

Interactive comment on “Characterization and testing of a new environmental chamber designed for emission aging studies” by A. Leskinen et al.

Anonymous Referee #1

Received and published: 19 September 2014

The manuscript describes and characterises a new photochemical aerosol chamber at the University of Eastern Finland. The subject and content of the manuscript is suitable for AMT, and should serve as a reference for future research at the reported facility. I believe the manuscript has the potential to be accepted for publication, but not before the authors address the following concerns and comments.

We thank the Referee for reviewing the manuscript carefully and for the valuable comments. Our answers to the comments are addressed below and the text will be corrected accordingly in the revised manuscript.

Major Comments:

Title: Although the title clearly states that the chamber is designed for emission aging studies, it does not provide any proof of concept evidence to show successful coupling of any type of emission sources to the chamber. What the manuscript presents is a description and characterisation of an environmental chamber. The title must be changed to remove any reference to emission studies unless the authors provide details on such studies. The fact that it is located within the ILMARI facility is not enough to justify the title.

We modified the title by leaving the “designed for emission aging studies” out.

Page 5932, line 5-8: It is not clear how the wall loss calculations were applied. The results in figure 2 and 3 emphasise the importance of size dependant chamber wall losses, therefore the authors should explain whether they have applied details size dependant loss corrections or have only used the polydisperse correction. It is clear from the reported results that the former should have been applied. In either case, this should be explained and discussed. The authors should also mention whether or not any attempts have been made to quantify, and correct for, the gas phase loss of the precursor.

We applied the size dependent wall loss corrections, because in the polydisperse sample coagulation may cause overestimation of wall losses.

At this point, we have not made attempts to correct for the gas phase losses or equilibrium between the gas phase and walls.

Pages 5933-5934, section 3.2: I presume that the Kuopio data is for the irradiance integrated across the whole wavelength range, not over the comparable range of the black lights <400nm? This needs to be clarified and stated in the manuscript. It surely has an implication on the chemistry. A wider discussion of the implication of the missing radiation at all wavelengths >400nm is required. More importantly, I am surprised that the employed backlights appear to be missing an atmospherically important part of the light spectrum between 300–340nm. This is critical for the production of OH from ozone photolysis and also important for the photolysis of other atmospherically relevant

VOCs. The authors need to clarify their choice of this specific type of light and discuss the implication on the photochemistry and aerosol yield.

The reported irradiance at ground level in Kuopio was calculated as an integral between 290-400 nm. For the same wavelength region as the lamps irradiate (340-400 nm) the integral irradiance at ground level in Kuopio would be  $20.2 \text{ W m}^{-2}$  on a sunny day and  $8.7 \text{ W m}^{-2}$  on a cloudy day, so the maximum irradiance of the lamps ( $29.7 \text{ W m}^{-2}$ ) exceeds that at ground level ( $20.2 \text{ W m}^{-2}$ ) in the wavelength region of 340-400 nm. The irradiance of 1/3 of the lamps ( $9.8 \text{ W m}^{-2}$ ) is still at the same level as that on a cloudy day on ground level in Kuopio ( $8.7 \text{ W m}^{-2}$ ). This is clarified in the manuscript.

The visible light region above 400 nm can be important especially for  $\alpha$ -dicarbonyls (e.g. glyoxal and methylglyoxal) photolysis and their following radical reactions. The same compounds have also been confirmed as products of toluene photooxidation. Missing the visible light region in toluene chamber experiments might have some effect on gas phase oxidation product yields and also SOA formation.

For the missing wavelengths between 300 and 340 nm we included discussion about lacking atmospherically relevant reactions, such as the  $\text{O}_3$  photolysis to  $\text{O}^1\text{D}$  and its further forming of OH radicals, and photolysis of aldehydes and ketones. The photolysis of these simple carbonyls can produce directly alkoxy radicals which react quickly with  $\text{O}_2$  to form more  $\text{HO}_2$  radicals. In high  $\text{NO}_x$  experiments (which is often the case with combustion aerosols) this can increase important OH radical production by converting  $\text{HO}_2$  to OH when  $\text{HO}_2$  reacts with NO.

