

## **Response to interactive comment by C. von Savigny on “Measuring FeO variation using astronomical spectroscopic observations” by Stefanie Unterguggenberger et al.**

### **General comments:**

*This is an interesting manuscript dealing with ground-based observations of two terrestrial nightglow emission features, i.e. the FeO orange bands and the well-known Na D-lines. The spectral observations were carried out with the X-shooter spectrograph at the Very Large Telescope in Chile. The FeO and Na emissions show similar diurnal and seasonal variations. Comparisons with WACCM model simulations allow empirical estimation of the (effective) quantum yields for the two emissions, which are not well known. The paper is of interest to the aeronomy community and is in general very well written. A few paragraphs and sentences are difficult to follow (see specific comments below). I don't have any major objections against the publication of this manuscript and recommend publication subject to minor revisions. I ask the authors to consider the specific comments listed below.*

### **Specific comments:**

*Page 3, line 20: "as A pseudo-continuum"*

The phrase was changed as proposed.

*Page 7, line 9: "We tested our results with respect to the data distribution over the year by introducing equally spaced bins"*

*I don't fully understand what you mean here? How many bins were used? How wide/long were they? Do they have to be equally spaced?*

The bins were equally spaced over the year with each bin having a width of 2 weeks, which left us with 26 data points over the year. For clarification the sentence was edited as follows:

'We tested our results with respect to the data distribution over the year by introducing equally spaced bins, spanning a fortnight.'

*Figure 2: I have some questions about this Figure:*

*(a) Is the ordinate label / unit correct? The plot shows the spectral intensity, so the unit should be  $R / (\text{wavelength unit})$ , e.g.  $R/\text{nm}$ , right? This applies to both panels.*

*(b) You write that the cyan line in the top panel corresponds to the FeO continuum, while the black line shows the raw spectrum. What is the origin of the offset between the two lines? Is it possible that the cyan line is offset by 100 R for better visibility? If yes, this is not mentioned, as far as I can tell.*

Yes, the label on the ordinate was wrong and has been corrected.

The offset between the black and the cyan spectrum results from the data reduction. With the help of the sky model we corrected the night-sky spectrum for zodiacal light, scattered star- and moonlight. This correction causes the offset between the two spectra. This information was added to the text.

*Page 9, line 19: Evans et al. found a NiO/FeO ratio of 0.05 to 0.3 and Gattinger et al. a ratio of 2.3. Is the large difference between these results understood.*

There was a typo with the second reference. Both measurements (OSIRIS and the space shuttle) were mentioned in Evans et al. (2011). This was corrected.

In the paper Evans et al. (2011) no answer was given to why they found these big discrepancies in their measurements. This information was added to the text: 'These differences were not discussed in detail in Evans et. al. (2011).'

*Page 9, line 26/27: "we find a maximum contribution of 31% to the mean peak"*

*I suggest adding "of the FeO emission" here (this is what you mean, right?)*

Indeed, in single spectra we could find a possible contribution of the main peak by NiO that

amounts to almost 1/3 of the total main peak intensity. This information was added to the text as follows:

'Using this peak to scale the laboratory NiO spectrum accordingly we find a maximum contribution to the FeO main peak intensity by NiO of 31%...'

*Page 10, line 2: "Scaling the main peak emission from Gattinger et al. (2011) to the whole spectrum we obtain a value of 3.9%"*

*I think some pieces of information are missing here. What "value" do you mean? Even after reading the sentence several times, I'm not sure I interpret it correctly. Please clarify.*

Due to other airglow contamination like different OH bands, NiO and NO+O it is difficult to measure the FeO spectrum. The most reliable part is the main peak. Since we wanted to see how much of the total FeO intensity is contained within the main peak, we took the theoretical FeO spectrum from Gattinger et al. (2011) and scaled it to the total FeO flux. Hence, the 3.9 % refer to the contribution of the main peak to the total FeO spectrum. '... FeO pseudo-continuum...' was added for clarification.

*Page 10, line 10: "where the main peak amounts to 3.3 +/-0.8%"*

*3.3 % of what? This is related to the previous point. Please clarify.*

The Gattinger spectrum spans a wavelength range from 0.5 to 0.72 micron. The main peak is only a small part of the total emission. Hence, if one is interested in the total intensity of the FeO emission, it is necessary to scale the main peak emission to the total emission of FeO. For a better comparison between the spectrum obtained by Gattinger and our reconstructed spectrum we compared the contribution of the main peak to the total pseudo-continuum.

We add '...of the total FeO emission ranging from 0.50 to 0.72 micron...' as clarification to the text.

*Page 11, line 6: "In general, the Na and FeO emission show similar diurnal variation within their combined errors, i.e. Figs. 4a, c, and d."*

*This statement is also true for 4b, and even more so than for, e.g. 4d or 4a. Next sentence: "The intensities of FeO and Na decline at the beginning of the night and rise towards sunrise" This is not true for 4b. I think you intend to only mean panels a, c d here, right? But this is not explicitly stated by this or the previous sentence (the phrase "i.e. Figs. 4a, c and d" does not imply that).*

Thank you very much for finding this. We corrected for the errors.

*Page 11, last line: "The best fit approach ( $\chi^2_{\min}$ ) relies on the grid size and does not provide uncertainties"*

*After reading the entire paragraph I understand what you mean, but there are different "best-fit" approaches. You create arrays with possible fit parameters and then determine  $\chi^2$  for each set of possible combinations. One may also use – and I think this is generally done – numerical routines to find the optimum fit values in a least-squares sense. I suggest mentioning at the beginning that you don't use a numerical scheme to minimize  $\chi^2$ . Otherwise, the reader has difficulties understanding what you mean by "relies on the grid size" – this is not correct for the numerical methods. Also the numerical methods will generally provide uncertainty estimates.*

A clarification was added to the text as follows:

'Since the best-fit approach ( $\chi^2_{\min}$ ) is not done with a numerical scheme but makes use of a parameter grid, it relies on the grid size and does not provide uncertainties.'

*Page 12, line 8: "parameter" -> "parameter"*

The typo was corrected.

Page 12, line 22: “stronger .. amplitude” -> “larger .. amplitude” ?

The word was corrected.

Page 13, line 8: “at the end of May”

Isn't it rather the end of April?

We checked the data again and the maximum is on DOY 116, which corresponds to the end of April. The correction was applied to the text.

Page 14, line 23: “by convolving” Is this really a convolution in the mathematical sense? This may well be the case, but I'm not entirely sure.

Convolved was changed into 'by combining in quadrature'.

Page 15, line 3: “convolving”

Same as above point.

Convolved was changed into 'by combining in quadrature'.

Page 15, line 9: “Fig, 9” -> “Fig. 9”

The typo was corrected.

Page 15, last sentence: *I think it's also worth mentioning that Clemesha et al. (1995) performed a minimization of the differences between the observed Na emission rates and model simulations, which resulted in a value of  $f = 0.093$ . Also, in our recent manuscript (von Savigny et al., First mesopause Na retrievals from satellite Na D-line nightglow observations, Geophys. Res. Lett., revised, 2016) we find an optimum value of  $f = 0.09$ , when comparing Na retrievals from SCIAMACHY Na nightglow observations with independent satellite observations (SCIAMACHY dayglow and GOMOS stellar occultation). I should point out that we varied  $f$  in steps of 0.01 to find the optimum value – an approach that can be refined. In any case, I find it encouraging that your results on the value of the effective quantum yield are in good overall agreement with the von Savigny et al. (2016) value and with Clemesha et al. (1995).*

The additional information was added at the end of the result section.

Fig. 4, caption, line 1: I suggest replacing “with respect to season” by “for different seasons”.

Same line: space in “.The” missing.

The space was added and the phrase changed to the suggested version.

Figure 5: The symbols (squares) are hardly visible in the printout. Please increase the symbol size.

The plot was edited.

Page 16, line 2: “airglow emissionS” ?

The typo was corrected.

Page 16, line 23: “None of the seasons showS”

The typo was corrected.

Page 23, table caption, line 2: “the relative value of A1 ..”

Suggest adding “in percent” to read “the relative value (in percent) ..”

Thank you for the suggestion, it was put into the table caption as 'in per cent' (British English).

*Reference list: the reference list contains a fair number of typos and inconsistencies. I probably didn't catch all of them. Please check the list again carefully. A general issue: periods are missing at the end of all references. In addition, the spacing between initials is not consistent between the references.*

We went through the references and corrected for mistakes and inconsistencies.

*Page 22, line 9: von Savigny (2012) is not cited in the manuscript, as far as can tell (But I'm certainly happy if you cite it ..)*

Sorry for that mistake. This citation was from an older version which still included OH measurements. However, your recent letter is now a part of the discussion section.

## **Response to interactive comment by T. P. Viehl on “Measuring FeO variation using astronomical spectroscopic observations” by Stefanie Unterguggenberger et al.**

### **General comments**

*The paper presents spectroscopic observations of FeO and Na nightglow emissions by the X-shooter instrument at the VLT / Paranal Observatory, Chile. The observations are analysed on diurnal as well as seasonal scales and compared to theoretical considerations. The seasonal variation of the emissions is very satisfactorily reproduced by an atmospheric chemistry model. This analysis reveals new insights about FeO in the MLT and the quantum yields of the relevant emissions.*

*The paper presents new data and insights which are relevant to the field and well suited for publication in ACP. The methods and assumptions are valid and clearly outlined. In general, the experiment and the calculations are sufficiently described. Some suggestions are given below to improve the description further. The authors give proper credit to related work and clearly indicate their own contribution. The overall presentation is well structured and clear. Some suggestions to improve the presentation further are given below. The title reflects the contents of the paper and the abstract provides a concise and complete summary.*

*I recommend publication of this interesting manuscript after minor revision and ask the authors to address the following comments and suggestions.*

### **Specific comments and suggestions**

*Page 2, line 24: Suggestion: change "source of THE metals" to simply "source of metals", "source of metal layers", "source of meteoric metals" or similar, as this is the first account of mentioning "the metals"*

Thanks for the suggestions. The phrase was changed to 'source of metal layers'.

*Page 3, line 12: It appears slightly odd to me to refer to sodium as "a good CANDIDATE" since observations of Na are well established and not only theoretically considered. Suggestion: "a good candidate" -> "well established", "commonly used", or similar*

'A good candidate' was meant with respect to astronomical techniques since the Na doublet can already be detected with small telescopes and low-to-medium resolution spectrographs. The phrase was changed to 'commonly used'.

*Page 5, line 16: Can you provide more information about the criteria of the "additional quality checks" applied to the data? Are these implemented in the pipeline (Modigliani et al., 2010) or are additional reductions performed, e.g., by discarding spectra with obvious distortions through technical problems?*

The spectra were furthermore checked for residuals introduced by the pipeline reduction (residuals related to higher orders, mentioned in the paper), contamination of the continuum by astronomical objects as well as a check on the reliability of the intensity measurements of various OH lines. Furthermore, the continuum was checked for unreasonable behaviour like steep sudden steps in the spectrum. A paragraph with this information was added to the manuscript.

*Page 5, lines 19/20: "...an adapted version of pipeline v2.6.8 of the ESO public pipeline..."*

*Suggestion: change to "...an adapted version of the public ESO pipeline v2.6.8..."*

The suggested change was implemented.

*Page 5, line 28: I'm not familiar with the term "echelle orders". I suggest changing to "higher diffraction orders of the echelle spectrometer" if this is what is meant. Furthermore, can it be easily explained how the pipeline (i.e., data processing) introduces these as opposed to the instrument? It might be worthwhile adding a further short explanatory sentence, since this influence does not seem to have been covered in the cited literature.*

Echelle order is indeed an astronomical term. At the position of its first occurrence it is now changed to the more detailed '...high diffraction orders of the echelle spectrograph...'. The main issue was the separation of sky and astronomical object. Applying different extraction methods implemented in the pipeline led to different results. X-shooter either traces the light profile of the astronomical source to separate the object from the sky or uses a predefined window to distinguish between sky and object.

We found that the difference between the spectra for the latter and the former method can be used to construct a template for the order-related contamination (periodic wave pattern). This template could then be scaled to the individual contamination patterns and finally be subtracted. Here we only considered the sky spectra obtained with the second approach which is more reliable for line emission.

