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ESTIMATION OF SHORT ODOR EVENTS BY USING CHEMICALLY REACTIVE ODORANTS ATMOSPHERIC DISPERSION MODELLING AROUND A PULP PAPER MILL

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Abstract: Odor episodes control due to low threshold perception odorants, as H_2S, is extremely difficult, as they are detected in very low concentrations. Traditionally, pulp paper mills using Kraft process produce TRS (Total Reduced Sulphur) odorants emissions, so their environment can be affected by odors. A model-based operational odor forecast system, namely *PrOlor*, was developed, tested and applied around ENCE-Pontevedra paper pulp mill in order to prevent any short odor event (less than 1 hour). This system includes WRF model coupled to CALMET model, to provide meteorological inputs to CALPUFF model. Both surface wind and temperature WRF and CALMET models outputs were validated against surface measurements, and statistics calculated by Openair software usually accomplished valid ranges. About CALPUFF performance, estimated odorant ground level concentrations were converted to short odor event intensity applying both peak-to-mean approach and Steven's Law. When forecast short odor events were compared to the 34 short odor events registered, 32 of them were caught by PrOlor.

Key words: *Odorants, Total Reduced Sulphur (TRS), Pulp Paper Mill, WRF, CALMET/CALPUFF*

INTRODUCTION

The use of atmospheric models to prevent odor events around wastewater treatment and industrial plants is increasing and improving nowadays (Carrera-Chapela et al., 2014) ENCE-Pontevedra paper pulp mill developed along the last six years several investments in order to reduce systematically its TRS emissions, to avoid persistent odor around it. However, due to the changeable conditions of its environment, the possibility of short and sporadic odor events (from seconds to minutes) remains.

In this work, PrOlor system is presented as an odor forecast system to prevent short odor events, based in WRF and CALMET/CALPUFF modelling systems. Models results were tested against meteorological measurements and qualitative environmental odor observations.

MATERIALS AND METHODS

PrOlor is a software system based in different atmospheric models running on Linux systems. For its feasible application, PrOlor includes a web-based interface for data analysis, daily odor forecast e-mail reports to the paper pulp mill staff by e-mail, back trajectory analysis and, also an app for mobile devices to check the zones where the odor thresholds should be superseded.

About the mathematical models and datasets applied, Figure 1 shows a flow diagram of PrOlor system. GFS model from US NCEP daily provides the input dataset to WRF (Weather Research & Forecast) model (Skamarock and Klemp, 2008), with the following physics parameterizations: Longwave RRTM (Radiation), MM5-Dudhia (Shortwave), YSU (with sfclay: Monin-Obukhov from MM5 MRF) for PBL, 5 layer MM5 LSM (Surface), Kain-Fritsch (Cumulus), and WSM6 for Microphysics. WRF is applied over four nested domains (Figure 2a) around the study area, with different horizontal resolutions: D1 (36x36 km^2), D2 (12x12 km^2), D3 (4x4 km^2), and D4 (study area, 1.3x1.3 km^2).

Using CALWRF interface (Figure 1), WRF forecast is applied as input dataset to CALMET (v. 6.334) meteorological diagnostic model (Scire et al., 2000a), to get hourly meteorological fields over the study area (D4 domain) with 250x250 m^2. This CALMET setup includes IKINE (kinematic module) and IOBR (procedure for adjusting vertical velocity) options. As Digital Elevation Model (DEM), Spanish Geographic Centre (CNIG) LIDAR 5x5 m^2 resolution elevation dataset is applied; 22 different land use categories, following the Land Cover Classification System (LCCS), are considered from the Global Cover Characterization (GLCC) dataset with 300x300 m^2 resolution Also, 12 vertical layers up to 4000 m are applied, with a telescopic distribution (thinner layers close to the surface) (Gonzalez et al., 2015).