The installation of the lamps were a compromise between the costs, safety, and desired  $\text{NO}_x$  reactions ( $\text{NO}_2$  photolysis, HONO photolysis), at the time we equipped the chamber facilities. Later, we have installed blacklight lamps that produce UV irradiation in the wavelength range of 310-400 nm. We have observed that both types of lamps are efficient in producing SOA.

Page 5935-5936: The discussion of yield values under seeded and un-seeded conditions is inconsistent. The reference to the rate constant in equation 2 is confusing as I don't see how is affected by light intensity. I presume the authors meant to refer the difference in light intensity and its effect on yield rather than the NO/O<sub>3</sub> reaction rate. This should be clarified. In addition, the reference to gas phase wall losses being more intense in the absence of seed particles (i.e. the authors data) should lead to lower yield, which is the opposite of what is being reported. I believe that the concept of yield, despite being widely used in the literature, is misleading and hard to quantify due to differences between chambers and in the way researchers apply wall loss corrections for particle mass and to an almost always absent characterisation of the tricky gas phase losses. Those are a few of the issues that make a yield value chamber specific, which is hard to directly compare to other chambers given the uncertainty associated with gas and particle phase wall loss corrections and the wide differences in light and oxidant characteristics across chambers.

The authors have indeed made a brief mention of the difficulty of comparing yield values from different chambers, but they only did so in the conclusion without elaborating on this in the main discussion. This needs to be addressed. Additionally, in order to establish the effect of seed on the yield values, the authors should ideally report their own seeded experiments yield values and compare to them.

We erroneously referred to the  $k$  in Equation 2 instead of referring to the  $j_{\text{NO}_2}$ . This is corrected in the manuscript.

We rephrased the paragraph discussing the obtained yield values and their comparison to those obtained at other laboratories in order to clarify the effect of gas phase wall losses. We also included discussion of the difficulty of comparing yields between different laboratories and facilities.

#### Other Comments:

Page 5923, line 23: Black lights are only one type of lights used in chamber. This should be changed to “artificial” lights so it is more inclusive.

Changed as suggested.

Page 5926, line 25: Is this aluminium plate exposed to the inside of the chamber or is it covered by Teflon. This should be clarified.

It is covered by Teflon. This is clarified in the manuscript.

Page 5930, line 26-28: What is the injection efficiency of this method? Would it be suitable for other VOCs over a range of volatilities? Have the authors considered using a gently heated glass bulb for this purpose?

We injected the toluene into an air stream of 100 L min<sup>-1</sup> in a 4 mm inner diameter tube. This corresponds 1.4 m s<sup>-1</sup> of air stream. Our estimation is that the fast air stream effectively evaporates the toluene. We agree with the Referee that heating would enhance the evaporation and thus the injection efficiency. However, as we measure the initial concentration of the injected compounds with PTR-MS and other gas analyzers, knowing the amount of evaporated compounds is not necessary, but only that measured directly from the chamber. Actually, our measured initial values have been quite close to the calculated values, and we are satisfied with our injection system.

Page 5934, section 3.3: The discussion of the temperature control means that the chamber is currently only operational with half of its lighting capacity at most. This implies that the characterisation results presented in the manuscript are currently partly not representative of the operational conditions of the chamber. The plan to upgrade the air conditioning unit which is mentioned at the end of the conclusion section should be clearly stated in the main body of the text to ensure that the reported characterisation are in agreement with the facility actual capabilities.

We have doubled the cooling capacity since the first

characterization experiments and now the temperature is well controlled also when all the lamps are on. In the characterization experiments described in this manuscript we have used only half of the lamps, also in the latter experiments, so we removed the discussion of upgrading the air conditioning from the manuscript.

Page 5749: The quality of Figure 5 is poor. The display should be expanded across the time axis to allow better visualisation of the data.

We improved the quality of Figure 5 (Fig. R1).

Page 5750: The quality of the Figure 6 is extremely poor. The display should be improved.

We improved the quality of Figure 6 (Fig. R2).

Page 5751: The authors should comment on the unexplained step changes in the data of the green trace (m/z99) around 150 and 240min. The data during this period is inconsistent with the rest of the data in the figure.

The step changes are due to a so far unidentified technical problem and we need to recheck the data and revise the figure accordingly.

