October , 2019
Subject: Manuscript to Annales Geophysicae

Dear Dr. Petr Pisoft

We are submitting our revised manuscript entitled "**A quasi-experimental coastal region eddy diffusivity applied in the APUGRID model**" to be published as an article in Annales Geophysicae. In the new version of the manuscript, we consider all questions raised by Referee 1 and 2 and provide a detailed item-by-item response to each of the reviewer's comments. Furthermore, we present more clearly the novelty of the paper: *"From the point of view of originality and novelty the present development, from some asymptotic equations and detailed turbulent spectral observations of the surface coastal internal boundary layer, provides a general methodology for obtaining algebraic expressions that reliably represent the eddy diffusivities in the coastal internal boundary layer."* *(line 73- page 3)*. We look forward to hearing about the review outcome.

Sincerely

Reply to Referee #1

First of all, we would like to sincerely thank the Reviewer for the useful comments and suggestions and analysis he gave to the manuscript.

This paper presents new information (eddy diffusivities) derived for a coastal region at southeast Brazil that can be used for air quality dispersion. The results are compared with the Copenhagen Experiment. There are few small mistakes (marked on the attached version). My main question is:

Our responses to the comments are given below:

why to compare results from a tropical region (although coastal) with a mid latitude results (Copenhagen)

The Copenhagen experimental site is limited by the Øresund coast, approximately 7 km east of the TV tower. Therefore, the turbulent effect acting on the tracer dispersion is an environment of the convective internal boundary layer (CIBL). The width of Øresund strait, the water portion separating Denmark and Sweden, is about 20 Km. On the western side of Øresund lies Copenhagen with its urban area. This area has high surface roughness due to the urban character. Thusly, this represents a turbulent environment occurring in a region with relatively cold water and warm land surface. As a consequence, the turbulent structure acting on the tracer dispersion can be considered as one present in the coastal inner boundary layer.

Our quasi-experimental convective eddy diffusivities for a coastal site were derived from the turbulent observations originated by differences in surface temperature and aerodynamic roughness occurring between land and water atmospheric environments. The important characteristic here is the fact that there is a CIBL in the tropical region (Brazil) and also in mid-latitude (Copenhagen). Furthermore, the principal aim of this study does not establish a comparison between the different eddy diffusivities parameterizations but, specifically to evaluate and test our quasi-experimental coastal eddy diffusivities with experimental concentrations results measured in a CIBL (Copenhagen diffusion experimental). Further, it is difficult to found in the literature coastal observed concentrations that allow the validation of our new coastal eddy diffusivities.

Also, I guess that a deeper discussion about the thermal stratification and the formation of an internal boundary layer (IBL) and its influence on the results are needed.

In the new version of the manuscript, we follow the reviewer suggestion. In the manuscript we add the following discussion:

The coastal internal boundary layers (CIBL) are generated by differences in surface temperature and aerodynamic roughness occurring between land and water atmospheric environments. Considering that a large number of power plants and industrial complexes and hence polluting installations are constructed in coastal regions it is necessary to obtain CIBL turbulent parameters that are employed in dispersion models to describe the coastal air pollution.

The growing interest in the dispersion issues regarding pollutants emission in coastal areas demands the knowledge of the turbulent structure of the planetary boundary layer in this region. However, the characteristics of the turbulence in these boundary layers vary complexly in space and time due to the sudden changes in the surface characteristics, as heat flux and roughness, in the sea-land interface.