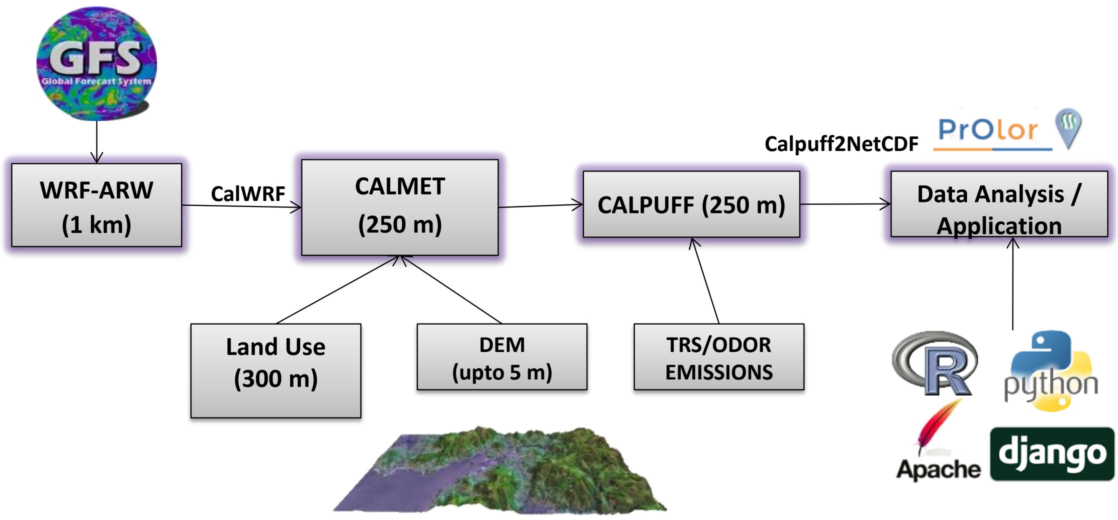


Figure 1. General scheme of PrOlor system, showing the models, input dataset, and data analysis and application modules.

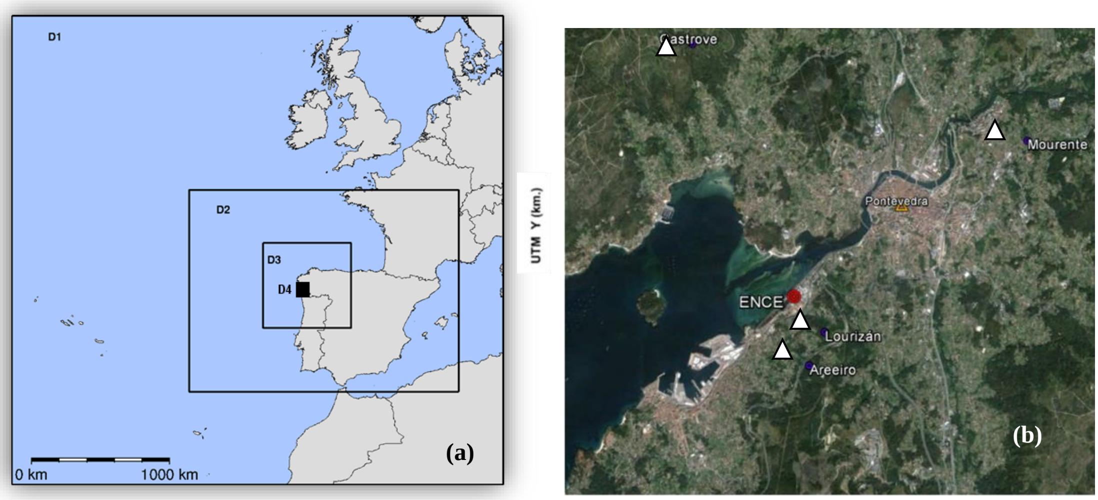


Figure 2. (a) WRF model nested domains at four different horizontal resolutio UTM X (km.) ler to achieve up to 1.3x1.3 km^2 resolution over the innest D4 domain; (b) study area (D4 domain), with location of the ENCE paper pulp mill, the four surface meteorological stations, and Pontevedra town urban area.

