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Interactive Comment

Interactive comment on "Broadband Cavity Enhanced Differential Optical Absorption Spectroscopy (CE-DOAS) – applicability and corrections" by U. Platt et al.

U. Platt et al.

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Response to referee comments on "Broadband Cavity Enhanced Differential Optical Absorption Spectroscopy (CE-DOAS) – applicability and corrections" by U. Platt et al., Atmos. Meas. Tech. Discuss., 1, S228–S230, 2009, (MS-NR: amtd-2008-0024)

Anonymous Referee #1

This is a very interesting paper that presents a systematic study of the applicability of the well-known and very successful DOAS analysis method to the new BB-CEAS experimental technique. I recommend the paper for publication but have some comments that are given below.



p. 483 The authors describe the great potential of BB-CEAS for atmospheric trace gas detection. The reference (Engeln et al., 1988) is wrong - it should be Engeln et al., 1998; moreover it is not at all a broad-band study as stated in the text but highly resolved using a diode laser - and I suggest to use here the reference: S. E. Fiedler et al., Chem. Phys. Lett. 371, 284-294 (2003) - the first use of BB-CEAS with an arc lamp.

Answer: We changed the reference (Engeln et al. 1998) and used Fiedler et al. 2003 as suggested.

p. 487 "In reality" should probably be "In practice" here the authors must cite the paper by R. A. Washenfelder et al., ACP 8, 7779-7793, 2008, also since these authors explicitly considered Rayleigh scattering. Furthermore, it is important to discuss here quantitatively the impact of using a broad-band LED for a ring-down experiment (as used in reference Meinen et al., 2008) that produces a multi-exponential decay – this must lead to substantial systematic errors. Same page (and elsewhere): I recommend using the words "effective light path" or "average light path" but not just "light path" or "light path length" to avoid confusion, throughout the paper.

Answer: We followed these recommendations: We added the reference to Washenfelder et al. 2008, used the term "effective light path" and added a discussion of the problems with ring-down time of broad-band light sources (in section 6., second enumeration, point 2). There we also refer to the manuscript by Meinen et al. (2008), where the problem and approaches to its solution are described.

General remarks: 1. The authors should point out very clearly that using DOAS for the analysis of BBCEAS data differs from previous studies (e.g. Ball et al., 2004; Venables et al., 2006; Gherman et al., 2008; Vaughan et al., 2008; Washenfelder et al., 2008) only by using the DOAS analysis method, but that the experimental part is based essentially on the BB-CEAS experimental set-up as published before by these other authors. The idea of using DOAS is the essential and most interesting point of

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this paper, but leads to important problems with the concept of "average" or "effective" light path – previous papers describing the use of BB-CEAS for atmospheric trace gas detection actually use other fitting approaches that do not need to solve this difficulty and thus to make such corrections.

Answer: We appreciate the reviewer's opinion that using DOAS for evaluation is an interesting point of our manuscript. However we maintain that it is not DOAS that 'leads to important problems', rather these problems are inherent to the technology of cavity enhanced absorption spectroscopy. We changed the discussion section to spell out more clearly what the problem with the effective light path is. We also note that previous studies have similar problems in determining the light path (or the mirror reflectivity).

2. It is necessary to point out clearly and thus to discuss ***quantitatively*** the benefit of using DOAS (e.g. in terms of sensitivity or accuracy) compared to the previous papers using the BB-CEAS equations described in the paper by Fiedler et al., 2003.

Answer: In the discussion section (section 6) we now point out that neglecting the distortion of the absorption band can lead to problems when weak absorbers (e.g. HONO) must be determined in the presence of strong overlying absorption structures (in this case of NO2) and give a quantitative example. Also if the total Optical Density is unknown, the BB-CEAS equation from Fiedler can not be used. An iterative analysis approach as mentioned in the paper has to be used.

3. In particular the authors must address here the very detailed comment made by D. Venables "Background extinction and concentration retrieval" (see http://www.cosis.net/copernicus/EGU/acpd/8/S5154/acpd-8-S5154_p.pdf) for the paper by Meinen et al. (2008). He shows that no such correction as discussed in the present paper is needed when the absolute absorption is used, as opposed to the differential absorption that needs such a correction. So this seems to be clearly a major ***disadvantage*** of using DOAS for the analysis of BB-CEAS data. In conclusion,

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this is an interesting paper and merits publication if the comments above are addressed in detail by the authors in a revised manuscript.

Answer: Using the total optical density (total absorption) is a possibility to correct for the light path reduction or to use a corrected equation, which is different to the basic equation of Lambert Beer. Also other corrections are possible as stated in the paper. We clarify that the total optical density is in general not known which result in problems which are discussed more clearly in our revised paper. However we maintain that it is not the DOAS approach that leads to the problems but rather that the difficulties are inherent to the technology of cavity enhanced absorption spectroscopy.