In the occurrence of sea-breeze, the stably stratified air mass over the water reaches the coast and starts to be heated by the land surface. Thus, a convective boundary rises from the surface developing a Thermal Internal Boundary Layer (TIBL) that increases in height as it advances over the land. The TIBL is topped by a stably stratified inversion layer that affects the atmospheric diffusion in coastal regions. Therefore, to improve the response of the dispersion models is necessary to provide a truthful description of the turbulence through the TIBL. In this sense, several observational experiments are performed using airborne, tethered balloons and fixed mast measurements techniques (Ogawa and Ohara, 1985; Durand et al., 1988; Smedman and Högström, 1983; Shao et al. 1991). Wind-tunnel experiments and numerical simulations are found in Meroney et al. (1975) and Hara et al. (2009). The experimental investigation that was performed by Martins et al.(2018) showed that the magnitudes of the coastal convective vertical eddy diffusivities are greater than those observed in the continental regions (far from coastal regions). Therefore, we believe that this strong vertical turbulence, occurring in the CIBL, can responsible for the enhanced dispersion contaminant and as a consequence such effect may decrease the contaminant concentration. This physical description taking into account the high magnitudes of the coastal eddy diffusivities allowed to obtain the fairly good results when the simulated concentrations were compared with those observed.

Also, the methodology is very short and there is only 1 figure and 1 table (It may be associated with the length permitted as it was a paper coming from a Proceedings).

In the new version of the manuscript, we improve the methodology follows your suggestion.
Two tables have been attached to the manuscript:

Table A1. Meteorological conditions during the Copenhagen dispersion experiments.

Exp.	U_{115m} (ms^{-1})	u_{10m} (ms^{-1})	U_{*} (ms^{-1})	L (m$)	σ_{w} (ms^{-1})	h (m)
1	3.4	2.1	0.37	-46	0.83	1980
2	10.6	4.9	0.74	-384	1.07	1920
3	5.0	2.4	0.39	-108	0.68	1120
4	4.6	2.5	0.39	-173	0.47	390
5	6.7	3.1	0.46	-577	0.71	820
6	13.0	7.2	1.07	-569	1.33	1300
7	7.6	4.1	0.65	-136	0.87	1850
8	9.4	4.2	0.70	-72	0.72	810
9	10.5	5.1	0.77	-382	0.98	2090

Table A3 – Ground level cross wind integrated concentration normalized by emission rate:

Run	Sampler distance (m)	Q(g/s)	Cy(μgm^{-2})	Cy/Q (Observed)*10^4 (sm^-2)	Cy/Q (Predicted)*10^4
1	1900	3.2	2074	6.48	8.44
1	3700	3.2	739	2.31	6.72
2	2100	3.2	1722	5.38	1.34
2	4200	3.2	944	2.95	1
3	1900	3.2	2624	8.20	8.88
3	3700	3.2	1990	6.22	7.34
3	5400	3.2	1376	4.30	4.34
4	4000	2.3	2682	11,66	10.27
5	2100	3.2	2150	6.71	7.98
5	4200	3.2	1869	5.84	6.59
5	6100	3.2	1590	4.96	2.81
6	2000	3.1	1228	3.96	3.3
6	4200	3.1	688	2.22	2.58
6	5900	3.1	567	1.83	1.19
7	2000	2.4	1608	6.7	3.7
7	4100	2.4	780	3.25	2.83
7	5300	2.4	535	2.22	1.73
8	1900	3.0	1248	4.16	5.19

8	3600	3.0	606	2.02	4.34
8	5300	3.0	456	1.52	2.67
9	2100	3.3	1511	4.58	4.28
9	4200	3.3	1026	3.11	3.21
9	6000	3.3	855	2.59	1.22

Supplementary:

How many profiles (daytime/nighttime, summer/winter time) have been used to derive those formulations?!

To derive our quasi-experimental convective eddy diffusivities profiles, 1-h observation wind velocity time series intervals are tested for quality control requirements. Unstable conditions were considered as daytime time series which $-150 \leq L < 0$, where L is Obukhov length. From a total of four months of observations (August–November 2016), 343 1-h unstable intervals are retained. The variances and time scale profiles used to estimate the K_α vertical profiles are obtained averaging the whole 343 individuals profiles.

Why this assumption?! What are the thermal stratification at Copenhagen experiment (mid latitude) and how this can be compared with SE Brazil?! Also, depending on the wind speed (if is around 10 m/s), probably the thermal stratification is close to the neutral! The authors should explain better this point.