CALPUFF (v. 6.42) (Scire et al., 2000b) Lagrangian dispersion model setup default options are selected, except for chemistry. First order chemical decay of each odorant is calculated during the CALPUFF simulation, considering typical atmospheric average lifetimes per odorant (Liang, 2008). As CALPUFF input, mean steady state TRS chemical emissions measurements from 3 point sources (stacks) and 4 area sources (water treatment plant) at the paper pulp mill were measured by using a Chromatech MEDOR

TRS model C51000 chromatograph. In these measurements H_2S and DMS were detected; otherwise, none significant DMDS and Methyl-SH emissions were observed.

As its main output, CALPUFF produces hourly odorants concentrations and odor levels are obtained over the same 3-dimensional grid applied in CALMET. These concentrations are applied as input dataset to estimate hourly odor levels by using the Stevens' Law (Gostelowrn et al., 2001). Also, as CALPUFF outputs are obtained in hourly-basis, short odor events (less than 1 hour) are estimated by using the peak-to-mean ratio, Eq (1) (Smith, 1973; Piringer et al., 2012),

$$\frac{C_p}{C_m} = \left(\frac{T_m}{T_p}\right)^U \qquad (1)$$

where C_p is the mean odorant concentration over the T_m integration time (typically, 1 hour), C_m is the peak (short) concentration, T_p is the integration time for C_p (typically, 30 seconds), and U depends on the atmospheric Pasquill stability (Piringer et al., 2012).

Finally, TRAJ2D back-trajectory module is applied to analize the origin of odor events, by using CALMET output and WIND2D processor.

RESULTS
PrOlor system runs every day to obtain an odor forecast 72 h in advance, and both average and peak hourly odorants concentrations (µg/m^3) and odor levels (OU/m^3) are predicted.

Both WRF and CALMET meteorological validations were done, from April, 1st 2014 to August, 31st 2014, against four surface meteorological stations measurements at the study area (Figure 2b); also, CALPUFF odor levels are validated against short odor events olfactometric observations (qualitative) at the study area.

About meteorological validations, hourly average wind speed and direction, temperature and relative humidity surface measurements were compared to both forecast results from WRF innest domain (D4) and from CALMET domain in "NOOBS" mode using WRF-D4 domain as CALMET input. Unfortunately, from the four meteorological surface stations available, only Castrove site provides valid wind measurements during this period; as other sites are affected by obstacles and they don't accomplished criteria for a valid winds validation.

Table 1. Statistics of hourly surface wind speed of WRF and CALMET results against measurements at Castrove site, 04/01/2014-08/31/2014. Green: pass benchmark; red: does not pass benchmarks. Absolute statistics in m·s^{-1}.

Model	n	FAC2	MB	MGE	NMB	NMGE	RMSE	r	COE	IOA
WRF	3672	0.60	-0.25	2.15	-0.07	0.57	2.96	0.32	0.03	0.52
CALMET	3672	0.77	-0.37	1.46	-0.10	0.39	2.03	0.73	0.34	0.67