Minor Corrections:

Abstract, line 3-4: change “belongs to” to “is part of”

Abstract, line 6: “are side by side” should be “are located side by side”

Page 5922, line 24: Remove “The” from the start of this sentence.

Page 5923, line 1-2: change “during the aging” to “during aging”

Page 5923, line 5: delete “the”

Page 5924, line 4-5: should be “vegetation, stacks or tailpipes”, also “the emission sources” should be “emission sources”. The article “the” is used far too many times at in-appropriate places throughout the introduction. This needs to be checked and corrected.

Page 5924, line 21-22: the phrase “and hopefully can help persons when planning new chambers in their work” should be deleted.

Page 5927, line 9: “Ammoniumsulphate” should be changed to “Ammonium sulphate”

Page 5934, line 14: Change “nor” to “not”

Page 5937, line 25: change “air conditioner” to “air conditioning unit”

These were corrected as suggested.

FIGURES

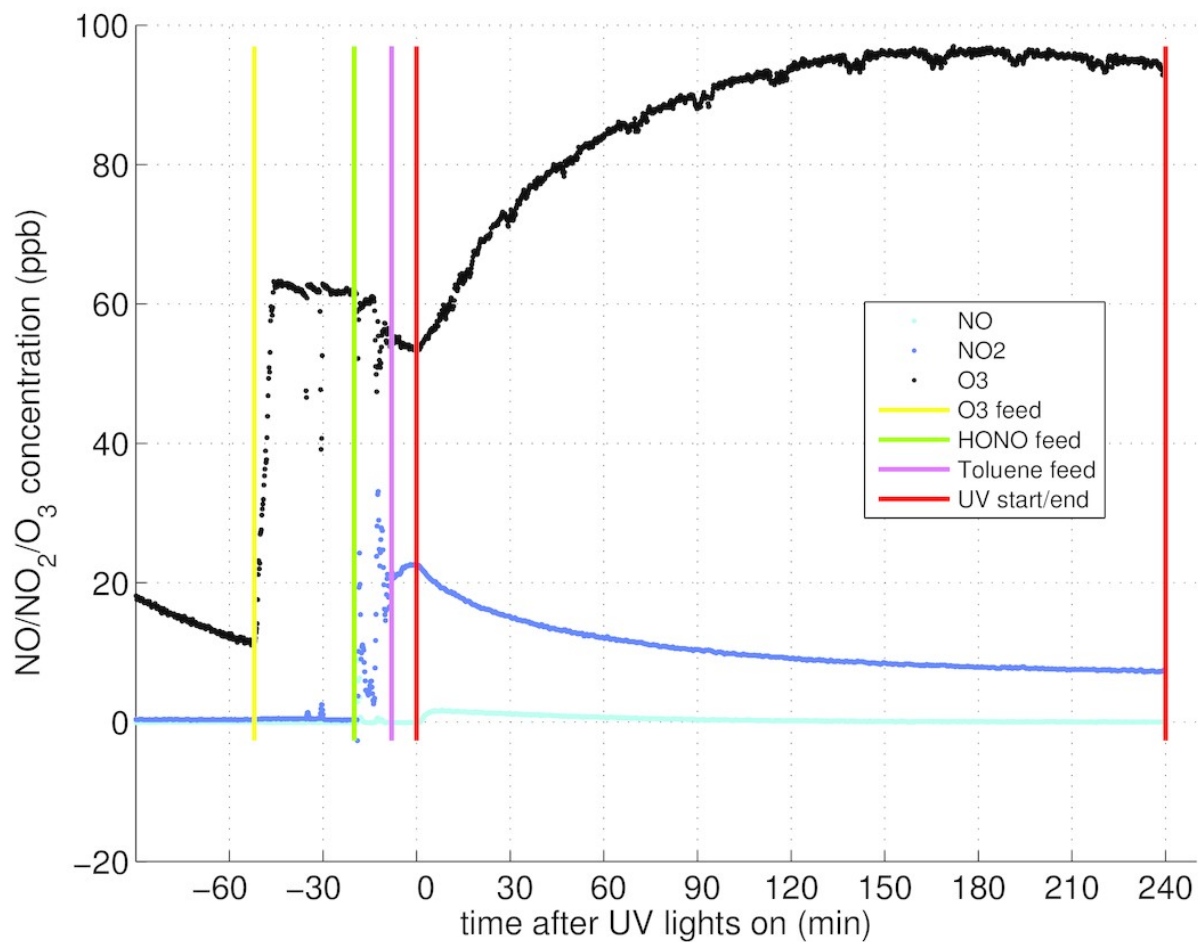
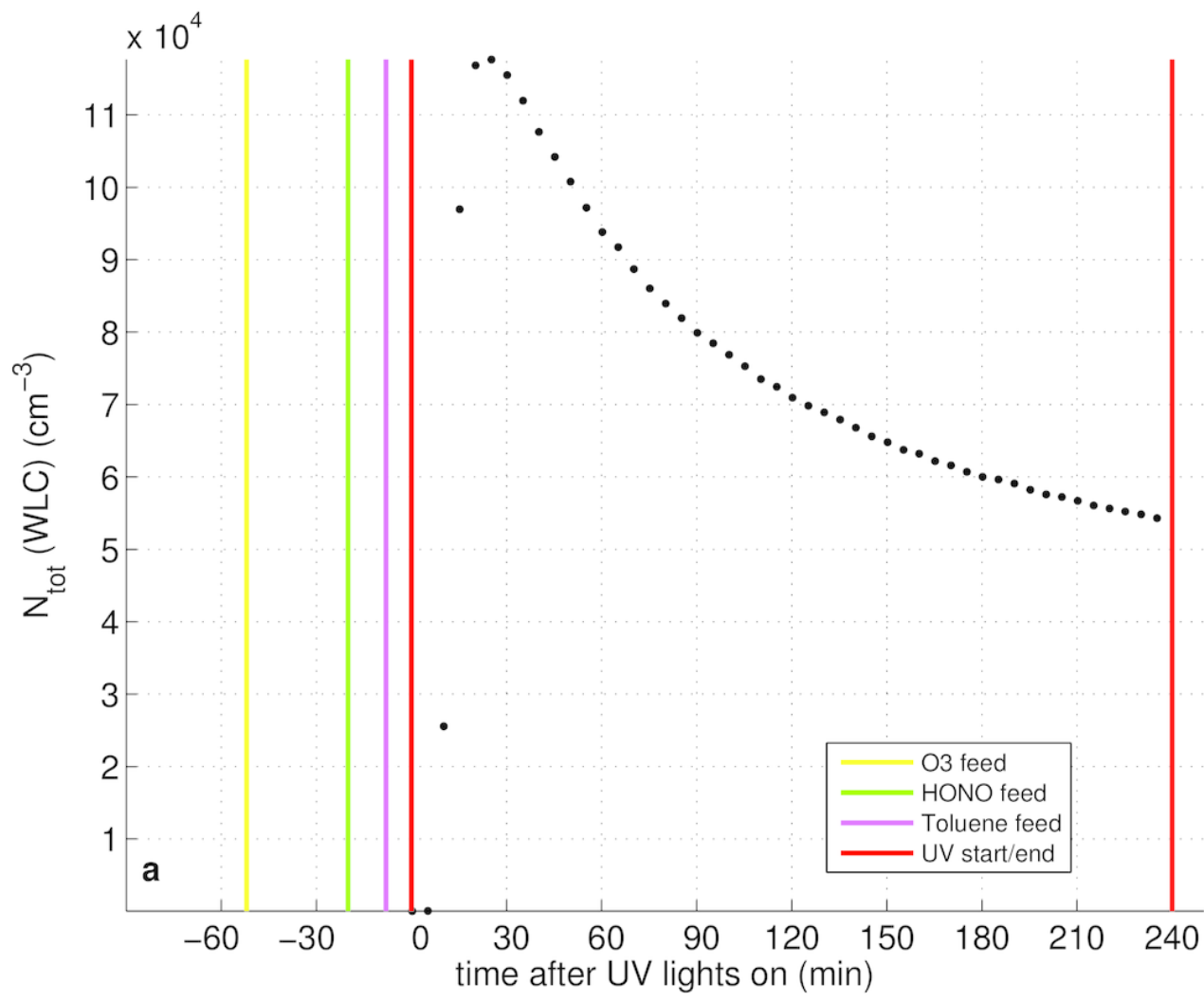
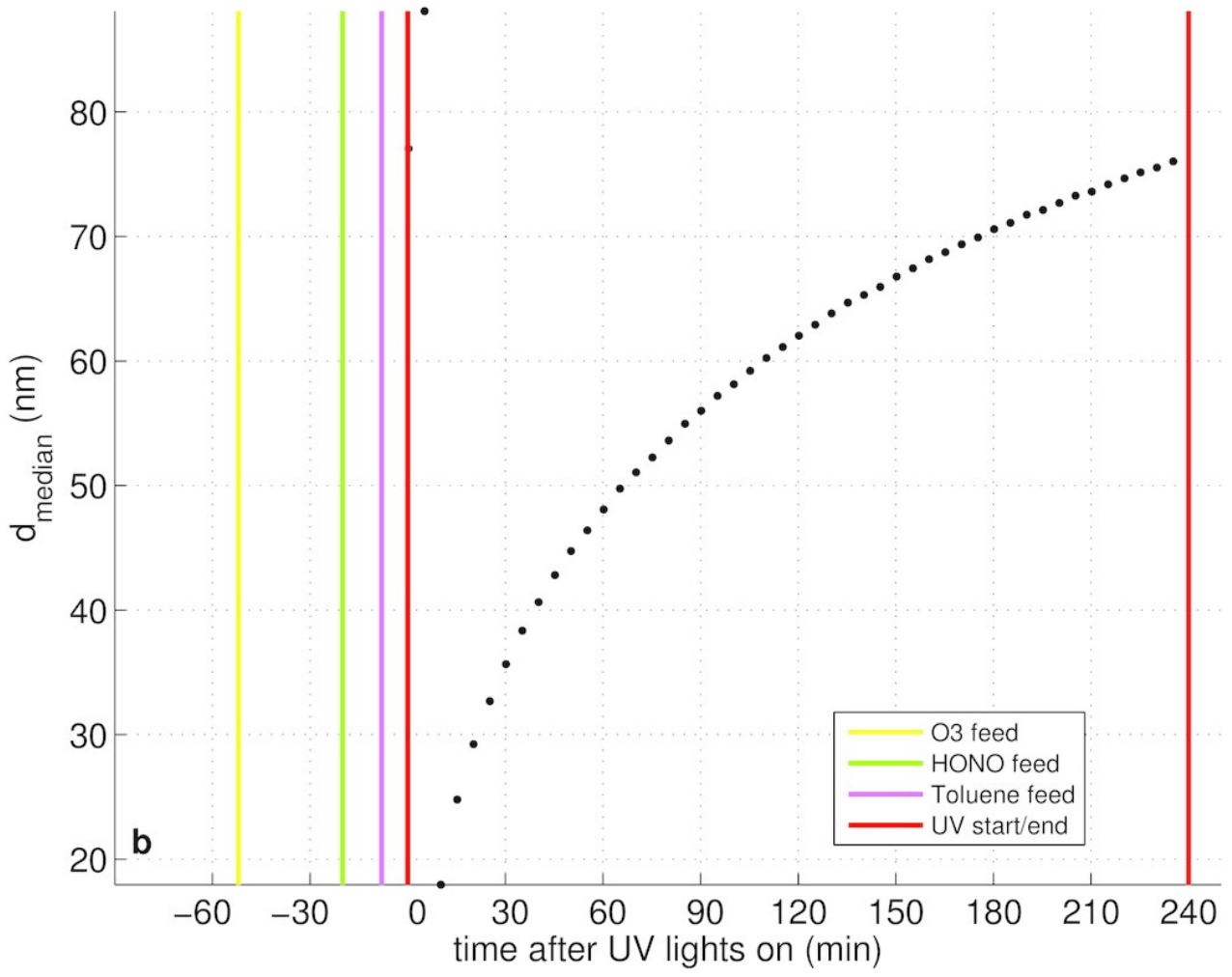