This information was also added to the manuscript: 'Comparing different extraction routines we found a systematic variation in flux with wavelength that shows minima at the central positions of the different echelle orders and maxima in the overlapping regions. A correction spectrum was determined by comparing differently extracted spectra. This spectrum was then scaled to the observation and subtracted. In addition, we checked for continuum contribution by astronomical objects, the reliability of the intensities of various OH lines and for unreasonable behaviour like sudden steps in the spectrum.'

*Page 6, line 12: "FeO is only a faint pseudo continuum component": this doesn't really make sense to me. Suggestion: change to "FeO has only a faint pseudo continuum component" or "the component of FeO to the observed pseudo continuum is only faint" depending on what you want to say here.*

The phrase was changed to '...FeO contributes to the airglow as a faint pseudo-continuum'.

*Page 6, lines 23&24 and Figure 2: In the text you refer to the exposure time as "roughly 1 hour" and the resolving power as "approx 7450". In the caption of Figure 2, however, the exposure time is given as precisely "3600 sec" and the resolving power as "7450" (without approx). Please clarify, e.g., by choosing either "roughly 1 hour" or "3600 sec", whichever is correct.*

It is indeed exactly an hour of observation time and a resolving power of approx 7450. The values are correct and the text changed accordingly.

*Page 7, line 2: Recommendation: change "this interval" to "the interval" as it is not referred to in the previous sentence.*

The suggested change was applied.

*Page 7, line 14: "which IS according to Gattinger et al. [2011] defined at" -> "which according to Gattinger et al. [2011] IS defined at" ?*

The suggested change was applied.

*Page 7, line 14: "FROM their selected wavelength range" -> "IN their selected wavelength range" ?*

The suggested change was applied.

*Page 7, lines 13/14: Here and throughout the manuscript there are several personal references to studies (i.e., "They found..." instead of "That study found..."). This very much is a stylistic choice of the authors, but I suggest to change those occurrences to the more neutral, impersonal form. In this example, I suggest changing "from their selected wavelength range" to "in the wavelength range of that study" or similar.*

Thank you very much for the comment. We left the text as it was in the original manuscript.

Page 7, line 15: *I recommend placing "of 6%" between "an error" and "for the FeO main peak"*  
The suggested change was applied.

Page 8, line 24: *While the observed FeO spectra indeed match the theoretical work of Gattinger et al. with "good overall agreement", I recommend to add a note that some parts show a difference in relative intensity of more than 50% (in particular at around 590 nm and 600 nm, well within the main peak).*

With this sentence we referred to the agreement of the five quintile spectra with each other. For clarification we added '... with each other ...'

Also your suggestion on the differences between the spectra was implemented.

Page 10, line 2/3: *"...we obtain a value of 3.9%" ...of what? Do you mean to say "...we find that FeO contributes 3.9% to the overall spectrum." ?*

Due to other airglow contamination like different OH bands, NiO and NO+O it is difficult to measure the FeO spectrum. The most reliable part is the main peak. Since we wanted to see how much of the total FeO intensity is contained within the main peak, we took the the theoretical FeO spectrum from Gattinger et al. (2011) and scaled it to the total FeO flux. Hence, the 3.9 % refer to the contribution of the main peak to the total FeO spectrum. '... FeO pseudo-continuum...' was added for clarification.

Page 10, line 27: *"...are the low statistic bins." Suggestion: change to "...have the lowest statistic." or "...contribute the fewest data points." or similar.*

The text was changed to 'contain the fewest data points'.

Page 11, line 6/7: *"show A similar" or "show similar ... variationS" ?*

The text was changed to '... show similar variations'.

Page 11, lines 11-15: *This description is not very clear to me. If 2010 shows a different behaviour than 2011&2012, does this mean the effect in those years would be even stronger than in the combined data shown or was 2010 excluded from the plot? Similarly, were the data from September and November 2011 excluded for the reason given or does this imply that the data from these months decreases the effect shown?*

For Fig. 4 all data points were used. Fig. 4 shows the average diurnal behaviour for the respective seasons in a time span of 3.5 years.

We also wanted to discuss the behaviour for the different years. However, the corresponding results are not as reliable as the complete picture since the sample size is much smaller.

Page 14, line 10: *Suggestion: "...rates were using the..." -> "...rates were CALCULATED / ESTIMATED using the..."*

The text was changed to '...rates were calculated using the ...'.

Page 16, line 7: *"The shape of the quintile spectra is almost identical." Identical to what or during which periods? I assume it is meant identical to each other.*

Indeed, we referred to the similarities of the quintile spectra among each other.

The phrase 'to each other' was added for clarification.

Figure 3: *Please use a lighter shade of grey for regions where the correction might not have been performed accurately. The contrast of the black and blue curves to the grey shaded areas is very low. It is furthermore slightly distracting to have features as prominent as the dark grey areas in the figure without a description in the figure or its caption.*

The shades were changed to a lighter grey.

## Technical comments

Page 6, line 6: *"and as well as": choose either "and" or "as well as"*  
The 'and' was eliminated.

Page 7, line 28: *"are discussed" -> "is discussed" ?*  
The phrase was changed to 'is discussed'.

Page 8, line 6: *"merge" -> "merged" or "merging"*  
The tense was changed.

Page 8, line 15: *"normalize" -> "normalized"*  
The tense was changed.

Page 8, line 15&16: *Throughout the manuscript, you seem to prefer British English over American English. While "normalized" is probably acceptable in BE, you might consider changing to "normalised" for consistency here.*  
The correction for British English was applied.

Page 12, lines 4/5: *"...between 0 and 0.65 x the maximum intensity" Change to "...between 0 and 0.65 OF the maximum intensity" or consider using percentages as done previously*  
The suggestion was included in the manuscript.

Page 12, line 20: *"...squareS the Bayesian..."*  
The s was added.

*Some comma errors, e.g. Page 16, line 6: "...with intensity, median..." Page 16, line 12/13: "...pointed out that..."*  
The suggestion was included in the manuscript.

Figure 4(d): *"Okt" -> "Oct"*  
The figure was changed.

# Measuring FeO variation using astronomical spectroscopic observations

Stefanie Unterguggenberger<sup>1</sup>, Stefan Noll<sup>1</sup>, Wuhu Feng<sup>2,3</sup>, John M. C. Plane<sup>2</sup>,  
Wolfgang Kausch<sup>4,1</sup>, Stefan Kimeswenger<sup>5,1</sup>, Amy Jones<sup>6,1</sup>, and Sabine Moehler<sup>7</sup>

<sup>1</sup>Institut für Astro- und Teilchenphysik, Universität Innsbruck, Technikerstr. 25/8, 6020 Innsbruck, Austria

<sup>2</sup>School of Chemistry, University of Leeds, Woodhouse Lane, Leed LS 9JT, United Kingdom

<sup>3</sup>National Centre for Atmospheric Science, University of Leeds, Woodhouse Lane, Leed LS 9JT, United Kingdom

<sup>4</sup>Institute for Astrophysics, University of Vienna, Türkenschanzstr. 17, 1180 Vienna, Austria

<sup>5</sup>Universidad Católica del Norte, Avenida Angamos 0610, Antofagasta, Chile

<sup>6</sup>Max Planck Institute for Astrophysics, Karl-Schwarzschild-Str. 1, 85748 Garching, Germany

<sup>7</sup>European Southern Observatory, Karl-Schwarzschild-Str. 2, 85748 Garching, Germany

*Correspondence to:* Stefanie Unterguggenberger (stefanie.unterguggenberger@uibk.ac.at)

## Abstract.

Airglow emission lines of OH, O<sub>2</sub>, O and Na are commonly used to probe the MLT (mesosphere/lower thermosphere) region of the atmosphere. Furthermore, molecules like electronically excited NO, NiO and FeO emit a (pseudo-) continuum. These continua are harder to investigate than  
5 atomic emission lines. So far, limb-sounding from space and a small number of ground-based low-to-medium resolution spectra have been used to measure FeO emission in the MLT. In this study the medium-to-high resolution echelle spectrograph X-shooter at the Very Large Telescope (VLT) in the Chilean Atacama desert (24° 37' S, 70° 24' W, 2 635 m) is used to study the FeO pseudo-continuum in the range from 0.5 to 0.72 μm based on 3 662 spectra. Variations of the FeO spectrum itself, as  
10 well as the diurnal and seasonal behaviour of the FeO and Na emission intensities are reported. These airglow emissions are linked by their common origin, meteoric ablation, and share O<sub>3</sub> as a common reactant. Major differences are found in the main emission peak of the FeO airglow spectrum between 0.58 and 0.61 μm, compared with a theoretical spectrum. The FeO and Na airglow intensities exhibit a similar nocturnal variation, and a semi-annual seasonal variation with equinoctial maxima.  
15 This is satisfactorily reproduced by a whole atmosphere chemistry climate model, if the quantum yields for the reactions of Fe and Na with O<sub>3</sub> are 13±3% and 11±2%, respectively. However, a comparison between the modelled O<sub>3</sub> in the upper mesosphere and measurements of O<sub>3</sub> made with the SABER satellite instrument suggests that these quantum yields may be a factor of ~2 smaller.

## 1 Introduction

20 The mesosphere lower thermosphere (MLT) is a layer of the atmosphere located between  $\sim 70$  to 110 km above the surface (Plane et al., 2015). The ablation of cosmic dust particles entering the atmosphere is the main source of ~~the metals~~ metal layers (Fe, Si, Mg, Na, K and Ca) in the MLT (e.g. Plane, 1991; Plane et al., 2015). These metals have been measured by space-based observation (e.g. Hedin & Gumbel, 2014; Fan et al., 2007; Evans et al., 2010; Dawkins et al., 2015; Langowski et al., 25 2015) and ground-based lidar (e.g. Höffner & Friedman, 2004, 2005; Gardner et al., 2005; Gardner et al., 2011; Lübken et al., 2011; Yi et al., 2009; Friedman et al., 2013) over a range of latitudes.

There are currently around 20 lidar stations worldwide observing Na, about 10 stations studying Fe, and three each for K and Ca/Ca<sup>+</sup> according to Plane et al. (2015). Yi et al. (2009) and Gardner et al. (2005) conducted studies of the variations of the Na and Fe layers at Wuhan, China (30° 34' N, 114° 30 17' E) and the South Pole, respectively. Yi et al. (2009) observed semi-annual variations of both Na and Fe, while Gardner et al. (2005) showed that at the South Pole there was a significant annual variation in both metals, with a summer minimum in Na and Fe density.

Another method that has been used to study the meteoric metals uses low-to-medium resolution spectroscopy of the nightglow. Na is ~~a good candidate~~ commonly used for this technique since its chemiluminescent emission can be measured as a doublet at 0.5890 and 0.5896  $\mu\text{m}$ . Atomic Na reacts with O<sub>3</sub> and forms NaO. The latter then reacts with atomic O to yield Na in the excited Na(<sup>2</sup>P<sub>3/2,1/2</sub>) states. In fact, both the ground state of NaO(<sup>2</sup>II) and the first excited state NaO(<sup>2</sup> $\Sigma^+$ ) are involved, but overall the quantum yield for photon emission arising from the Na + O<sub>3</sub> reaction should be 16.6% on the statistical basis of correlating electronic states, which is in accordance with 40 rocket-borne and laboratory measurements (Plane et al., 2012).

Chemiluminescent emission from electronically excited FeO appears as a pseudo-continuum at wavelengths between 0.5 and 0.72  $\mu\text{m}$ , termed the "orange arc" bands. The emission is produced by the reaction Fe + O<sub>3</sub> with a quantum yield of  $\sim 2\%$ , measured in a laboratory study (West & Broida, 1975). Being part of the night-sky continuum emission implies that it is also contaminated 45 by other airglow continua (e.g. NO+O (Khomich et al., 2008) and NiO (Evans et al., 2011)), and astronomical sources such as scattered star- and moonlight, and zodiacal light.