We believe that the dispersion process near to the surface does not depend with the latitude. The micrometeorological parameters that control the dispersion process are the same in mid-latitude and SE Brazil.

The presence of a slightly convective stratified boundary layer can be seen in u and *v* turbulent energy spectra (Kaimal et al., 1972; Martins et al.,2018). In this situation, it can be observed in spectral curves a structure that contains two peaks; one low-frequency peak and one high-frequency peak. This reflects the impact of the larger convective eddies on the turbulent structure (Garrat, 1992). Although the Linhares-ES CIBL data has been collected in the different latitude of the Copenhagen data the mean wind speed vertical profile as can be seen in Fig.1 also presents in high levels velocity magnitudes of the order of 10 m/s.
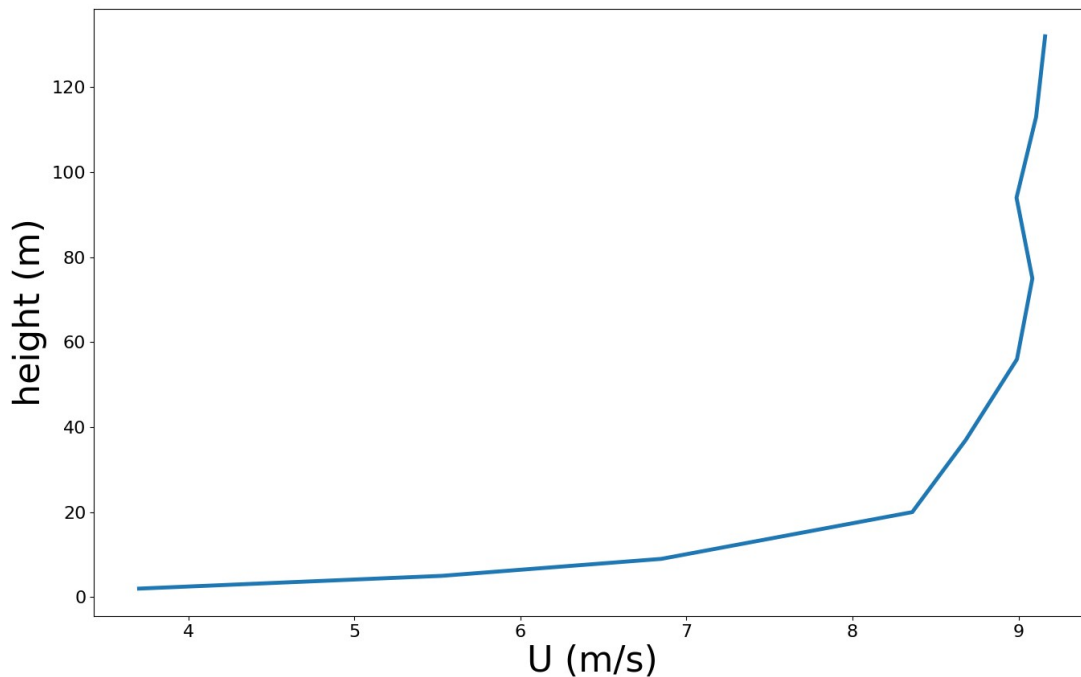
Fig.1: Mean wind speed vertical profile from CIBL Linhares-ES data.

Only to be coastal region is not a good example for the results to be compared, I guess.

Our quasi-experimental convective eddy diffusivities for a coastal site were derived from the turbulent observations originated by differences in surface temperature and aerodynamic roughness occurring between land and water atmospheric environments. The important characteristic here is the fact that there is a CIBL in the tropical region (Brazil) and also in mid-latitude (Copenhagen). Furthermore, the principal aim of this study does not to establish a comparison between the different eddy diffusivities parameterizations but, specifically to evaluate and test our quasi-experimental coastal eddy diffusivities with experimental concentrations results measured in a CIBL (Copenhagen diffusion experimental). Further, it is difficult to found in the literature coastal observed concentrations that allow the validation of our new coastal eddy diffusivities.