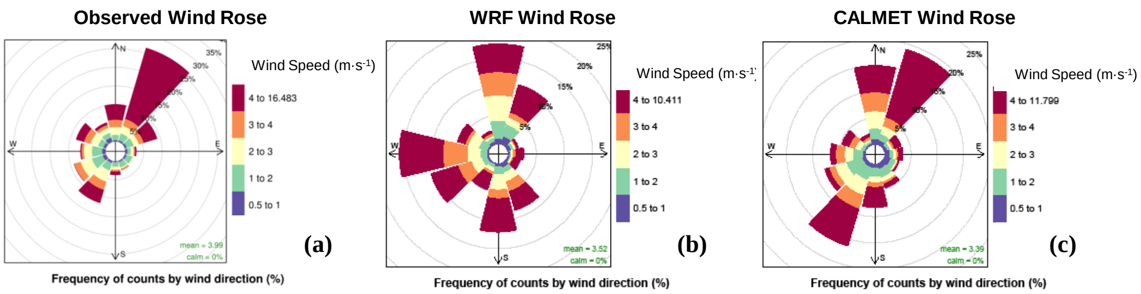
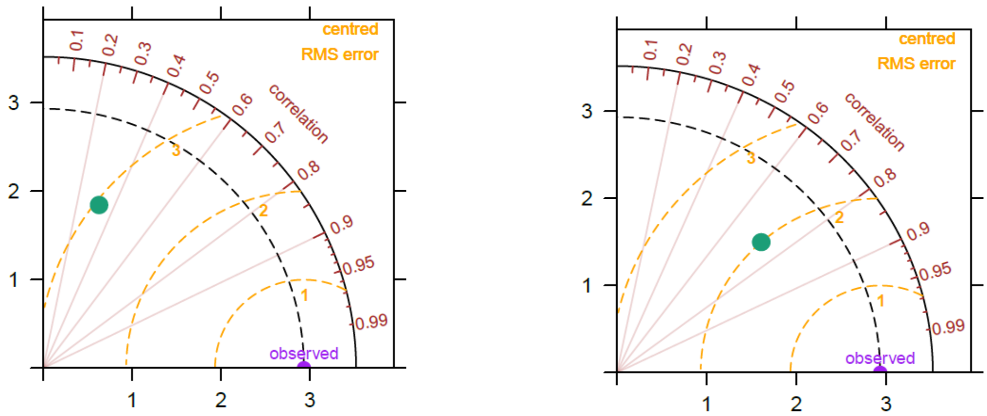


Figure 3. Wind roses at Castrove site: (a) observed, (b) WRF model, and (c) CALMET model, 04/01/2014-08/31/2014

Validation dataset was calculated by using Openair module of R freeware software (Carslaw and Ropkins, 2012). The different statistics were recommended by Chang and Hanna (2004) and Emery et al. (2001) for the validation of meteorological models (to be applied as input to air quality models). Table 1 shows WRF and CALMET wind speed outputs statistics against Castrove site measurements: considering Emery et al. (2001) benchmarks, that is, IOA>0.6, RMSE<2.0 $m \cdot s^{-1}$ CALMET output is practically in agreement to measurements (just CALMET RMSE 2.03 $m \cdot s^{-1}$, a bit out of range); and, CALMET statistics always improve WRF statistics. Only WRF MB and NMB are lower than CALMET statistics, but all values are very low, so differences are not significant.

About wind direction, Emery et al. (2001) consider a more liberal benchmark, as low wind speeds can produce unrealistic wind directions. Therefore, a qualitative wind roses comparison is shown in Figure 3 at the Castrove site: again CALMET wind direction frequencies are more similar to the observed wind rose than WRF output, showing the necessity of applying CALMET model with higher horizontal resolution to achieve accurate meteorological fields as CALPUFF input. However, CALMET seems to overestimate northern and southwestern wind speed at this site: these differences also increases the wind speed CALMET RMSE (Table 1), but they can be explained by some barriers around Castrove meteorological tower (mainly, trees), that cannot be considered by CALMET.

Taylor diagrams (Figure 4) also shows the improvement of wind speed CALMET output at Castrove site over WRF output, as a graphical combination of RMSE, standard deviation, and Pearson product moment correlation coefficient (r).