Figure R1: The evolution of NO, NO<sub>2</sub>, and O<sub>3</sub> concentrations in the chamber in the experiment T130910.





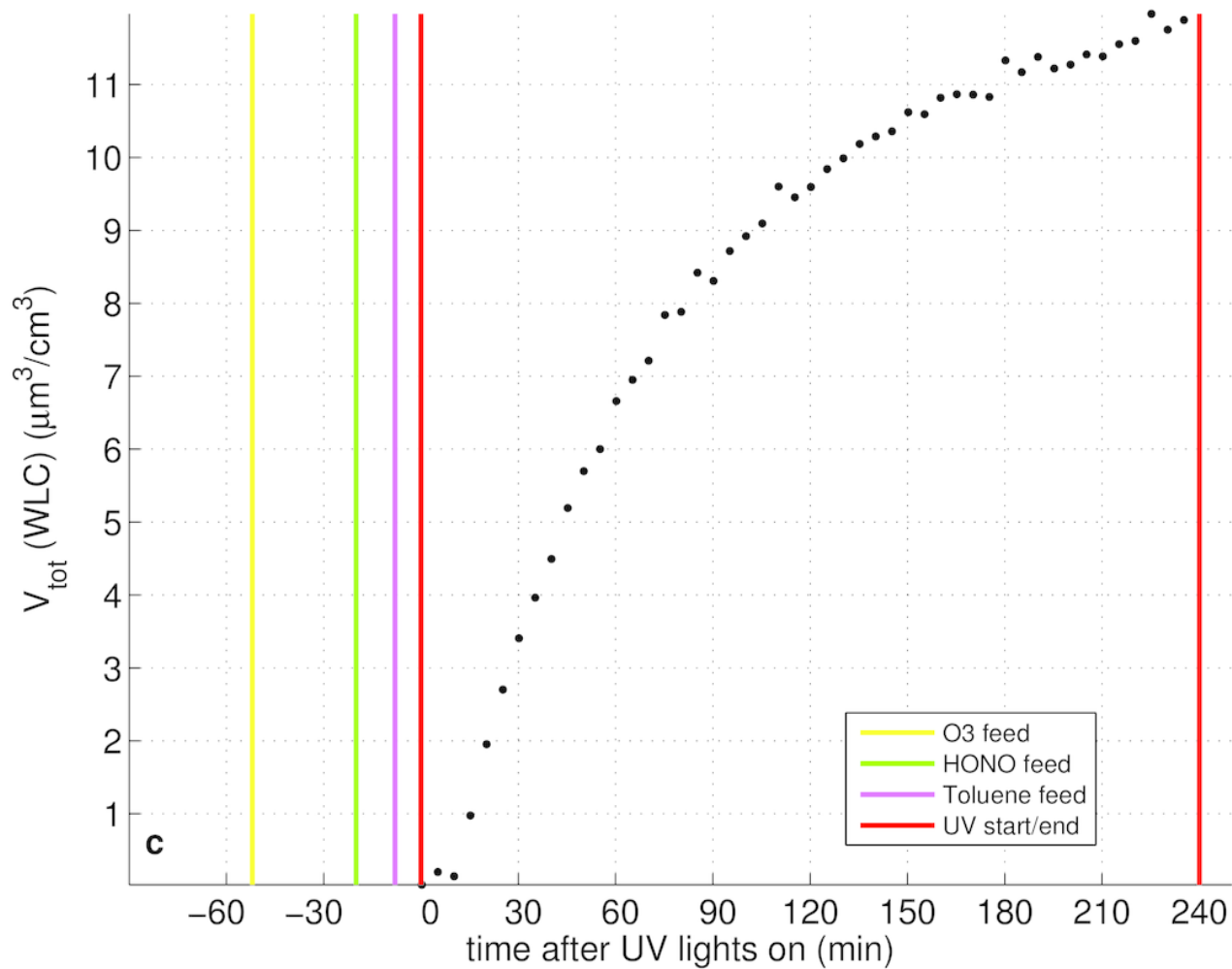


Figure R2: The evolution of (a) aerosol number concentration (corrected for wall losses), (b) median diameter, and (c) calculated volume concentration (corrected for wall losses) in the chamber in the experiment T130910.