The following references have been added to the text:

REFERENCES:

OGAWA, Yasushi; OHARA, Toshima. The turbulent structure of the internal boundary layer near the shore. Boundary-Layer Meteorology, v. 31, n. 4, p. 369-384, 1985.

DURAND, Pierre; DRUILHET, Aime; BRIERE, Serge. A sea-land transition observed during the COAST experiment. Journal of the atmospheric sciences, v. 46, n. 1, p. 96-116, 1989.

GARRATT, J. et al. The atmospheric boundary layer. cambridge atmospheric and space science series. Cambridge University Press, Cambridge, v. 416, p. 444, 1992.

Kaimal JC, Finnigan JJ. 1994. Atmospheric Boundary Layer Flows. Oxford University Press. 289 pp.

Martins, L. G. N., Degrazia, G. A., Acevedo, O. C., Puhales, F. S., de Oliveira, P. E., Teichrieb, C. A., and da Silva, S. M.: Quasi-Experimental Determination of Turbulent Dispersion Parameters for Different Stability Conditions from a Tall Micrometeorological Tower, Journal of Applied Meteorology and Climatology, 57, 1729–1745, 2018.

SMEDMAN, Ann-Sofi; HOEGSTROEM, Ulf. Turbulent characteristics of a shallow convective internal boundary layer. Boundary-Layer Meteorology, v. 25, n. 3, p. 271-287, 1983.

SHAO, Yaping; HACKER, Jörg M.; SCHWERDTFEGER, Peter. The structure of turbulence in a coastal atmospheric boundary layer. Quarterly Journal of the Royal Meteorological Society, v. 117, n. 502, p. 1299-1324, 1991.

HARA, Tomohiro et al. Wind-tunnel and numerical simulations of the coastal thermal internal boundary layer. Boundary-layer meteorology, v. 130, n. 3, p. 365-381, 2009.

Please also note the supplement to this comment: angeo-2019-85-RC1-supplement

Page 2: In the new version of the manuscript the sentence "In the present study **we use** eddy diffusivities that were derived from..." was removed.

Page 3: it is missing the year of McRae et al. and Y (2006) should come earlier then R (2010)

In the new version of the manuscript the references have been corrected: "(McRae et al., 1982; Yordanov et al., 2006; Rizza et al., 2010)".

(Long Jr and Pepper; Rizza et al.,2010) - year??? 1981!

In the new version of the manuscript we added the year of reference: " (Long and Pepper, 1981)".

How many profiles (daytime/nighttime, summer/winter time) have been used to derive those formulations?!

In the new version of the manuscript we have introduced the sentence (page 5, line 117):
 "*To obtain such profiles, 1-h observation wind velocity time series intervals are tested for quality control requirements. Unstable conditions were considered as daytime time series which −150 ≤L< 0. From a total of four months of observations (August - November 2016), 343 1-h unstable intervals are 120 retained. The variances and time scales profiles used to estimate the K_i vertical profiles are obtained averaging the whole 343 individuals profiles.*"

(Gryning and Lyck) – year?!

In the new version of the manuscript we added *"(Gryning and Lyck, 1984)"*.

Why this assumption?! What are the thermal stratification at Copenhagen experiment (mid latitude) and how this can be compared with SE Brazil?! Also, depending on the wind speed (if is around 10 m/s), probably the thermal stratification is close to the neutral! The authors should explain better this point. Only to be coastal region is not a good example for the results to be compared, I guess.

In new version of manuscript the sentence was better explained. The following sentence was was better explained (page 2 – line 35) :

"The coastal internal boundary layers (CIBL) are generated by differences in surface temperature and aerodynamic roughness occurring between land and water atmospheric environments. Considering that a large number of power plants and industrial complexes and hence polluting installations are constructed in coastal regions it is necessary to obtain CIBL turbulent parameters that are employed in dispersion models to describe the coastal air pollution.