Two previous studies have employed spectroscopy to measure the FeO airglow emission. Evans et al. (2010) used the OSIRIS (Optical Spectrograph and InfraRed Imager System) spectrometer on the Odin satellite to detect the feature in the night-sky continuum. They found that the spectral 50 shape of FeO from their study matched the laboratory spectrum of West & Broida (1975). Gattinger et al. (2011) calculated a theoretical spectrum, using laboratory data and the spectra obtained from OSIRIS. These studies were followed by Saran et al. (2011) who used the ground-based ESI spectrograph (resolving power  $\lambda/\Delta\lambda \sim 7\,000$ ,  $\lambda = 0.39$  to 1.1  $\mu\text{m}$ ) at the Keck observatory (19° 49.6' N, 155° 28.5' W) to detect FeO contribution to the night-sky spectrum. Data from five nights in 55 March 2000 and four nights during October of the same year were presented. This study showed

that the diurnal behaviour of Na and FeO are closely related. This is not surprising since the two emissions share the same source, meteoric ablation of cosmic dust and involve reactions with O<sub>3</sub>. Saran et al. (2011) investigated the intra-annual change of the FeO emission strength with spectra taken in March and October 2009 as well as spectra from February and June 2010 taken at Kitt Peak  
60 (31° 57.5' N, 111° 35.8' W). They found a clearly visible change in the FeO pseudo-continuum with the seasons.

In this paper we investigate the FeO airglow continuum with respect to the already well studied Na emission. We used all publicly available data from the X-shooter echelle spectrograph at Cerro  
65 Paranal (24° 37' S, 70° 24' W, 2 635 m) (Vernet et al., 2011) from October 2009 to March 2013, compiling a sample of 3 662 spectra with higher resolution than previous studies (Evans et al., 2010; Saran et al., 2011).

With our sample it is possible to investigate differences between the observed spectra and the theoretical one provided by Gattinger et al. (2011) (see Sect. 3.1.2). The resolution of X-shooter enables  
70 us not just to distinguish between the different features of the FeO emission but also to study finer structures within the FeO emission. The diurnal variability (3.2) and seasonal variability (3.3) of the FeO and Na emissions are then reported, and the seasonal variability is compared with the predictions of a whole atmosphere chemistry climate model (3.4).

## 2 Observations and data set

75 The spectra were taken with the Very Large Telescope (VLT) operated by the European Southern Observatory (ESO). These four 8-meter class telescopes are located in the Chilean Atacama desert at an altitude of 2 635 m on the top of Cerro Paranal. Since the VLT is an astronomical research facility we do not have dedicated airglow observations, but use the observed astronomical data. The Earth's atmosphere leaves its fingerprint in every spectrum taken at the facility. Especially valuable  
80 are long-slit spectra since they contain a portion of the night-sky in addition to the astronomical science object. X-shooter is a medium-to-high resolution spectrograph with a field of view between  $0.4 \times 11 \text{ arcsec}^2$  and  $5 \times 11 \text{ arcsec}^2$ . It is a unique instrument since it covers a wavelength range from 0.3 to 2.5  $\mu\text{m}$  simultaneously with a resolving power ranging from 3 000 to 18 000, depending on the covered wavelength range and slit width. While the wavelength range is covered with one shot, the  
85 spectrum is split into three so-called arms: the UV to blue part of the spectrum (UVB, 0.3-0.56  $\mu\text{m}$ ), the "visual" regime (VIS, 0.56-1.02  $\mu\text{m}$ ), and the near infrared (NIR, 1.02-2.5  $\mu\text{m}$ ). To study FeO emission (0.5 - 0.72  $\mu\text{m}$ ) the VIS arm was used. X-shooter is a frequently used instrument, so there is comprehensive coverage over several years. Figure 1 shows the available data that had a minimum exposure time of 10 minutes, and passed additional quality checks after the data reduction.  
90 An exposure time of 10 minutes provides a sufficient signal-to-noise (S/N) to reliably detect FeO

emission. For the data reduction, an adapted version of [the public ESO pipeline v2.6.8](#) ~~of the ESO public pipeline~~ (Modigliani et al., 2010) was used, which allowed us to use data of almost all observing modes to determine the sky spectrum (Vernet et al., 2011; Noll et al., 2015). The reduction results in a two dimensional (2D) sky spectrum which was then collapsed to a 1D sky spectrum using a median along the spatial direction. The absolute intensity calibration was performed using spectra of spectrophotometric standard stars (Moehler et al., 2014), which were corrected for molecular absorptions (Smette et al., 2015; Kausch et al., 2015) and atmospheric extinction (Patat et al., 2011). For more details see Noll et al. (2015). In addition to Noll et al. (2015) we also performed a continuum correction. We corrected for the influence of residuals related to the ~~echelle orders~~ [high diffraction orders of the echelle spectrograph](#) introduced by the pipeline. [Comparing different extraction routines we found a systematic variation in flux with wavelength that shows minima at the central positions of the different echelle orders and maxima in the overlapping regions. A correction spectrum was determined by comparing differently extracted spectra. This spectrum was then scaled to the observation and subtracted. In addition, we checked for continuum contribution by astronomical objects, the reliability of the intensities of various OH lines and for unreasonable behaviour like sudden steps in the spectrum.](#)

Our quality checks leave us with a sample of 3 662 spectra (see Fig. 1). Over the whole period from October 2009 and March 2013, 33%, 32% and 22% of the data were taken in 2011, 2010 and 2012, respectively, while 2009 and 2013 account for 13%. Each month from April to August contributes between 5 to 8% to the sample. The most prominent months are December and January with 10%, ~~and~~ as well as March and September with 13%. This uneven distribution is due to the observation schedule of the VLT.

Four months of UVB arm spectra (January, April, July and October 2010) were used as a control sample in Sect. 3.1.2. This sample consists of 223 spectra with each of them having a counterpart in the VIS arm.

### 3 Methods and Results

Compared to other airglow emissions such as Na and O, FeO ~~is only contributes to the airglow as~~ a faint pseudo-continuum ~~component~~. Consequently, there are two issues to be taken care of when measuring the FeO emission intensity in the X-shooter spectra: first, sufficient integration time (see Sect. 2); second, the subtraction of any other emission in the wavelength region of the FeO emission. This includes contributions from zodiacal light, scattered star- and moonlight. These components were corrected by using the sky model described in Noll et al. (2012) and Jones et al. (2013). The airglow emission lines were corrected by fitting a Gaussian function to define the width of each line. Median values of predefined continuum windows, with close proximity to each emission line, were used to interpolate the corresponding wavelength range. Figure 2 illustrates the result before

and after the subtraction of the airglow emission lines as well as additional background components such as zodiacal light, scattered star- and moonlight. The structure of the FeO spectrum can be clearly identified in Fig. 2, panel (b). The spectrum has an exposure time of ~~roughly~~ 1 hour and is in the medium range ( $\lambda/\Delta\lambda \approx 7\ 450$ ) of the X-shooter resolving power.

130 Figure 2 also illustrates that the most prominent section of the FeO emission is between 0.58 and 0.61  $\mu\text{m}$ , where the main emission peak is located. In this window only Na and OH(8-2) have to be subtracted. The other parts of the FeO emission bands have a higher contamination of airglow emission lines and have a lower S/N. Hence, the integrated intensity measurements presented below are from ~~this~~ the interval around the main peak. The continuum for the intensity measurements is  
135 defined from the minima on each side of the main peak. Since the minima are narrow regions and their depth is variable, they are the dominant error source. The magnitude of this error was estimated using a Monte Carlo method. By varying the width and position of the continua on both sides of the peak and calculating the respective intensities, the uncertainty in the integrated peak intensity was derived. The winter months, June to August, contain fewer spectra than the rest of the year (see Fig.  
140 1). Hence we tested if any bias was introduced by the uneven distribution. We tested our results with respect to the data distribution over the year by introducing equally spaced bins, spanning a fortnight. Using these bins, our results only changed within the error (see Sect. 3.3). In comparison, Saran et al. (2011) investigated the FeO intensity in a window between 0.56 and 0.62  $\mu\text{m}$ . They subtracted the Na and OH(8-2) emission and the continuum level, which ~~is~~ according to Gattinger et al. (2011) is  
145 defined at 0.5  $\mu\text{m}$  ~~from~~ in their selected wavelength range. We estimated an error of 6% for the FeO main peak measurements ~~of 6%~~ by testing the possible influence of other continuum components (NiO, NO+O) as well as the choice of the side minima of the main peak.

The intensity of the Na doublet was measured by summing the intensities of Na D<sub>1</sub> and Na D<sub>2</sub> and subtracting the underlying continuum. The continuum was obtained individually for each line by a  
150 fit of a Gaussian to the lines and using the offset of the obtained parameters as continuum value. FeO and Na intensity measurement were corrected for the van Rhijn effect (see Noll et al., 2015).

In the following sections we investigate the deviation of the observed FeO spectrum from the one derived by Gattinger et al. (2011) with respect to the FeO emission strength intensity (Sect. 3.1). In  
155 Sect. 3.2 the diurnal variability of the FeO emission in the four different seasons is examined and compared with the results from Na. In Sect. 3.3 the seasonal behaviour of the FeO and Na intensities ~~are~~ is discussed and compared with the study of Takahashi et al. (1995). Finally, we compare in Sect. 3.4 the observational results to the predictions of a Whole Atmosphere Chemistry Climate Model (WACCM).

## 160 3.1 Variability of the FeO spectrum

### 3.1.1 Methods

To investigate the variability of the FeO emission, we sorted the 3 662 available spectra according to their main peak intensity by dividing them into five bins (quintiles) and ~~merge~~ merged these spectra into a median spectrum for each bin. Figure 3a illustrates the different median FeO spectra.

165 The first quintile spectrum (blue line in Fig. 3), is the one with the lowest intensity, whereas the fifth quintile spectrum (red) is the one with the median spectrum of the highest intensity. The fifth quintile spectrum is well represented in all years, with the most prominent months March, April, September and October. The spectra of the first and second quintile bin are evenly distributed over all the years and mainly originate from the months December and January (50% of the total number of spectra).

170 To compare the median spectra to the theoretical spectrum of Gattinger et al. (2011) we ~~normalize~~ normalised the theoretical spectrum to the mean intensity in the main peak. Then the median spectra were ~~normalized~~ normalised by scaling their main peak to the unit area of the theoretical main peak (see Fig. 3b). In the following we concentrate on the first and fifth quintile spectrum. For Fig. 3c we subtracted the theoretical spectrum from the median spectra.

175 The regions shaded in grey in Fig. 3 are regions where deviations between the theoretical and the median spectra have to be taken with caution since residuals of strong absorption features from molecular absorption ( $O_2$ ), scattered star-, moon- and zodiacal light or airglow emission lines may not have been properly corrected.

### 3.1.2 Results

180 In general, the five quintile spectra show a good overall agreement with each other in terms of shape and emission pattern (see Fig. 3b). We found that they can be easily reproduced by any other quintile spectrum by multiplying them with a constant factor (see Fig. 3b). This indicates either a continuum contribution of e.g. NO+O and NiO that scales directly with the FeO emission or that the continuum contribution is very weak and hence does hardly contribute to the FeO spectrum. It should also be  
185 kept in mind that by subtracting the different components of the sky model and the residuals of the X-shooter pipeline an overcorrection is another possibility.

Comparing our median spectra with the theoretical one derived from Gattinger et al. (2011) we find a good agreement in general (Fig. 3b). However, there are significant differences within and in close proximity to the main peak (0.585 and 0.615  $\mu\text{m}$ ) which can amount up to 50% as illustrated in Fig.

190 3c. The theoretical reference spectrum shows a decrease of the main peak from 0.595 to 0.585  $\mu\text{m}$  whereas we find the main peak to be extended until 0.585  $\mu\text{m}$ . Part of the excess could be attributed to the residuals of Na emission lines and the OH(8-2) band, but the excess window is broader than these features. Furthermore, the theoretical spectrum shows structures within the main peak (0.595 and 0.600  $\mu\text{m}$ ). Our median spectra show less structure. The higher the intensity of the quintile spec-

195 trum the smoother the main peak, which is indicated by the excess in flux at  $0.59\ \mu\text{m}$  in Fig. 3c. One more deviation can be seen between  $0.615$  and  $0.626\ \mu\text{m}$ . A possible explanation for the deviation could be a contamination by NiO. Evans et al. (2011) showed that NiO emission can be found in the same wavelength regime as the FeO emission. They found a variation in the ratio of NiO/FeO emission from 0.05 to 0.3 using data from the OSIRIS spectrograph, and a ratio of 2.3 was obtained  
200 on board a space shuttle(see Gattinger et al., 2011). These differences were not discussed in detail in Evans et al. (2011). The NiO emission overlaps with FeO emission in the VIS arm and cannot be separated. We tested our sample for NiO emission by using spectra from the UVB arm. The FeO emission starts at  $0.5\ \mu\text{m}$  (Gattinger et al., 2011), whereas NiO extends further into the blue down to about  $0.465\ \mu\text{m}$  (Burgard et al., 2006). Hence we studied the UVB for distinctive features and  
205 compared them to the NiO spectrum by Burgard et al. (2006). We found one peak between  $0.495$  and  $0.508\ \mu\text{m}$ . Using this peak to scale the laboratory NiO spectrum accordingly we find a maximum contribution ~~of to the FeO main peak intensity by NiO of 31% to the main peak%~~, while the average contribution is in the order of  $\sim 2\%$ . However, this estimate has to be treated with caution, since we could not find any correlation between the possible NiO emission and the FeO emission or any other  
210 distinct NiO emission signatures in either the UVB or VIS arms.

