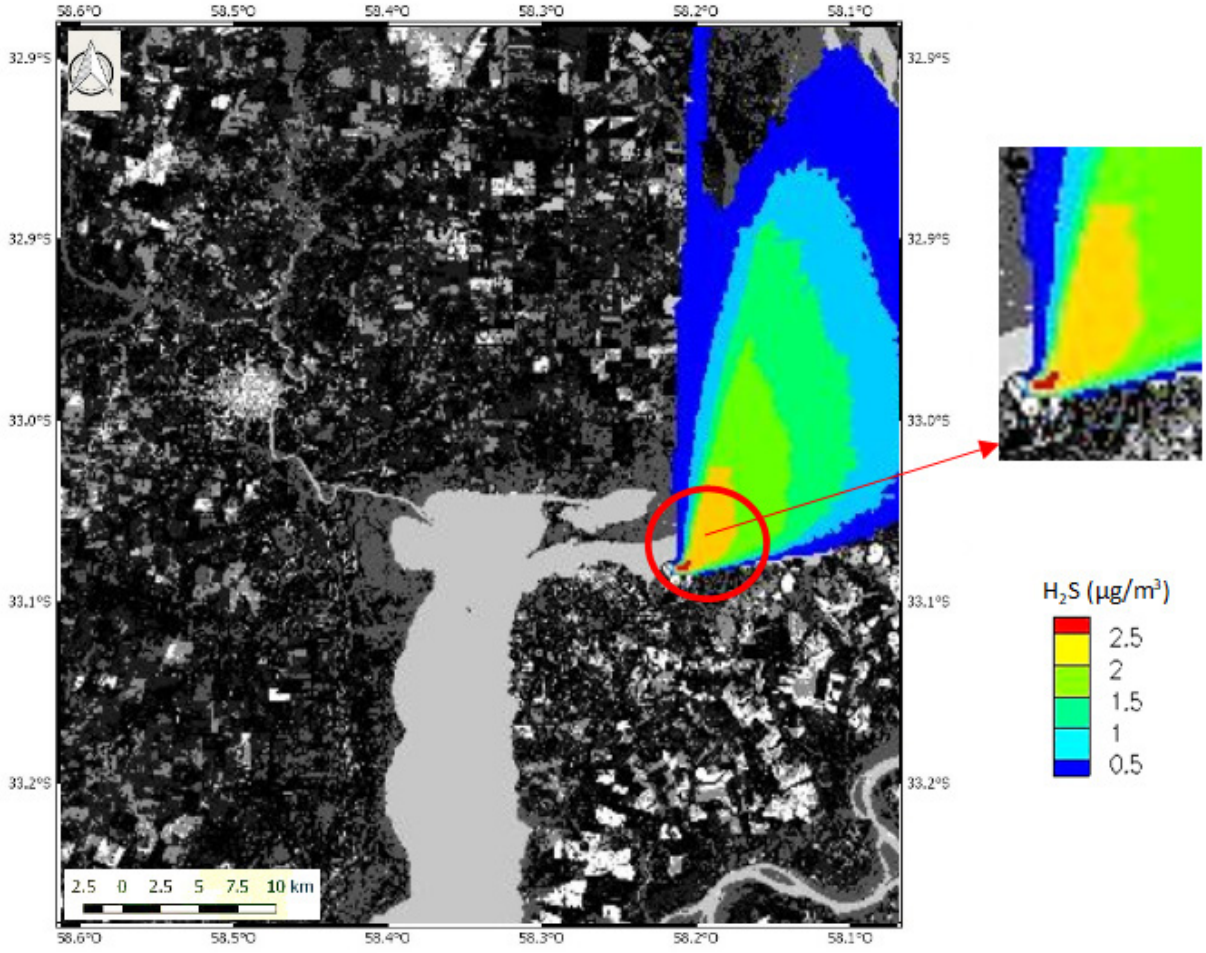

Figure 3: H_2S concentration in µg m $^{-3}$ calculated on November 30, 2009 from 4:00 a.m. to 5:00 a.m., by the ARPS with chemical reaction.

Complementary, the results are compared with those got by Orcellet et al., (2016) with the original version of ARPS. It is important mentioned that in both version the same input data was used.

In the Fig. 4, is possible to appreciate the difference in the plume transverse extension. This is because the original version, simulate the dispersion of a conservative pollutant, no decay, so the substance is transported by the wind further away. In change, the new version includes the substances chemical parameter and incorporate the main atmospheric reaction, so the pollutant is transported and transformed, during the modeling time, according with the direct reaction constant.