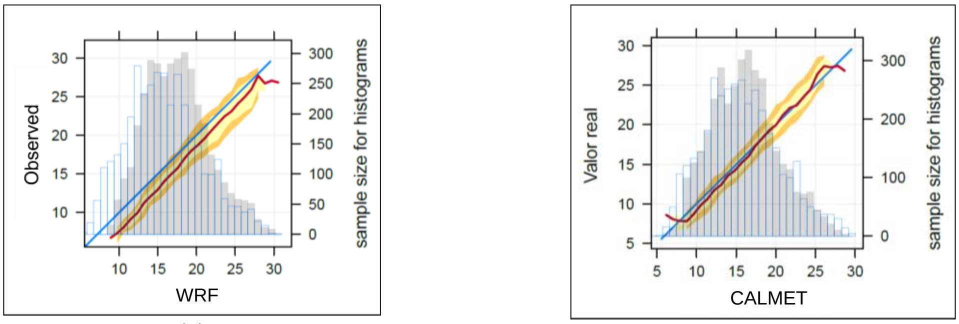
(a) **(b)**

Figure 4. Taylor Diagrams of wind speed at Castrove site: (a) WRF output and (b) CALMET output, against hourly measurements along 04/01/2014-08/31/2014 period.

Table 2. Statistics of hourly surface temperature of WRF and CALMET results against measurements at the four sites, 04/01/2014-08/31/2014. Green: pass benchmark; red: does not pass benchmarks. Absolute statistics in ºC.

	WRF					CALMET				
SITE	**MB**	**MGE**	**IOA**	**RMSE**	**R**	**MB**	**MGE**	**IOA**	**RMSE**	**R**
Areeiro	0.68	1.48	0.80	1.99	0.91	-0.02	1.61	0.78	2.07	0.89
Castrove	1.68	2.04	0.73	2.37	0.94	0.02	1.18	0.85	1.49	0.95
Lourizán	0.30	1.80	0.77	2.38	0.87	-0.03	1.89	0.76	2.42	0.87
Mourente	-0.85	1.76	0.76	2.09	0.91	0.00	1.33	0.82	1.79	0.92

About surface temperature (Table 2), again CALMET provides better statistics than WRF at the four sites, achieving all the statistical benchmarks suggested by Emery et al. (2001): MB<±0.5 ºC, MGE<2 ºC, and IOA>0.7.



(a) **(b)**

Figure 5. Quantile diagrams of surface temperature at Castrove site: (a) WRF output and (b) CALMET output, against hourly measurements along 04/01/2014-08/31/2014 period.

As an example, Figure 5 shows surface temperature quantile diagrams at Castrove site CALMET output histogram (Figure 5b, gray bars) and observed data histogram (blue bars) are more similar that WRF output histogram (Figure 5a, gray bars); also CALMET median (red line), 25/75 percentile (yellow area), and 10/90 percentile (orange area) in Figure 5b are very close to the perfect model (blue line), and closer than WRF results (Figure 5a).

About the odor forecast validation, as odorants ambient concentrations observations are not available, a register of short odor events based in olfactometric qualitative observations from the paper pulp mill staff was set. Every observed odor event was reported to a database using a Smartphone app, to register its time and location. 34 short odor events were reported during the validation period; and, 32 of those events were forecast by PrOlor, near to the reported location and at the same daily period (morning, afternoon, night). For the remaining 2 events, one of them was caused by an accidental increase in H_2S emissions at stripping process.

CONCLUSIONS

Operational ambient odor PrOlor system for the simulation and forecast of short odor events around a pulp paper mill, based in meteorological models (WRF, CALMET) and a CALPUFF Lagrangian dispersion model, was developed and validated around ENCE-Pontevedra paper pulp mill,. About meteorological forecast validation, CALMET output (with WRF output as meteorological input) passed the statistical benchmarks for wind and temperature by Emery et al. (2001). About ambient odor validation, 34 short events were registered along 5 months by the paper pulp mill staff outside its plant; CALPUFF in PrOlor agreed in 32 of those events; and, one of failed event was due to a fugitive H_2S emission from the paper pulp mill, as PrOlor forecast is based in mean historical emissions measurements. Although no explanation was found for another failed event, it could be related to the mixing layer depth estimation, as it is a significant parameter in the short term plume dispersion at the PBL.

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