Scaling the main peak emission from Gattinger et al. (2011) to the whole ~~spectrum~~ FeO pseudo-continuum we obtain a value of  $3.9\%$ . To compare this to our measured spectra we reconstructed a FeO spectrum from our sample. First, we calculated a median spectrum of the whole sample. The VIS arm spectra do not extend further to the blue than  $0.56\ \mu\text{m}$ , so we extended it from  $0.56\ \mu\text{m}$  to  $0.5\ \mu\text{m}$  by scaling  
215 the corresponding part of the theoretical spectrum accordingly. The grey-shaded regions in Fig. 3 were replaced in the same way. Our median spectrum from  $0.68$  to  $0.72\ \mu\text{m}$  is heavily influenced by further airglow emission. Hence this part was also replaced by the scaled theoretical spectrum. This procedure provided us with a FeO spectrum, where the main peak amounts to  $3.3\pm 0.8\%$  of the total FeO emission ranging from  $0.50$  to  $0.72\ \mu\text{m}$ . For the estimated error we took scaling errors of the  
220 theoretical spectrum to the overall median spectrum into account as well as contamination by the NiO and NO+O continuum.

The same tests were done with a FeO laboratory spectrum by Jenniskens et al. (2000). This spectrum showed a shift in the main peak of  $5\ \text{nm}$  compared to our median spectra. Furthermore, the main peak in Jenniskens et al. (2000) is more prominent than in our median spectra. The ratio of the  
225 main peak to the whole spectral range would be  $12\%$  which is a factor of four larger than what we estimated from our median spectra. Also the side peaks on the red side of the main peak are hardly traced at all. The overall agreement of the laboratory spectrum to our median spectrum is worse than the agreement with the theoretically derived one.

## 3.2 Diurnal variability

### 230 3.2.1 Methods

The sample is sufficiently well distributed over the different seasons to study the nocturnal behaviour of the FeO and Na emission. For clearer statistics the night was divided into five bins (in local time) by using 21:00, 23:00, 1:00 and 3:00 as delimiters. The number of data points within each bin is highly variable and varying between 110 and 316. In general, the bins at the beginning and end of the night ~~are the low statistic bins~~ contain the fewest data points. The error bars were derived from the standard deviations of the measurements. For a clearer comparison, the relative intensities are plotted normalised to the nightly mean. All seasons we refer to are related to the southern hemisphere.

### 3.2.2 Results

In Fig. 4 we illustrate the nocturnal behaviour of FeO and Na during the four seasons at Cerro Paranal in the Atacama desert for the complete sample. In general, the Na and FeO emission show similar diurnal ~~variation~~ variations within their combined errors, ~~i.e.~~ (see Figs. 4 a, c and d to c). The intensities of FeO and Na decline at the beginning of the night and rise towards sunrise (see Figs. 4 a, c, d). These panels also show that the relative intensity of Na is strongest at the end of the night, while the relative FeO intensity is either at the same level or lower than at the beginning of the night. Figure 4b shows a steady decline of the relative FeO and Na intensities throughout the night. ~~The~~ Studying the individual years, a decline in relative intensity is found in the same period of the year in 2011 and 2012, while 2010 shows a rise towards the morning. The data from September to November in 2011 do not comply with 2010 and 2012, since there is a steep decline towards the final bin of the night.

### 250 3.3 Seasonal variability

#### 3.3.1 Methods

The annual and semi-annual variations of the FeO and Na intensities were determined by fitting the data to the following expression (e.g. Takahashi et al., 1995):

$$F(t) = A_0 + A_1 \cdot \cos\left(\frac{2\pi(t - \varphi_1)}{365}\right) + A_2 \cdot \cos\left(\frac{2\pi(t - \varphi_2)}{182.5}\right) \quad (1)$$

255 where  $A_1$  and  $A_2$  are the amplitudes of the annual and semi-annual oscillations, respectively, and  $\varphi_1$  and  $\varphi_2$  describe their corresponding phases. The parameter  $A_0$  denotes the annual mean. ~~The~~ Since the best-fit approach ( $\chi_{\min}^2$ ) is not done with a numerical scheme but makes use of a parameter grid, it relies on the grid size and does not provide uncertainties. Hence, we used Bayesian statistics to confirm the regression best fit and to derive the uncertainties for our results.

260 For this, we created a grid containing different combinations of the five parameters  $A_0$ ,  $A_1$ ,  $A_2$ ,  $\varphi_1$  and  $\varphi_2$ .  $\varphi$  was varied from 0 to 365 days and the amplitudes  $A$  between 0 and 0.65 ~~✗~~of the maximum intensity of the FeO or Na emission. For each of the created models above, we calculated the likelihood as follows:

$$L = e^{-(\chi^2 - \chi_{\min}^2)/2} \quad (2)$$

265 where  $\chi^2$  is the value and  $\chi_{\min}^2$  is the minimum  $\chi^2$  within the grid of ~~parameter~~parameter sets. The results of Eq. 2 are then used to obtain the probability of the best parameter set by,

$$P_{\text{par}} = \frac{\sum L_{\text{par}}}{\sum L}. \quad (3)$$

$L_{\text{par}}$  are the likelihoods, where one parameter of Eq. 1 is held constant and all others are varied.  $P_{\text{par}}$  is the derived probability of a given parameter set. Equation 3 does not contain the prior term  
270 since all models are assumed to have the same weight which results in a flat prior. Using Eq. 3 we are able to find a maximum within the parameter space corresponding to the most likely parameter set.

Table 1 shows the results of these calculations, with the mean value being a weighted mean and  $\sigma$  giving the standard deviation of the probability distribution.

### 275 3.3.2 Results

Figure 5 shows the measured intensities for the FeO main peak (Fig. 5a) and Na (Fig. 5b). The solid lines show the results of the least squares fit of Eq. 1, and the ~~square~~squares the Bayesian solution. FeO has a ~~stronger~~larger semi-annual amplitude in the best-fit solution, whereas the amplitudes for Na are equal and only show a dominating semi-annual amplitude using the Bayesian analysis.  
280 The relative intensity change derived between  $A_1$  and  $A_2$  in Na ( $A_1$ : 25%,  $A_2$ : 30%) tends to be less prominent than the change in FeO ( $A_1$ : 17%  $A_2$ : 27%). Taking the errors of the Bayesian analysis into account (see Tbl. 1) we cannot exclude that  $A_1$  and  $A_2$  are equally strong for FeO and Na.

Comparing the phases of Na and FeO derived with both methods we find them to be in good agreement within the error. FeO and Na show their global minimum at the beginning of February and  
285 their second minimum at the end of August, while the maxima can be found at the end of ~~May~~April and the beginning of November when combining the annual and semi-annual components.

The results for the Na emission can also be compared with the study of Takahashi et al. (1995), which used the same model (see Eq. 1) and was carried out at a similar latitude (Cachoeira Paulista; 22° 39' S). They reported Na amplitudes relative to the annual mean of  $A_1 = 28\%$  and  $A_2 = 41\%$ .

290 The semi-annual amplitude is clearly the dominant component. Fukuyama (1976, 1977) and Wiens & Weill (1973) examined the latitude dependency of the relative strengths of the annual and semi-annual amplitude of the emission intensities of Na and other MLT airglow emissions. Their studies

showed that the semi-annual oscillation decreases at higher latitudes. Comparing Na relative amplitudes of Cerro Paranal ( $A_1$ : 25%,  $A_2$ : 30%) with Cachoeira Paulista ( $A_1$ : 28%,  $A_2$ : 41%), we find that the results for  $A_1$  are in good agreement. On the other hand, the difference in latitude is probably too small to explain the discrepancies in  $A_2$ . However, differences in the sampling, observing period or longitude could be responsible for equally strong  $A_1$  and  $A_2$  at Cerro Paranal. Comparing the phases of sodium from Takahashi et al. (1995) with our study, the annual and the semi-annual phase are in agreement within the errors.

## 3.4 Models

### 3.4.1 Methods

Here we use the Whole Atmosphere Community Climate model (WACCM), in which the injection through meteoric ablation and chemistry of Na (Marsh et al., 2013) and Fe (Feng et al., 2013) have been included, to simulate the Na and FeO emission intensities at Cerro Paranal in the Chilean Atacama desert. WACCM is a coupled chemistry climate model which consists of a fully interactive chemistry and dynamics from the surface to an upper boundary at  $6.0 \times 10^{-6}$  hPa ( $\sim 140$  km) (Marsh et al., 2013). The model was run with specified dynamics (termed as SD-WACCM) using ECMWF-Interim analyses (Dee et al., 2011) below 50-60 km from 2004-2015. The horizontal resolution is  $1.9^\circ$  latitude  $\times$   $2.5^\circ$  longitude, with 88 vertical levels with a vertical resolution of approximately 3.5 km in the MLT region. The photolysis, neutral and ion-molecule chemistry as well as meteoric input function are described in Plane et al. (2015).

The airglow intensities were calculated by integrating the FeO and Na volume emission rates between 80 and 100 km. The volume emission rates were calculated using the modelled concentrations of Fe, Na and  $O_3$ , and the reaction rate coefficients for  $Fe + O_3$  and  $Na + O_3$  at the modelled temperatures. The airglow intensities were calculated daily at local midnight from 1 January 2009 to 31 December 2015, thus covering the period of the observations.

### 3.4.2 Results

Figure 6 shows a comparison of the nightly-averaged observations of FeO emission, considering a 3.9% contribution of the main peak to the total emission (see Sect. 3.1.2), with the model at local midnight. The modelled intensities are scaled by a factor of 0.13 to produce a correlation plot (lower panel) with a slope of 1 when forced through the origin. That is a quantum yield of  $13 \pm 3\%$  for the  $Fe + O_3$  reaction, which is much closer to the laboratory measurement of West & Broida (1975) (2-6%) than the previous modelling study of Saran et al. (2011) (100%). The error of the quantum yield was estimated by convolving combining in quadrature the 22% uncertainty in the  $Fe + O_3$  reaction rate coefficient (Helmer et al., 1994), a 6% uncertainty in the absolute calibration of the observed FeO\*

intensity, and a 2% uncertainty from the correlation plot in Fig. 6. Figure 7 is the analogous plot for the Na airglow emission intensity. The modelled intensities are scaled by a factor of 0.11 to produce a correlation plot (lower panel) with a slope of 1 when forced through the origin. The corresponding quantum yield of  $11 \pm 2\%$  for the Na + O<sub>3</sub> reaction is really an effective quantum yield, since photons at 0.5890 and 0.5896  $\mu\text{m}$  are produced from both the <sup>2</sup>Π and <sup>2</sup>Σ<sup>+</sup> states of NaO reacting with O (Plane et al., 2012). The uncertainty in the Na quantum yield is estimated by ~~convolving~~ combining in quadrature the 12% uncertainty in the Na + O<sub>3</sub> reaction rate coefficient (Plane et al., 1993) with a 6% absolute calibration uncertainty and 2% uncertainty in the correlation plot (see Fig. 7). In both cases, the model captures well the semi-annual seasonal variation of the airglow intensities, with equinoctial maxima which correspond to peaks in MLT O<sub>3</sub> density (Thomas et al., 1984). Note that the autumnal peak of the FeO emission intensity in March/April is larger than the vernal peak in September/October. The reason for this is elucidated in Fig. 8, which shows that the injection flux of meteoric Fe peaks in March/April (Feng et al., 2013). This coincides with maxima in both the atomic Fe and O<sub>3</sub> density in WACCM (shown at a representative height of 87 km in Fig. 8). Since the FeO emission intensity is proportional to the product of [Fe] and [O<sub>3</sub>], it maximises in autumn between March and May. In September to November, the secondary O<sub>3</sub> peak is offset by a low Fe density, as the Fe injection flux is near minimum. The same considerations apply to the seasonal variation of the Na emission intensity. A final point to note is that there is evidence that WACCM may underestimate the O<sub>3</sub> concentration in the airglow region between 86 and 89 km, as a result of insufficiently rapid downward transport of atomic O from the thermosphere (Smith et al., 2015). We have therefore compared the WACCM night-time O<sub>3</sub> at 24° S with SABER for the period of the present study. The modelled O<sub>3</sub> is on average between 45 and 56% lower than SABER. This suggests that the quantum yields estimated in this study could be lower by a factor of ~2. This would bring the FeO quantum yield into even better agreement with the laboratory study of West & Broida (1975). The Na quantum yield would then be close to lower end of the range of 0.05 - 0.2 that was estimated from a combined rocket-borne and lidar experiment (Clemesha et al., 1995). Furthermore, a minimisation between the measured data and the model values was performed. This resulted in a quantum yield of 0.093. von Savigny et al. (2017) retrieved Na profiles from SCIAMACHY (Imaging Absorption spectroMeter for Atmospheric CHartography, see Burrows et al., 1995) observations. Choosing the quantum yield to be 0.09 led to the best fit of their model. These values are in good agreement with our result.