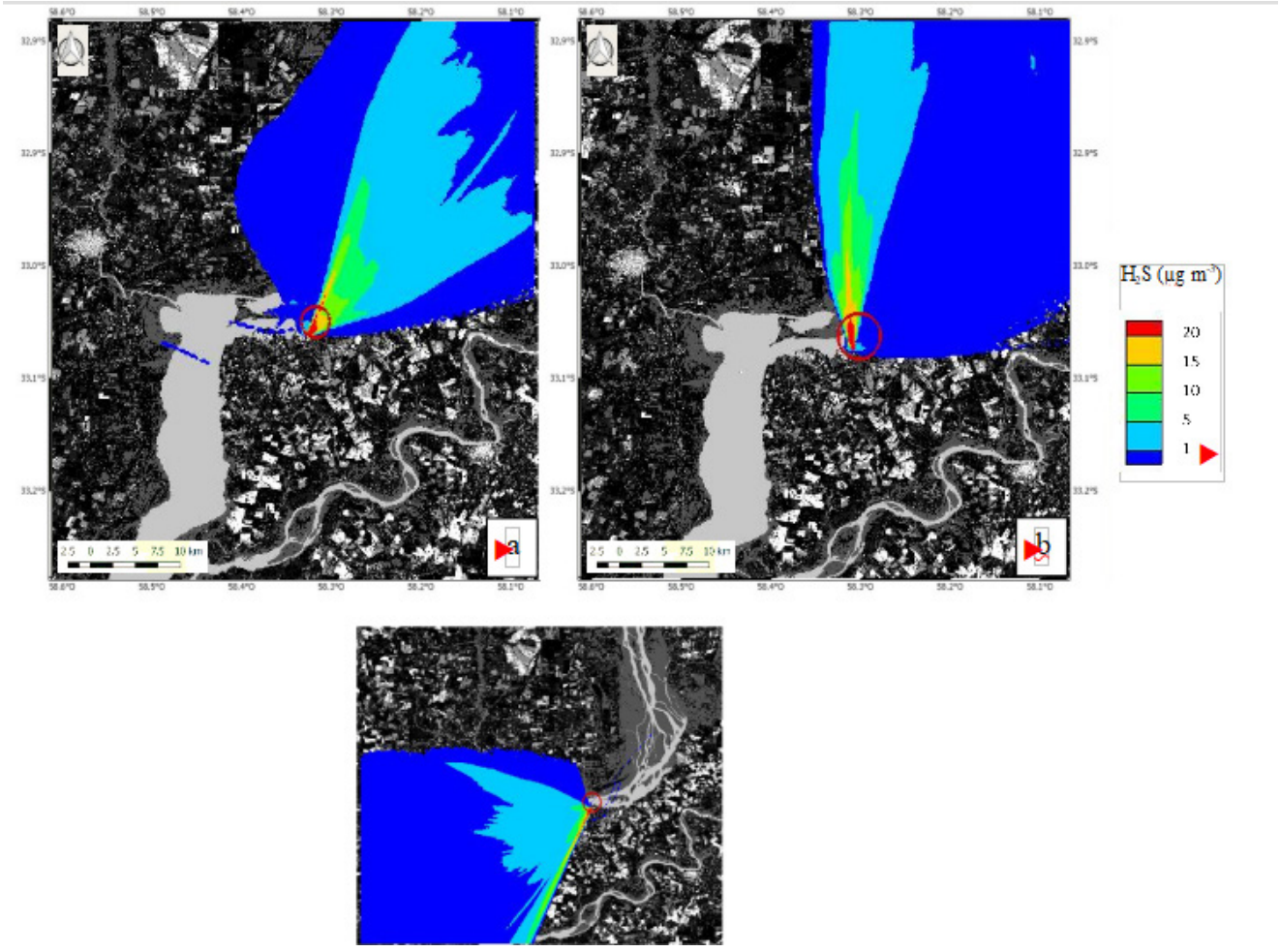

Figure 4: H_2S concentration in µg m^{-3} calculated on: a) October 12, 2009 from 9:00 a.m. to 10:00 a.m and b) November 30, 2009 from 4:00 p.m. to 5:00 p.m., by the original ARPS version. (Orcellet et al., 2016)

Likewise, the concentration of H_2S obtained by de the original version are greater than the chemical version, in the events simulated. Specifically, in the complaint record place, the concentration is ten time higher, than the values measured by de EMP

In change, the H_2S values estimated by the ARPS chemical model are very close to the actual concentrations resulting from the analysis of the air samples obtained by the EMP at the time the complaint was verified.

Table 6 shows a summary of the results obtained for the two events for each model.