The growing interest in the dispersion issues regarding pollutants emission in coastal areas demands the knowledge of the turbulent structure of the planetary boundary layer in this region. However, the characteristics of the turbulence in these boundary layers vary complexly in space and time due to the sudden changes in the surface characteristics, as heat flux and roughness, in the sea-land interface.

In the occurrence of sea-breeze, the stably stratified air mass over the water reaches the coast and starts to be heated by the land surface. Thus, a convective boundary rises from the surface developing a Thermal Internal Boundary Layer (TIBL) that increases in height as it advances over the land. The TIBL is topped by a stably stratified inversion layer that affects the atmospheric diffusion in coastal regions. Therefore, to improve the response of the dispersion models is necessary to provide a truthful description of the turbulence through the TIBL. In this sense, several observational experiments are performed using airborne, tethered balloons and fixed mast measurements techniques (Ogawa and Ohara, 1985; Durand et al., 1988; Smedman and Högström, 1983; Shao et al. 1991). Wind-tunnel experiments and numerical simulations are found in Meroney et al. (1975) and Hara et al. (2009). The experimental investigation that was performed by Martins et al.(2018) showed that the magnitudes of the coastal convective vertical eddy diffusivities are greater than those observed in the continental regions (far from coastal regions). Therefore, we believe that this strong vertical turbulence, occurring in the CIBL, can responsible for the enhanced dispersion contaminant and as a consequence such effect may decrease the contaminant concentration. This physical description taking into account the high magnitudes of the coastal eddy diffusivities allowed to obtain the fairly good results when the simulated concentrations were compared with those observed."

Reply to Referee #2

First of all, we would like to sincerely thank the Reviewer for the useful comments and suggestions and analysis he gave to the manuscript.

In this work, the authors incorporate new parameterizations of turbulent diffusivities developed for coastal profiles in Brazil into a pollutant diffusion model. The validation data came from an air pollution experiment developed in a coastal area of Denmark. Only unstable conditions are considered. The theme is original and suitable for the journal.

Major comments:

1. Although the original idea of the work is appropriate, the advantage of introducing these profiles in the proposed model is not demonstrated. The authors should first make a brief description of the original way in which there is solved the Eulerian pollutant diffusion equation in the model to understand the advantage of using the profiles developed in Brazil. In addition, the results obtained with the original model and those obtained with the modification of this work should be shown in Figure 1, to observe the improvements introduced.

2. On the other hand, in the introduction there is presented both methodological issues and information on the data used. These topics should be incorporated in the data and methodology section. The introduction should be enriched with a detail of the background that indicates the lack of information or of methodological development that leads to the aim of the work.

In the new version of the manuscript, we follow the reviewer suggestions. Our responses to the comments 1 e 2 of Referee #2 are given below:

The Eulerian dispersion models solve the advection-diffusion equation and can employ distinct turbulent parameterizations using different numerical methods.
Despite the limitation of the K-models they are used in different atmospheric conditions because the eddy diffusivities describe the turbulent transport in an Eulerian framework. In this case, almost all measurements are Eulerian in character. These Eulerian models generate results that agree with observational data as well as any more complex. The reliability of the K-models depends on the way the eddy diffusivities is determined based on the turbulent structure of the planetary boundary layer (Ulke, 2000).
It is important to note that the Eulerian model APUGRID is already a well developed Eulerian dispersion model. In this model is enough to have turbulent parameterizations to obtain simulated contaminant concentrations. In our case, we use detailed turbulent data of coastal internal boundary layers and some equations (from Taylor Statistical diffusion Theory) to obtain quasi-experimental eddy diffusivities.
Therefore, the principal aim of this study does not establish a comparison between the different eddy diffusivities parameterizations but, specifically to evaluate and test our quasi-experimental coastal eddy diffusivities with experimental concentrations results

measured in a CIBL (Copenhagen diffusion experimental). Further, it is difficult to found in the literature coastal observed concentrations that allow the validation of our new coastal eddy diffusivities.