#### 4 Conclusions

Astronomical data are a valuable addition to the study of airglow ~~emission~~ emissions. Astronomical facilities provide long-time archives of medium-to-high resolution spectra. Using the X-shooter archive data we compiled a sample of 3 662 spectra showing FeO emission with a minimum expo-

sure time of 10 min.

To study the variation of the FeO spectrum with intensity, median spectra for different intensities were created (see Sect. 3.1.2). The shape of the quintile spectra is almost identical to each other.

365 They can be transformed into each other by multiplying with a constant factor. Comparing the median spectra to a theoretical spectrum by Gattinger et al. (2011) we found three major deviations: a broader main peak, less structure in the main peak and a possible additional emission peak between 0.615 and 0.626  $\mu\text{m}$ . Reasons for the deviations could be additional airglow emission from NiO and NO+O (Evans et al., 2011). Evans et al. (2011) pointed out that the ratio of NiO and FeO is highly variable (0.3-2.3). In this study we found the maximum and average possible contamination of NiO to be  $\sim 30\%$  and  $\sim 2\%$  of the FeO main peak emission, respectively. To explain the broader main peak one could consider collisional excitation and deactivation. However, the radiative lifetime ( $\sim 400$  ns) is much smaller than the collisional lifetime ( $\sim 200$   $\mu\text{s}$ ) (see Gattinger et al., 2011). On the other hand, uncertainties in the molecular parameters as well as uncertainties in the population distribution of the FeO levels by the Fe+O<sub>3</sub> reaction may cause further deviations from the measured spectrum. To find the reason for the excess in the measured spectra compared to Gattinger et al. (2011) further simulations of the FeO spectrum are needed.

The diurnal variability of the FeO emission was studied with respect to the four seasons (Sect. 3.2.2). In general, FeO and Na show a very similar behaviour. None of the seasons ~~show~~ shows a sudden drop of the FeO emission at the end of the night as observed by Saran et al. (2011). This may be due to the better time resolution of Saran et al. (2011) at the end of the night. In general, it has to be noted that the behaviour of the seasons can vary strongly between the different years.

Finally, we studied the seasonal variation of the FeO emission (Sect. 3.3.2). We derived the annual and semi-annual amplitudes and phases of FeO and compared these results with the analogous parameters derived for Na. We compared our results for sodium with the study of Takahashi et al. (1995), who found a dominant semi-annual amplitude for Na. Possible reasons for this difference in the relative strength of the annual and semi-annual amplitudes could be a change in latitude (e.g. Fukuyama, 1976, 1977; Wiens & Weill, 1973), longitude, a difference in the sampling or the observing period. Other studies (e.g. Fukuyama, 1976, 1977; Wiens & Weill, 1973) showed that the dominance of the semi-annual amplitude decreases with increasing latitude. These results were satisfactorily reproduced by a whole atmosphere chemistry climate model (see Sect. 3.4), which revealed that a  $13\pm 3\%$  quantum yield for the Fe+O<sub>3</sub> reaction best fitted the entire observational data set, although this may be too large by a factor of 2 since there is evidence that the O<sub>3</sub> density in the upper mesosphere predicted by WACCM is about 50% too small. Using the reconstructed spectrum (see Sect. 3.1.2) as reference instead of the Gattinger et al. (2011) template we derive a quantum yield of  $16\pm 6\%$ .

## 5 Data availability

The WACCM Na and Fe model output has been archived at University of Leeds Petal library (<http://www.petal.leeds.ac.uk>) and can be obtained by emailing J.M.C. Plane or W. Feng.

400 The observational data used for the plots in this paper are available as a zip file at Atmospheric Chemistry and Physics.

*Acknowledgements.* This project made use of the ESO Science Archive Facility. X-shooter spectra from different observing programmes of the period from October 2009 to March 2013 were analysed. This publication is supported by the Austrian Science Fund (FWF). S. Unterguggenberger and S. Noll receive funding from the  
405 FWF project P26130. W. Kausch is funded by the project IS538003 (Hochschulraumstrukturmittel) provided by the Austrian Ministry for Research (BMWFV). W. Feng and J. M. C. Plane are funded by the European Research Council (project number 291332 - CODITA).

## References

- Burgard, D., Abraham, J., Allen, A., Craft, J., Foley, W., Robinson, J., Wells, B., Xu, C., and Stedman, D.:  
410 Chemiluminescent reactions of nickel, iron, and cobalt carbonyls with ozone, *Appl. Spectrosc.*, 60, 99-102,  
doi:10.1366/000370206775382730, ~~2006~~ 2006.
- Burrows, J. P., Hölzle, E., Goede, A. P. H., Visser, H., and Fricke, W.: *SCIAMACHY-scanning imaging absorption spectrometer for atmospheric chartography*, *Acta Astronaut.*, 35, 445-451, doi:10.1016/0094-5765(94)00278-T, 1995.
- 415 Clemesha, B. R., Simonich, D. M., Takahasi, H., and Melo, S. M. L.: Experimental evidence for photochemical control of the atmospheric sodium layer, *J. Geophys. Res.-Atmos.*, 100, 18909-18916,  
doi:10.1029/95JD01708, ~~1995~~ 1995.
- Dawkins, E. C. M., ~~J. M. C.~~ Plane, J. M. C., ~~M. P.~~ Chipperfield, M. P., and Feng, W.: The near-global mesospheric potassium layer: Observations and modeling, *J. Geophys. Res.-Atmos.*, 120, 7975-7987,  
420 doi:10.1002/2015JD023212, ~~2015~~ 2015.
- Dee, D. P., Uppala, S. M., Simmons, A. J., Berrisford, P., Poli, P., Kobayashi, S., Andrae, U., Balmaseda, M. A., Balsamo, G., Bauer, P., Bechtold, P., Beljaars, A. C. M., van de Berg, L., Bidlot, J., Bormann, N., Delsol, C., Dragani, R., Fuentes, M., Geer, A. J., Haimberger, L., Healy, S. B., Hersbach, H., Hólm, E. V., Isaksen, L., Kållberg, P., Köhler, M., Matricardi, M., McNally, A. P., Monge-Sanz, B. M., Morcrette, J.-J., Park,  
425 B.-K., Peubey, C., de Rosnay, P., Tavolato, C., Thépaut, J.-N., and Vitart, F.: The ERA-Interim reanalysis: configuration and performance of the data assimilation system-, *Q.J.R. Meteorol. Soc.*, 137, 553-597-,  
doi:10.1002/qj.828, ~~2011~~ 2011.
- Evans, W. F. J., Gattinger, R. L., Slinger, T. G., Saran, D. V., Degenstein, D. A., and Llewellyn, E. J.: Discovery of the FeO orange bands in the terrestrial night airglow spectrum obtained with OSIRIS on the Odin  
430 spacecraft, *Geophys. Res. Lett.*, 37, L22105, doi:10.1029/2010GL045310, ~~2010~~ 2010.
- Evans, W. F. J., Gattinger, R. L., Broadfoot, A. L., and Llewellyn, E. J.: The observation of chemiluminescent NiO emissions in the laboratory and in the night airglow, *Atmos. Chem. Phys.*, 11, 9595-9603,  
doi:10.5194/acp-11-9595-2011, ~~2011~~ 2011.
- Fan, Z. Y., Plane, J. M. C., Gumbel, J., Stegman, J., and Llewellyn, E. J.: Satellite measurements of the global  
435 mesospheric sodium layer, *Atmos. Chem. Phys.*, 7, 4107-4115, doi:10.5194/acp-7-4107-2007, ~~2007~~ 2007.
- Feng, W., Marsh, D. R., Chipperfield, M. P., Janches, D., Höffner, J., Yi, F., and Plane, J. M. C.: A global atmospheric model of meteoric iron, *J. Geophys. Res.-Atmos.*, 118, 9456-9474, doi:10.1002/jgrd.50708,  
~~2013~~ 2013.
- Friedman, J. S., Chu, X. Z., Brum, C. G. M., and Lu, X. J.: Observation of a thermospheric descending layer of  
440 neutral K over Arecibo, *J. Atmos. Sol.-Terr. PhyPhys.*, 104, 253-259, doi:10.1016/j.jastp.2013.03.002, ~~2013~~ 2013.
- Fukuyama, K.: Airglow variations and dynamics in the lower thermosphere and upper mesosphere-I. Diurnal variation and its seasonal dependency, *J. Atmos. Sol.-Terr. PhyPhys.*, 38, 1279-1287, doi:10.1016/0021-9169(76)90136-7, ~~1976~~ 1976.
- 445 Fukuyama, K. J.: Airglow variations and dynamics in the lower thermosphere and upper mesosphere-II. Seasonal long-term variation, *J. Atmos. Sol.-Terr. PhyPhys.*, 39, 1-14, doi:10.1016/0021-9169(77)90038-1, ~~1977~~ 1977.