Table 6: comparison of the concentrations calculated with ARPS model in both version, air concentration of H_2S in µg m^{-3}, measured by EMP and odor threshold.

Date	ARPS chemical raction	ARPS original	H_2S Concentration	Odor threshold
Oct 12 2009	1.5 - 2	> 20	1.37	0.7
Nov 30 2009	2-2.5	> 20	2.27	0.7

4. DISCUSSION

The ARPS model constitutes a complex atmospheric modeling system of regional scope, which involves specific variables (topographic, meteorological, etc.) generated for the purposes of the case study. Above all, the potentiality of the use of this model for the areas of the Río Uruguay where the geographical conditions originate particular phenomena of transport and dispersion of pollutants stands out.

In this work, completely ARPS model is used, considering multiple sources, gas exit speed, chemical transformation and forecast meteorological data specific to the region.

The study case corresponds to pulp mill gaseous emission and consider all H_2S three active point sources and one diffuse source).

The incorporation of all the H_2S sources allows simulate the total gaseous release, applying the calculation of gas exit speed to the active emission of point source and passive emanation of diffuse source. In this way, the plume simulates correspond to the total average emission H_2S for the time considering (one hour) at 1.50 m level.

The events of bad odor are evaluated to check the plume impact and the concentration levels.

The result show that in the two events studied, the plume affects directly the place (International Bridge) where the complaint was recorder. The H_2S concentrations, calculated by ARPS model to the October 12 and November 30, 2009, are higher than the established odor threshold, for this reason the bad smell could have been perceived by the local population. Likewise, the range of values obtained by the model simulation include the values measured on site.

Complementary, comparing these result with those of the original version, it possible check that this last, overestimate the plume extension and the concentration values, for that its use would be limited to simulate conservative pollutant. In this case, the model uncertainty, are considered similar, because use exactly the same input data, for that, the difference in the results cannot be attributed to it.

In conclusion, comparing the two models presented, ARPS model with chemical reaction, is the better free and unregister alternative to predict concentration of reactive substances.

This version of ARPS model, has the potentiality to be used in zones with similar geographic characteristics. Likewise, ARPS model is an open code, write in Fortran 77, so it is easily editable, for that it is possible modify the meteorological condition and complex terrain data to apply the version in different studied cases. Multiple chemical reactions can be included without additional scalar equations, in order to estimate the concentration of other reactive species.

CONCLUSIONS

A turbulent boundary layer flow is computed using the LES code ARPS 4.5.2. A LES coupled with a Lagrangian stochastic model has been applied to the study of reactive scalar dispersion downwind of a localized source of H_2S. This model, that simulates atmospheric transport and diffusion of pollutant, allows calculating the concentrations of the compound of interest taking into account, chemical transformation reactions in the atmosphere.

The results of this model application provides good description of the plumes for event of bad odor records in the zone.

The ability to incorporate weather forecast information, generated to the specific region, to forced meteorological conditions of ARPS, allows obtain better results, applying this preventively.

Comparing the results with those original version, is possible to appreciate the difference in the plume transverse extension. This is because the original version, simulate the dispersion of a conservative pollutant, no decay, so the substance is transported by the wind further away. In change, the new version includes the substances chemical parameter and incorporate the main atmospheric reaction, so the pollutant is transported and transformed, during the modeling time, according with the direct reaction constant.

The values resulting from the analysis of the air samples, obtained at the time of the verification of the registered complaints, are within the concentration range estimated by the new model version; however, the original version

overestimate the values. Which allow affirming that the chemical reaction model specifically adapts to the simulation of these events, could be used to predict possible episodes of bad smells.

This model is presented that as an alternative to the widely used, Gaussian models, considering that these last, provide poor results in situations with low wind speeds, where the three-dimensional diffusion is significant. Unfortunately, these situations have proven to be the most dangerous ones in real-life atmospheric dispersion problems as they are often connected to a stably stratified atmosphere or low-level inversions.

The model is a free, unregister, valid and useful tool to simulate atmospheric pollution episodes that involve non-conservative pollutants, that is, chemical species that, when in contact with the atmospheric components, react, and giving rise to the formation of other compounds. Likewise, ARPS model, is an open code, it can be easily modified, and adapted to particular conditions, so constitutes an instrument of environmental impact assessment and environmental risk analysis.

It is possible used the developed modeling system in cases of diagnosis and prognosis of real situations and even emergencies, with an appropriate level of precision for studies of this type.

DECLARATIONS

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Competing interests: the authors declare that they have not had competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability: the data generated and analyzed during the current study are available from the corresponding author on a reasonable request.

Code availability: code application is free

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