For the new version of the manuscript we enrich the introduction with this definition of the CIBL:

The coastal internal boundary layers (CIBL) are generated by differences in surface temperature and aerodynamic roughness occurring between land and water atmospheric environments. Considering that a large number of power plants and industrial complexes and hence polluting installations are constructed in coastal regions it is necessary to obtain CIBL turbulent parameters that are employed in dispersion models to describe the coastal air pollution.

The growing interest in the dispersion issues regarding pollutants emission in coastal areas demands the knowledge of the turbulent structure of the planetary boundary layer in this region. However, the characteristics of the turbulence in these boundary layers vary complexly in space and time due to the sudden changes in the surface characteristics, as heat flux and roughness, in the sea-land interface. In the occurrence of sea-breeze, the stably stratified air mass over the water reaches the coast and starts to be heated by the land surface. Thus, a convective boundary rises from the surface developing a Thermal Internal Boundary Layer (TIBL) that increases in height as it advances over the land. The TIBL is topped by a stably stratified inversion layer that affects the atmospheric diffusion in coastal regions. Therefore, to improve the response of the dispersion models is necessary to provide a truthful description of the turbulence through the TIBL. In this sense, several observational experiments are performed using airborne, tethered balloons and fixed mast measurements techniques (Ogawa and Ohara, 1985; Durand et al., 1988; Smedman and Högström, 1983; Shao et al. 1991). Wind-tunnel experiments and numerical simulations are found in Meroney et al. (1975) and Hara et al. (2009).

The aim should be written more clearly.

For the new version of the manuscript we rewrote the aim more clearly:

In this present study, we use eddy diffusivities that were derived from the observations of the turbulent wind components (u, v, w) in a convective CIBL to simulate the dispersion of contaminant released from an elevated continuous point source in a coastal region.

The turbulent observations were performed at a 140 m micrometeorological tower positioned 240 m north of a natural gas power plant and 4 km southwest of the ocean coastal environment) in the city of Linhares (southeastern Brazil). The turbulent wind data were obtained from high-frequency measurements (10 Hz) accomplished by tridimensional sonic anemometers at heights of 1, 2, 5, 9, 20, 37, 56, 75, 94, 113 and 132 m. Therefore, the study of Martins et al., 2018 uses these measurements and some few mathematical

relations to determine turbulent dispersion parameters (Taylor Statistical diffusion Theory, Degrazia et al., 2000)

Differently, of previous studies in which the vertical profiles of turbulent parameters have been calculated using surface observations to throughout similarity-based relationship, our eddy diffusivities were locally calculated from the detailed measurements taken (accomplished) along the entire vertical extension occupied by the surface internal boundary layer. As a consequence, they can be called quasi-experimental eddy diffusivities. This work aims to obtain algebraic formulation from the fitting curves, that reproduce the observed vertical profile of these quasi-experimental convective eddy diffusivities. As a test and to evaluate the quasi-experimental eddy diffusivities for a convective CIBL we substitute these turbulent diffusion parameters into Eq. 3 to simulate the contaminant concentration originated from an elevated continuous point source in a coastal environment. The simulated concentrations are compared to those measured in the Copenhagen diffusion experiment.

3. It is not clear from the beginning of the methodological description that only unstable conditions will be considered. Authors should make it explicit.

In the new version of the manuscript, we write more clearly the stability conditions associated with the quasi-experimental eddy diffusivities. Please see the answer above (1 e 2).

Nor is variable C adequately described, since by its units (Fig. 1) I understand that it is a concentration per emission and surface area unit. Is that correct?

Yes, is correct, c^Y represents the ground-level cross wind integrated concentration normalized by the emission rate (C/Q) (s m^{-2}).

It is also not known if the pollutant diffused is a gas (which?) or it is particulate matter.

The tracer sulphur hexa fluoride (SF6) used in the Copenhagen dispersion experiments, was released at a height of 115 m from the TV tower in the Gladsaxe (Copenhagen) and the ground level contaminant concentrations were measured at 3 arcs located in the distance of 2000 to 6000 m from the elevated continuous point source.