- Gardner, C. S., Chu, X., Espy, P. J., Plane, J. M. C., Marsh, [and](#) D. R., Janches, D. J.: Seasonal variations of the mesospheric Fe layer at Rothera, Antarctica (67.5° S, 68.° W), *J. Geophys. Res.*, 116, D02304, doi:10.1029/2010JD014655, [2011-2011](#).
- Gardner, C. S., Plane, J. M. C., Pan, W. L., Vondrak, T., Murray, B. J., [and](#) Chu, X. Z.: Seasonal variations of the Na and Fe layers at the South Pole and their implications for the chemistry and general circulation of the polar mesosphere, *J. Geophys. Res.*, 110, D10302, doi:10.1029/2004JD005670, [2005-2005](#).
- Gattinger, R. L., Evans, W. F. J., Degenstein, D. A., [and](#) Llewellyn, E. J.: A spectral model of the FeO orange bands with a comparison between a laboratory spectrum and a night airglow spectrum observed by OSIRIS on Odin, *Can. J. of Phys.*, 89, 239-248, doi:10.1139/P11-003, [2011-2011](#).
- Helmer, M., [and](#) Plane, J. M. C.: Experimental and theoretical study of the reaction  $\text{Fe} + \text{O}_2 + \text{N}_2 \rightarrow \text{FeO}_2 + \text{N}_2$ , *J. Chem. Soc. Faraday Trans.*, 90, 395-401, doi:10.1039/ft9949000395, [1994-1994](#).
- Helmer, M., Plane, J. M. C., Quian, J., [and](#) Gardner, C. S.: A model of meteoric iron in the upper atmosphere, *J. Geophys. Res.*, 103, 10913-10925, doi:10.1029/97JD03075, [1998-1998](#).
- Höffner, J., [and](#) Friedman, J. S.: The mesospheric metal layer topside: a possible connection to meteoroids, *Atmos. Chem. Phys.* [3](#), [4](#), 801-808, doi:10.5194/acp-4-801-2004, [2004-2004](#).
- Höffner, J., [and](#) Friedman, J. S.: The mesospheric metal layer topside: Examples of simultaneous metal observations, *J. Atmos. Sol.-Terr. PhyPhys.*, 67, 1226-1237, doi:10.1016/j.jastp.2005.06.010, [2005-2005](#).
- Hedin, J., [and](#) Gumbel, J.: The global mesospheric sodium layer observed by Odin/OSIRIS in 2004-2009, *J. Atmos. Sol.-Terr. PhyPhys.*, 73, [73](#), 2221-2227, doi:10.1016/j.jastp/2010.10.008, [2011-2011](#).
- Jenniskens, P., Lacey, M., Allan, B. J., Self, D., [and](#) Plane, J. M. C.: FeO "orange arc" emission detected in optical spectrum of leonid persistent train, *Earth Moon and Planets*, [82-3](#), [429-34882](#), [429-438](#), doi:10.1023/A:1017079725808, [2000-2000](#).
- Jones, A., Noll, S., Kausch, W., Szyszka, C., [and](#) Kimeswenger, S.: An advanced scattered moonlight model for Cerro Paranal, *Astron. Astrophys.*, 560, A91, doi:10.1051/0004-6361/201322433, [2013-2013](#).
- Kausch, W., Noll, S., Smette, A., Kimeswenger, S., Barden, M., Szyszka, C., Jones, A. M., Sana, H., Horst, H., [and](#) Kerber, F.: Molecfit: a general tool for telluric absorption correction, II. Quantitative evaluation on ESOVLT/X-shooter spectra, *Astron. Astrophys.*, 576, A78, doi:10.1051/0004-6361/201423909, 2015.
- Khomich, V. Y., Semenov, A. I., [and](#) Shefov, N. N.: *Airglow as an Indicator of Upper Atmospheric Structure and Dynamics*, Springer, Berlin, Germany, 2008.
- Langowski, M. P., [von Savigny, C.](#), [Burrows, J. P.](#), [Feng, W.](#), [Plane, J. M. C.](#), [Marsh, D. R.](#), [Janches, D.](#), [Sinnhuber, M.](#), [Aikin, A. C.](#), [Liebing, P.](#) ([2015](#)): Global investigation of the Mg atom and ion layers using SCIAMACHY/Envisat observations between 70 and 150km altitude and WACCM-Mg model results, *Atmos. Chem. Phys.*, 15, 273-295, doi:10.5194/acp-15-273-2015, [2015-2015](#).
- Lübken, F. J., Höffner, J., Viehl, T. P., Kaifler, B., [and](#) Morris, R. J.: First measurements of thermal tides in the summer mesopause region at Antarctic latitudes, *Geophys. Res. Lett.*, 38, L24806, doi:10.1029/2011GL050045, [2011-2011](#).
- Marsh, D. R., Janches, D., Feng, W., [and](#) Plane, J. M. C.: A global model of meteoric sodium, *J. Geophys. Res.-Atmos.*, 118, 11442-11452, doi:10.1002/jgrd.50870, [2013-2013](#).

- Marsh, D. R., Mills, M. J., Kinnison, D. E., Lamarque, J. ~~FF~~, Calvo, N., and Polvani, L.M.: Climate change from 1850 to 2005 simulated in CESM1 (WACCM), *J. Clim.*, 26, 7372-7391, doi:10.1175/JCLI-D-12-00558.1, ~~2013~~ 2013.
- 490 Modigliani, A., Goldoni, P., Royer, F., Haigron, R., Guglielmi, L., Francois, P., Horrobin, M., Bristow, P., Vernet, J., Moehler, S., Kerber, F., Ballester, P., Mason, E., and Christensen, L.: The X-shooter pipeline, *SPIE Proc. Ser.*, 7737, 773728, doi:10.1117/12.857211, ~~2010~~ 2010.
- Moehler, S., Modigliani, A., Freudling, W., Giammichele, N., Gianninas, A., Gonneau, A., Kausch, W., Lançon, A., Noll, S., Rauch, T., and Vinther, J.: Flux calibration of medium-resolution spectra from 300 nm to 2500 nm: Model reference spectra and telluric correction, *Astron. Astrophys.*, 568, A9, doi:10.1051/0004-  
495 6361/201423790, ~~2014~~ 2014.
- Noll, S., Kausch, W., Barden, M., Jones, A. M., Szyska, C., Kimeswenger, S., and Vinther, J.: An atmospheric radiation model for Cerro Paranal: I. The optical spectral range, *Astron. Astrophys.*, 543, A92, doi:10.1051/0004-6361/201219040, ~~2012~~ 2012.
- Noll, S., Kausch, W., Kimeswenger, S., Unterguggenberger, S., and Jones, A. M.: OH populations and temperatures from simultaneous spectroscopic observations of 25 bands, *Atmos. Chem. Phys.*, 15, 3647-3669, doi:10.5194/acp-15-3647-2015, ~~2015~~ 2015.
- 500 Noll, S., Kausch, W., Kimeswenger, S., Unterguggenberger, S., and Jones, A. M.: Comparison of VLT/X-shooter OH and O<sub>2</sub> rotational temperatures with consideration of TIMED/SABER emission and temperature profiles, *Atmos. Chem. Phys.*, 16, 5021-5042, doi:10.5194/acp-16-5021-2016, ~~2016~~ 2016.
- 505 Patat, F., Moehler, S., O'Brien, K., Pompei, E., Bensby, T., Carraro, G., de Ugarte Postigo, A., Fox, A., Gavignaud, I., James, G., Korhonen, H., Ledoux, C., Randall, S., Sana, H., Smoker, J., Stefl, S., and Szeifert, T.: Optical atmospheric extinction over Cerro Paranal, *Astron. Astrophys.*, 527, A91, doi:10.1051/0004-6361/201015537, ~~2011~~ 2011.
- Plane, J. M. C.: The chemistry of meteoric metals in the Earth's upper atmosphere, *Rev. Phys. Chem.*, 10, 55-106, doi:10.1080/01442359109353254, ~~1991~~ 1991.
- 510 Plane, J. M. C., Feng, W. H., and Dawkins E. C. M.: The Mesosphere and Metals: Chemistry and Changes, *Chem. Rev.*, 115, 4497-4541, doi:10.1021/cr500501m, ~~2015~~ 2015.
- Plane, J. M. C., Nien, C. F., Allen, M. R., and Helmer, M.: A kinetic investigation of the reactions Na + O<sub>3</sub> and NaO + O<sub>3</sub> over the temperature-range 207-377 K, *J. Phys. Chem.*, 97, 4459-4467, doi:10.1021/j100119a033, ~~1993~~ 1993.
- 515 Plane, J. M. C., Oetjen, H., de Miranda, M., Saiz-Lopez, A., Gausa, M., and Williams B.: On the sodium D line emission in the terrestrial nightglow, *J. Atmos. Sol.-Terr. Phys.*, 74, 181-188, ~~2012~~ 2012.
- Saran, D. V., ~~Slanger, T. G.~~ Slanger, T. G., Feng, W., and Plane, J. M. C.: FeO emission in the mesosphere: Detectability, diurnal behavior, and modeling, *J. Geophys. Res.-Atmos.*, 116, D12303, doi:10.1029/2011JD015662, ~~2011~~ 2011.
- 520 Slanger, T. G., Cosby, P. C., Huestis, D. L., Saiz-Lopez, A., Murray, B. J., O'Sullivan, D. A., Plane, J. M. C., Prieto, C. A., Martin-Torres, F. J., and Jenniskens, P.: Variability of the mesospheric nightglow sodium D2/D1 ratio, *J. Geophys. Res.* ~~2005~~, 110, D23302, doi:10.1029/2005JD006078, ~~2005~~ 2005.
- 525 Smette, A., Sana, H., Noll, S., Horst, H., Kausch, W., Kimeswenger, S., Barden, M., Szyska, C., Jones, A. M., Gallenne, A., Vinther, J., Ballester, P., and Taylor, J.: Molecfit: ~~a~~ A general tool for telluric absorption

- correction. I. Method and application to ESO instruments, *Astron. Astrophys.*, 576, A77, doi:10.1051/0004-6361/201423932, [2015-2015](#).
- Smith, A. K., Lopez-Puertas, M., Xu, J. Y. ~~and Mlynzak,~~ ~~and Mlynyczak,~~ M. G.: The heating efficiency of the exothermic reaction  $H + O_3$  in the mesosphere, *J. Geophys. Res.-Atmos.*, 120, 12739-12747, doi:10.1002/2015JD024061, [2015-2015](#).
- 530 Takahashi, H., Clemensha, B. ~~R.~~, ~~and~~ Batista, P. ~~P.~~: Predominant semi-annual oscillation of the upper mesospheric airglow intensities and temperatures in the equatorial region, *J. Atmos. Terr. Phys.*, 57, 407-414, doi:10.1016/0021-9169(94)E0006-9, [1995-1995](#).
- Thomas, R. J., Barth, C. A., and Solomon, S.: Seasonal variations of ozone in the upper mesosphere and gravity waves, *Geophys. Res. Lett.*, 11, 673-676, doi:10.1029/GL011i007p00673, [1984-1984](#).
- 535 Vernet, J., Dekker, D'Odorico, S., Kaper, L., Kjaergaard, P., Hammer, F., Randich, S., Zerbi, F., Groot, P. ~~M.~~, Hjørth, J., Guinouard, I., Navarro R., Adolfse, T., Albers, P. ~~W.~~, Amans, J. ~~PP.~~, Andersen, J. ~~J.~~, Andersen, M. ~~I.~~, Binetruy, P., Bristow, P., Castillo, R., Chemla, F., Christensen, L., Conconi, P., Conzelmann, R., Dam, J., De Caprio, V., De Ugarte Postigo, A., Delabre, B., Di Marcantonio, P., Downing, M., Elswijk, E., Finger,
- 540 G., Fischer, G., Flores, H., François, P., Goldoni, P., Guglielmi, L., Haignon, R., Hanenburg, H., Hendriks, I., Horrobin, M., Horville, D., Jessen, N. ~~C.~~, Kerber, F., Kern, L., Kiekebusch, M., Kleszcz, P., Klougart, J., Kragt, J., Larsen, H. ~~H.~~, Lizon, J. ~~L.~~, Lucuix, C., Mainieri, V., Manuputy, R., Martayan, C., Mason, E., Mazzoleni, R., Michaelsen, N., Modigliani, A., Moehler, S., Møller, P., Norup Sørensen, A., Nørregaard, P., Péroux, C., Patat, F., Pena, E., Pragt, J., Reinero, C., Rigal, F., Riva, M., Roelfsema, R., Royer, F., Sacco,
- 545 G., Santin, P., Schoenmaker, T., Spano, P., Sweers, E., Ter Horst, R., Tintori, M., Tromp, N., van Dael, P., van der Vliet, H., Venema, L., Vidali, M., Vinther, J., Vola, P., Winters, R., Wistisen, D., Wulterkens, G., and Zacchei, A.: X-shooter, the new wide band intermediate resolution spectrograph at the ESO Very Large Telescope, *Astron. Astrophys.*, 536, A105, doi:10.1051/0004-6361/201117752, [2011-2011](#).
- von Savigny, C., ~~McDade, I. C., Eichman, K. U., and Langowski, M. P., Zilker, B.~~ Burrows, J. P.: ~~On the dependence of the OH Meinel emission altitude on vibrational level: SCIAMACHY observations and model simulations, Atmos. Chem. Phys., Fussen, D., and Sofieva, V. F.: First mesopause Na retrievals from satellite Na D-line nightglow observations, Geophys. Res. Lett., 43, 12,8813-8828~~ [651-12,658](#), doi:~~10.5194/10.1002/aep-12-8813-2012, 2012-2016~~ [GL071313, 2017](#).
- 550 West, J. B., ~~and~~ Broida H. P.: Chemiluminescence and ~~Photoluminescence—of—Diatomic Iron-Oxid~~ [photoluminescence of diatomic iron oxide](#), *J. Chem. Phys.*, 62, 2566-2574, doi:10.1063/1.430837, [1975-1975](#).
- Wiens, R. H., and Weill, G.: Diurnal, annual and solar cycle ~~variationsof~~ [variations of](#) the hydroxyl and sodium nightglow intensities in the Europe-Africa sector, *Planet. Space Sci.*, 21, 1011-1027, doi:10.1016/0032-0633(73)90147-5, [1973-1973](#).
- 560 Yi, F., Yu, C., Zhang, S., Yue, X., He, Y., Huang, C., Zhang, Y., and Huang, K.: Seasonal variations of the nocturnal mesospheric Na and Fe layers at 30° N, *J. Geophys. Res.*, 114, D01301, doi:10.1029/2008JD010344, [2009-2009](#).

**Table 1.** Coefficients of harmonic analysis

Method		$A_0$	$A_1$	$A_2$	$\varphi_1$	$\varphi_2$
		[R]	[R]	[R]	[DOY]	[DOY]
FeO	best fit	22.3	3.6 (16)	7.1 (31)	180	108
	mean	23.2	4.0 (17)	6.2 (27)	177	106
	$\sigma$	1.1	1.9	1.6	35	8
Na	best fit	40.4	9.9 (25)	9.9 (25)	192	108
	mean	39.9	9.9 (25)	11.9 (30)	191	108
	$\sigma$	1.1	0.5	2.4	8	1
	Cachoeira Paulista	33	9.2 (28)	16.3 (41)	192	109

$A_0$  denotes the annual mean intensity in Rayleigh.

$A_1$  is the amplitude of the annual oscillation in Rayleigh. In parentheses the relative value of  $A_1$  to  $A_0$  is given in per cent.

$A_2$  is the amplitude of the semi-annual oscillation in Rayleigh. The values in parentheses are the same as for  $A_1$ .

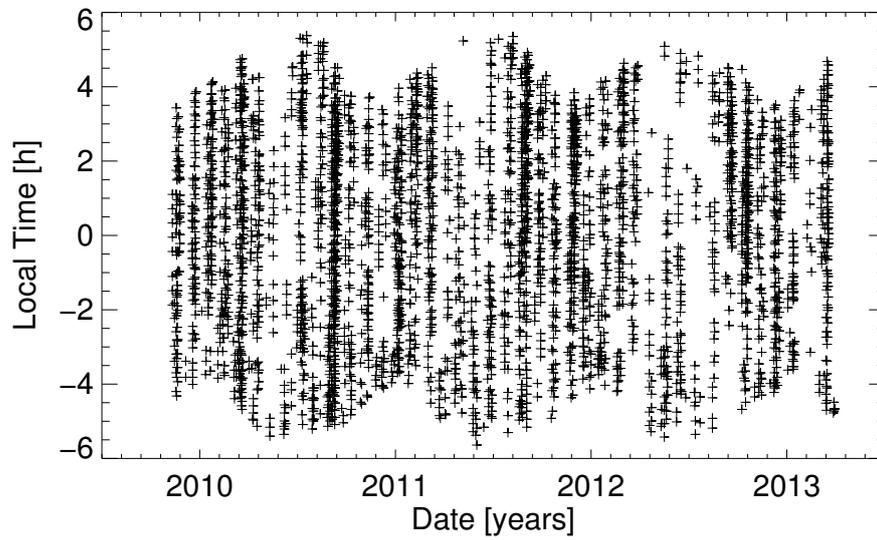
$\varphi_1$  is the phase shift of the annual oscillation in DOY.

$\varphi_2$  is the phase shift of the semi-annual oscillation in DOY.

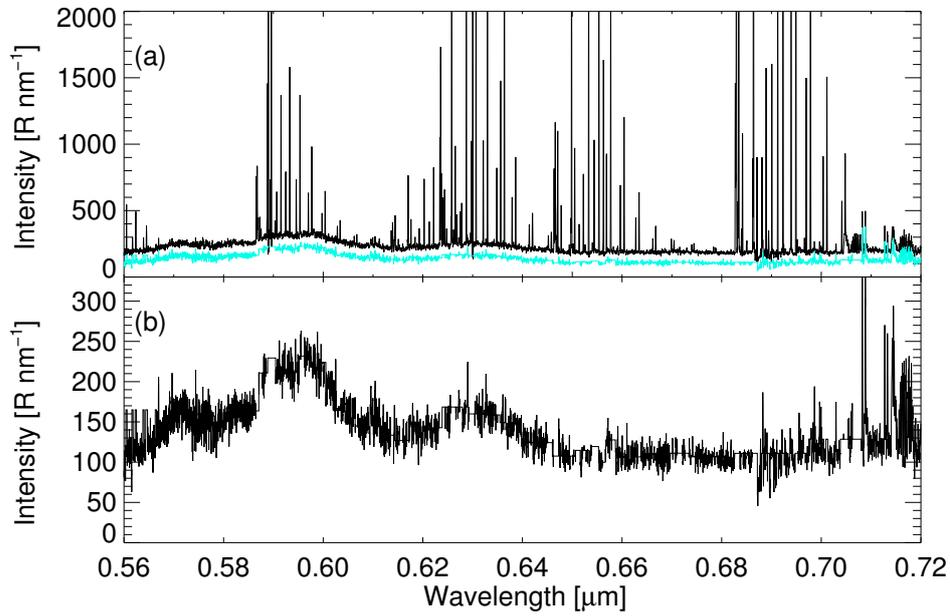
The column 'Method' refers to the fit used for the model. Best fit was achieved with a least squares fit.

Mean is the value retrieved with a Bayesian approach with  $\sigma$  as the standard deviation.

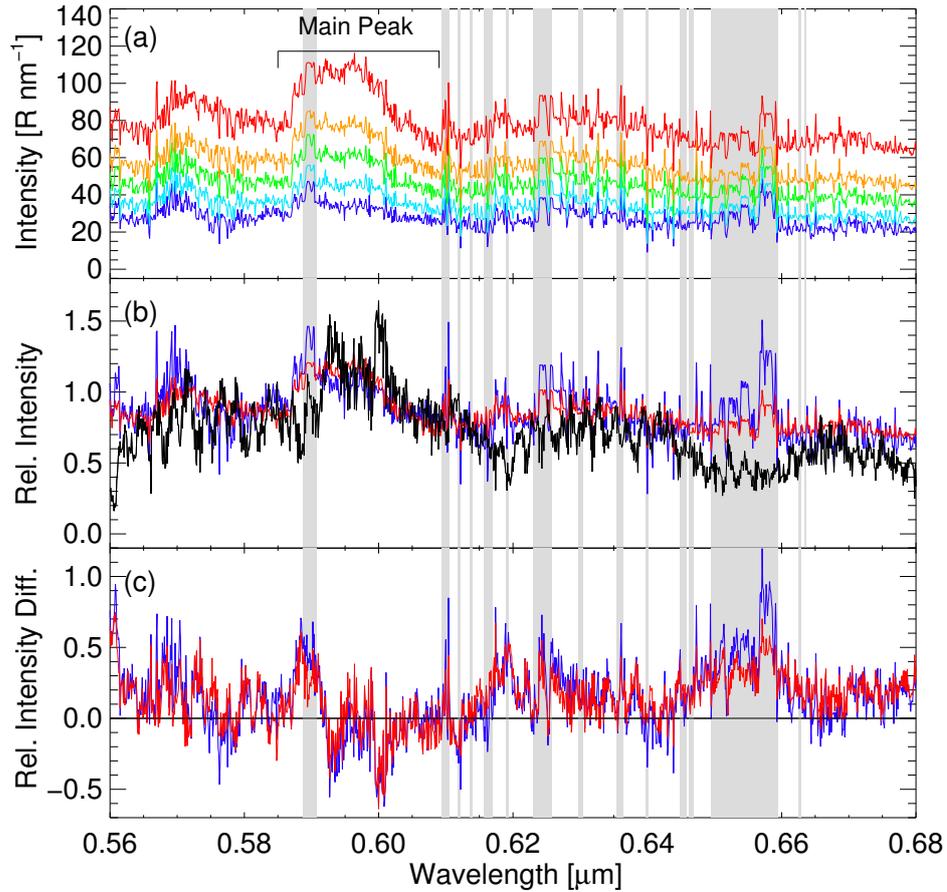
The comparison data are from Cachoeira Paulista (Takahashi et al., 1995).



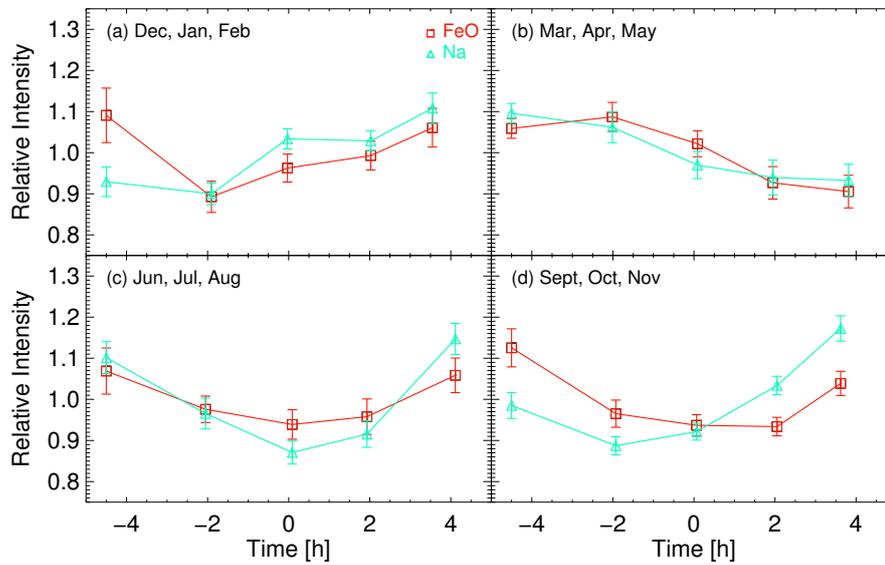
**Figure 1.** Coverage of the X-shooter data set between October 2009 and March 2013. The black crosses show all available X-shooter observations which have an exposure time of at least 10 min. The ordinate shows the observing time with 0 labelling local midnight.



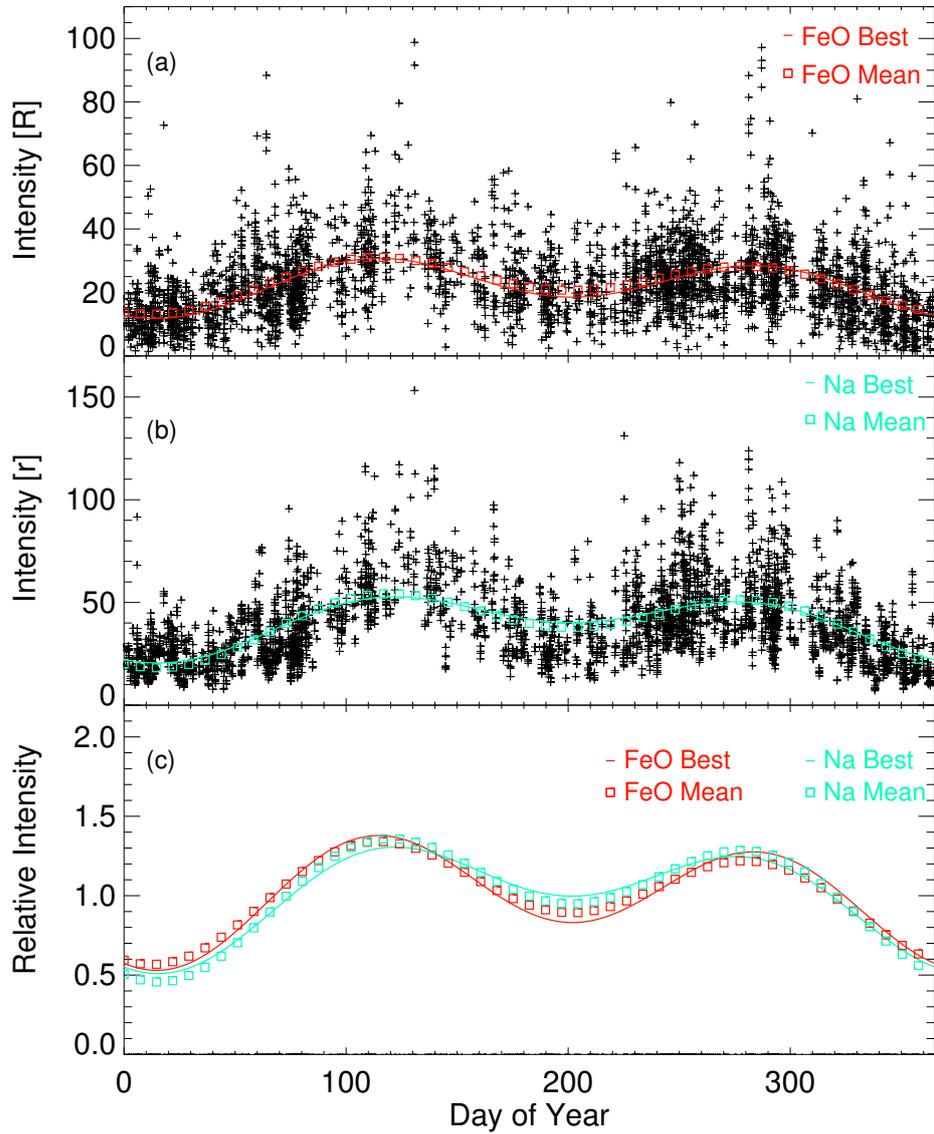
**Figure 2.** Example of a FeO spectrum. Panel (a) displays a raw night-sky spectrum with all its emissions. The FeO continuum, with possible contamination by NiO and NO+O, is overplotted in cyan. ~~Panel (b) shows~~ The difference is due to the same spectrum after removal of all airglow emission lines, zodiacal light, scattered star and ~~moon light~~ moonlight. ~~The Panel (b) shows the same FeO spectrum.~~ It has an exposure time of 3 600 sec and a resolving power of about 7 450. The ordinate shows the emission intensity in Rayleighs per nm ( $1R = 10^6 \text{ photons cm}^{-2} \text{ s}^{-1}$ ) while the abscissa shows the FeO emission regime in  $\mu\text{m}$ .