4. The authors should better describe how they chose the Copenhagen experiment cases for the model validation.

The Copenhagen experimental site is limited by the Øresund coast, approximately 7 km east of the TV tower. Therefore, the turbulent effect acting on the tracer dispersion is an environment of the convective internal boundary layer (CIBL). The width of Øresund strait, the water portion separating Denmark and Sweden, is about 20 Km. On the western side of Øresund lies Copenhagen with its urban area. This area has high surface roughness due to the urban character. Thusly, this represents a turbulent environment occurring in a region with relatively cold water and warm land surface. As a consequence, the turbulent structure acting on the tracer dispersion can be considered as one present in the coastal inner boundary layer.

Our quasi-experimental convective eddy diffusivities for a coastal site were derived from the turbulent observations originated by differences in surface temperature and

aerodynamic roughness occurring between land and water atmospheric environments. The important characteristic here is the fact that there is a CIBL in the tropical region (Brazil) and also in mid-latitude (Copenhagen)

For example, did they consider ranges of Instabilities? It is measured by which variable? In addition, which were the atmospheric boundary layer characteristics in these cases? Were these characteristics decisive in the choice of cases?

Yes, the stability parameter used in our study was the Monin Obukhov length.
  To derive our quasi-experimental convective eddy diffusivities profiles, 1-h observation wind velocity time series intervals are tested for quality control requirements. Unstable conditions were considered as daytime time series which $-150 \leq L < 0$, where L is Obukhov length. From a total of four months of observations (August–November 2016), 343 1-h unstable intervals are retained. The variances and time scale profiles used to estimate the K_α vertical profiles are obtained averaging the whole 343 individuals profiles.
  Although some Copenhagen dispersion experiments occurred in conditions quasi-neutral the L parameter was negative. The presence of a slightly convective stratified boundary layer can be seen in *u* and *v t*urbulent energy spectra (Kaimal et al., 1972; Martins et al.,2018). In this situation, it can be observed in spectral curves a structure that contains two peaks; one low-frequency peak and one high-frequency peak. This reflects the impact of the larger convective eddies on the turbulent structure (Garrat, 1992).

Although the Linhares-ES CIBL data has been collected in the different latitude of the Copenhagen data the mean wind speed vertical profile as can be seen in Fig.1 also presents in high levels velocity magnitudes of the order of 10 m/s.
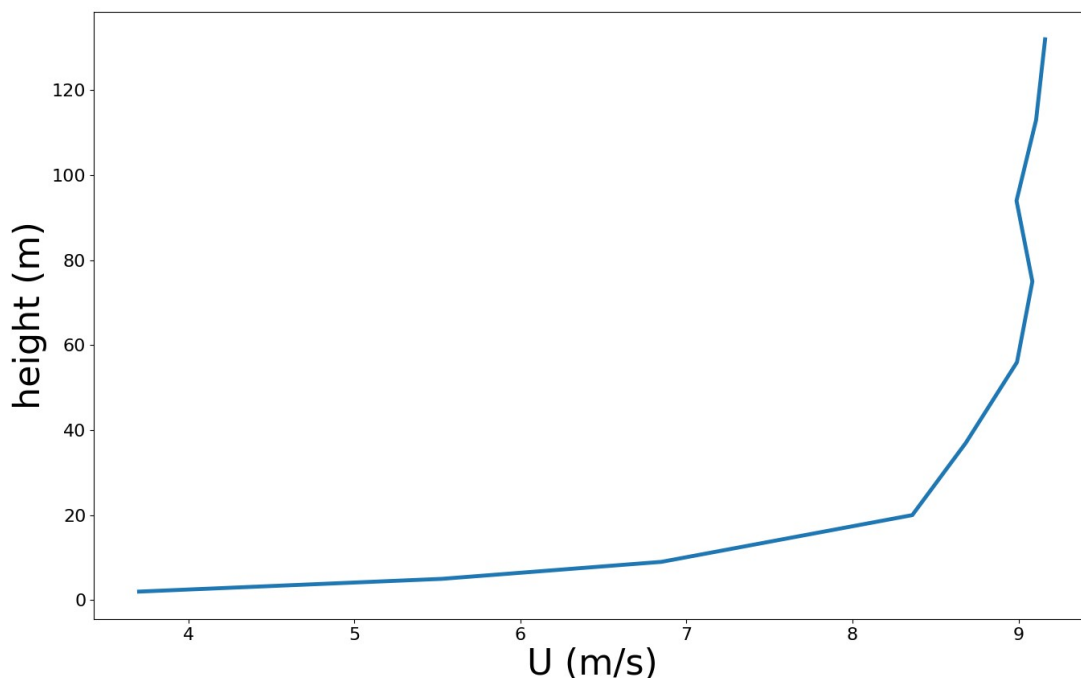
Fig.1: Mean wind speed vertical profile from CIBL Linhares-ES data.