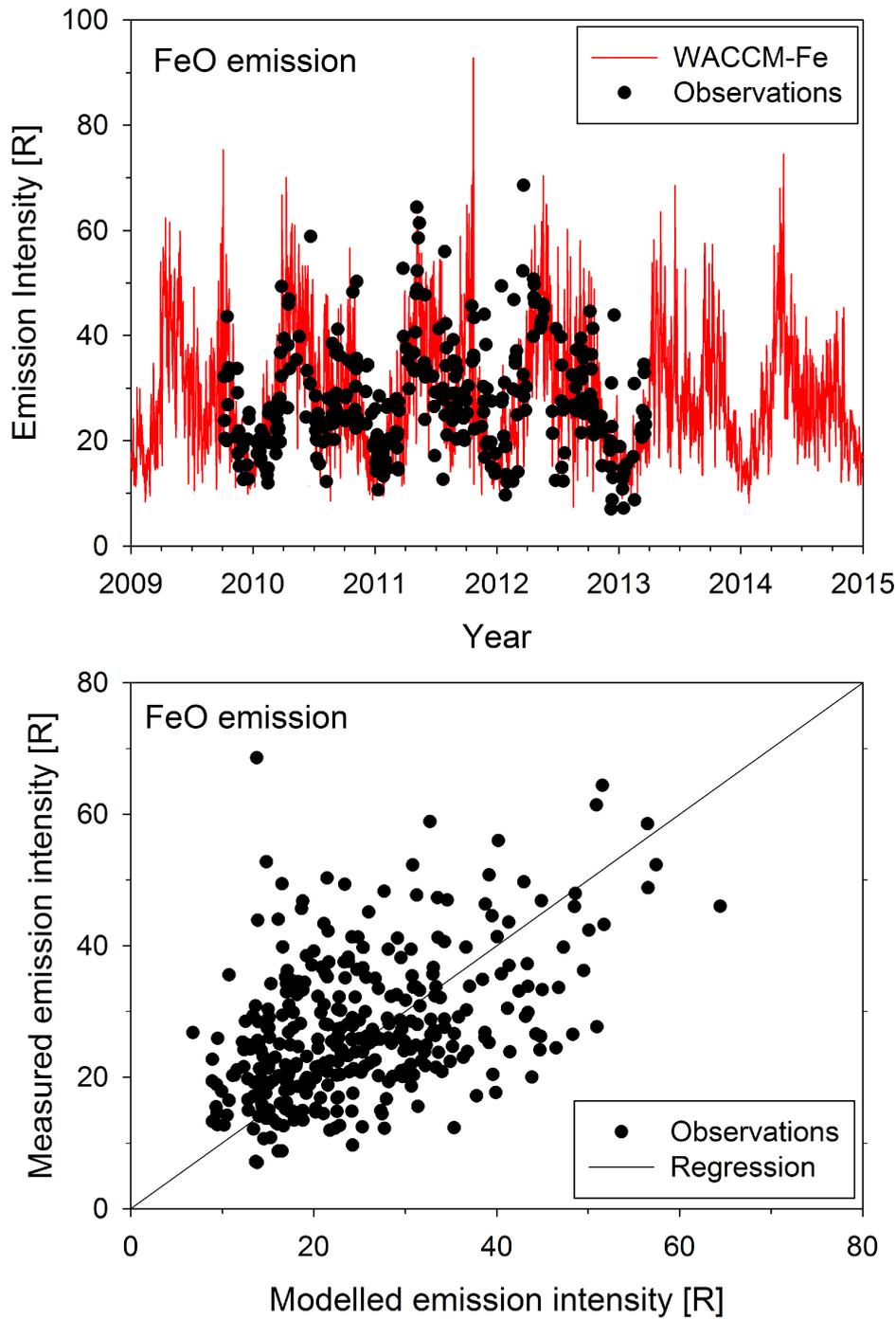
**Figure 3.** Panel (a) displays the five median spectra. Panel (b) illustrates the highest and the lowest quintile median spectra from panel (a) as well as the theoretical spectrum from Gattinger et al. (2011) in black (see Sect. 3.1.1), with the average main peak emission normalised to one. Panel (c) displays the deviation of the two selected median spectra from the theoretical spectrum by subtracting the theoretical spectrum from the median spectra. The colours of the quintile spectra range from blue (median spectrum of the lowest intensity spectra) to red (median spectrum of the highest intensity spectra).



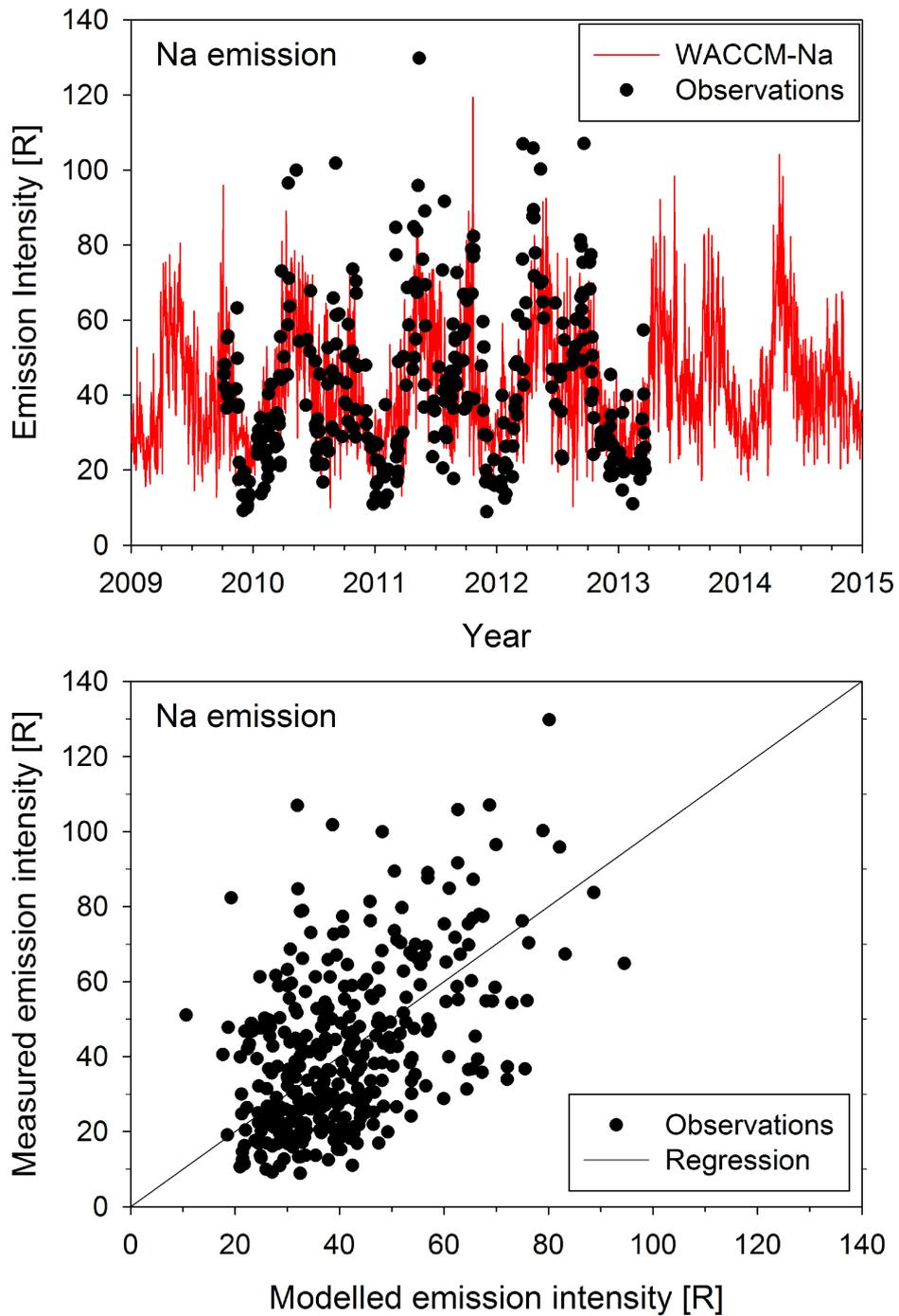
**Figure 4.** Diurnal variability with respect to season for different seasons. The colours indicate the emitter: FeO (red squares), Na (cyan triangles). The symbols are placed at the mean time of all the measurements in each bin with respect to midnight. The ordinate shows the intensities relative to the nocturnal average.



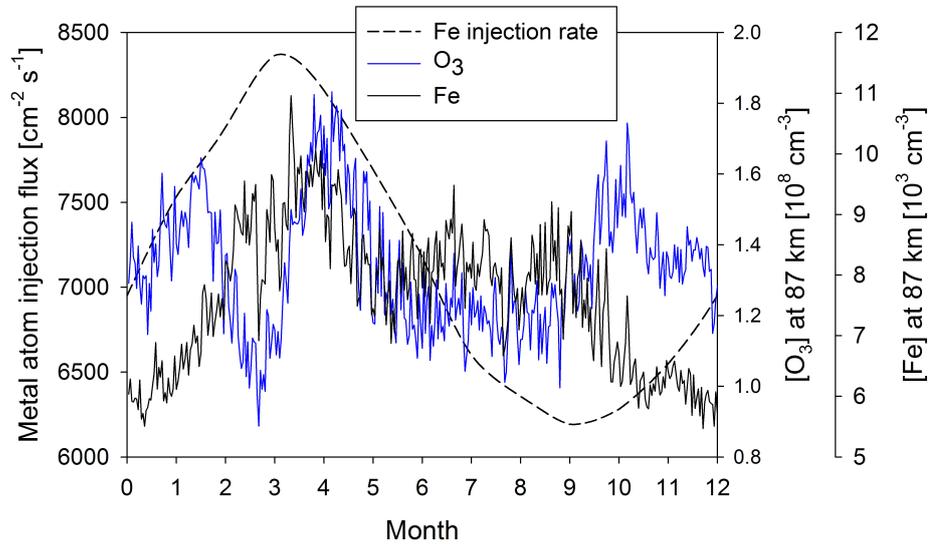
**Figure 5.** Harmonic Analysis: This figure shows the results of the harmonic analysis of FeO in panel a and Na in panel b. The best-fit approach is plotted with a solid line, while the squares indicate the Bayesian (mean) solution. The coefficients of the best fit and mean are given in Table 1. Panel c compares the behaviour of FeO and Na relative to their annual mean. The colours, lines and symbols are the same as in the panels above.



**Figure 6.** Comparison of the measured and modelled FeO emission intensity. Top panel: absolute intensities over the period 2009-2015. Bottom panel: correlation between the measured and modelled intensities. Note that the modelled intensities are scaled to produce a 1:1 regression line through the origin.



**Figure 7.** Comparison of the measured and modelled Na emission intensity. Top panel: absolute intensities over the period 2009-2015. Bottom panel: correlation between the measured and modelled intensities. Note that the modelled intensities are scaled to produce a 1:1 regression line through the origin.



**Figure 8.** Monthly variations of the injection flux of Fe from meteoric ablation, and the concentrations of O<sub>3</sub> and Fe at 87 km (averaged from 2009 to 2015) predicted by WACCM.