Minor comments: 1.The years in citations and in the bibliography mentioned at lines 44,50, 55 and 86 are missing. In 26 the correct citation is Panofsky and Dutton (1984).

In the new version, we corrected the citations.

2. Describe what is S in Eq. 1.

In the new version, we described the variable: S represents a source term.

3. In line 43, APUGRID is a model or a numerical method?

Is a numeric dispersion model. Rizza U., G.Gioia, C.Mangia, and G.R.Marra, 2003. Development of a grid dispersion model in a large-eddy-simulation-generated PBL, Il Nuovo Cimento, 26C, 3, 297-309.

YORDANOV, D. et al. EVALUATION OF WIND AND TURBULENT PARAMETERISATIONS FOR SHORT RANGE AIR POLLUTION MODELING. **Bulgarian Geophysical Journal**, v. 32, p. 107-123, 2006.

4. In Eq. 7, u is a mean or an instantaneous value?

In Eq. 7 u is the mean value. We corrected in the new version of the manuscript

5. In Eq. 8, which is the difference between u ÌˇE y U ÌˇE?

The u represents the mean wind speed.

6. Add a citation for Eq. 12. 8.

In equation 7 we added the following reference:

DEGRAZIA, Gervasio; ANFOSSI, Domenico. Estimation of the Kolmogorov constant C0 from classical statistical diffusion theory. **Atmospheric Environment**, v. 32, n. 20, p. 3611-3614, 1998.

HANNA, Steven R. Lagrangian and Eulerian time-scale relations in the daytime boundary layer. **Journal of Applied Meteorology**, v. 20, n. 3, p. 242-249, 1981.

Variables units are missing in Table A1.

These variables represent statistical indices. In the new version of the manuscript, we explain these variables. Please see the answer to the next question.

In addition, variable COR is used in the table and R (line 99) is used in the text. Please, unify nomenclature. I suggest adding in the Table Caption the definition of the variables.

We agree with the reviewer. In the new version of the manuscript, we add the following definition of the statistic indices.

The Normalized mean square error (NMSE) is defined by the following equation:

$$NMSE = \frac{\overline{(C_{obs} - C_{pre})^2}}{\overline{C_{obs}C_{pre}}}$$

where C is the analyzed quantity (concentration) and the subscripts "OBS" and "PREV" represent the observed and the predicted values respectively.

The fractional bias (FB) is defined by:

$$FB = \frac{(\overline{C_{obs}} - \overline{C_{pre}})}{0.5(\overline{C_{obs}} + \overline{C_{pre}})}$$

The fractional standard deviation (FS) is defined by

$$FS = \frac{2(\sigma_{obs} - \sigma_{pre})}{(\sigma_{obs} + \sigma_{pre})}$$

The Correlation coefficient (COR) is defined by

$$COR = \frac{\overline{(C_{obs} - C_{pre})(C_{obs} - C_{pre})}}{\sigma_{obs}\sigma_{pre}}$$