Anonymous Referee #2 Received and published: 2 February 2009

General Comments: This paper describes the theoretical operating principal behind a new instrument using cavity enhanced absorption spectroscopy. The paper follows on a description of the instrument itself, which appeared in ACPD in 2008 (Meinen et al.). The two papers may be regarded as companions since the first makes reference to this paper for quantitative reduction of data. The general topic of this paper is of substantial interest, no so much because the technique of cavity enhanced absorption is itself new, but because the paper outlines a method by which a true open path instrument of this type may be operated, i.e., in which the background light intensity at the detector (i.e., the intensity in the absence of absorbing trace gases, or I0) is not known. This is akin to the operating principals of DOAS instruments, in which the variation of the background intensity with wavelength is taken as a slowly varying function of wavelength so that the more rapidly varying trace gas absorptions may be fit without a separate measurement of I0, which is generally not possible in a long path DOAS arrangement. That said, there are, in my opinion, several difficulties with the mathematical development presented in this paper. Some sections are either incorrect (to my understanding, at least) or else not sufficiently clarified so as to be readily reproduced by the reader. Furthermore, there is insufficient justification for some of the approaches used. For example, the main thrust of the paper is to apply the formalisms conventional to long

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path DOAS to the mathematical development of a formalism for cavity enhanced absorption spectroscopy (CEAS). Long path DOAS instruments operate with a fixed path length that allows ready separation of background intensity from intensity variation due to trace gas absorption. In cavity enhanced spectroscopy, the light path between two highly reflective mirrors is not a fixed quantity, a fact that forces somewhat different mathematical treatment. This paper defines the path length for CEAS in an averaged sense, and then uses this concept to draw analogous relationships between CEAS and DOAS. The approach appears to obscure, or at least disregard, a simpler mathematical treatment for CEAS already available in the literature, and the reasons for the departure with the accepted CEAS formalism require better justification than is given here. I would certainly invite a response and further discussion on these points and on the more specific comments below. As stated above, I feel that the general topic addressed here is substantive, and if my criticisms are incorrect or based on a misunderstanding of the mathematics, I would happily see them corrected. In this case, some response to the points below and some clarifications on certain other points would make the manuscript acceptable for publication.

Answer: We like to thank the reviewer for the positive comments on our manuscript. As for the "a simpler mathematical treatment for CEAS already available in the literature", this refers to the use of the absorptivity (absorption per unit length, usually called alpha). However this quantity is calculated from the reduction of the intensity compared to some initial value with this reduction being proportional to (alpha) * (effective light path). So in our opinion this "simpler" approach only hides the underlying problem, i.e. the precise definition of the light path. We rearranged the derivation of the light path length (now equations 24 to 26 in combination with 31), we also removed the appendix of the manuscript.

We also removed Figure 3 (correction factor, numbering of the original ACPD version) and added a new Figure 2 (reduction of optical pathlength in a cavity as function of the optical density DCE, new numbering). The remaining figures are essentially un-

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changed except for minor additions/corrections as noted in the responses to the individual remarks of the reviewers.

Specific comments: Page 484, minor comment on equations 1-5: The quantities given in these equations are all wavelength dependent (i.e., R, rho, etc.) and it would be helpful if that were explicitly noted at the outset, i.e., that the development given here and in the following equations is for a single wavelength point in a spectrum, and the spectral dependence is considered at a later point in the paper. It is also worth pointing out here that the "average" path is identical to the 1/e path length for an exponential decrease in light intensity with path. The latter is the more conventional terminology, though the two are equivalent.

Answer: We follow the recommendations of the reviewer and note that the above quantities are wavelength dependent. With respect to the effective path length and 1/e path length, they are in fact not identical as pointed out in equations 24 to 26 and 31. In fact the average light path as calculated in the appendix of the original (ACPD) version of our manuscript is not equal to the effective light path for the absorption if compared to Lambert Beer absorption. We now stress that the effective light path is the one to be used in the evaluation of the trace gas concentration (section 4 of the revised manuscript).

Page 485, equation 6: The equation includes only a loss term and no source for light entering the cavity from an external source, which seems to be the case that describes the broadband spectroscopy apparatus. As written, the equation would more appropriate for describing a ring-down apparatus than a spectrometer with a continuous (rather than pulsed or modulated) light source.

Answer: The equation (No. 11 in the revised manuscript) only describes the decay of the intensity, the text is changed to reflect this. Also if the equation represents ring down spectroscopy, it is important for the following broad band spectroscopy, as it can be seen as continuous light pulses entering the cavity.

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Page 486, equation 13: This is the same as equation (5) on page 484, which was given by inspection. Some condensation of the development would seem appropriate here to reduce the number of equations.

Answer: The equations was removed, the flow of the derivation was simplified overall.

Page 487, equations 14-15. These are confusing, as are the curves drawn in Figure 2. For example, the quantity lin0(n) is not given in Figure 2, though there is a quantity lin(n0) in the figure. Are these the same? It is also not clear what the distinction between n0 and n is in the figure caption. Is n0 intended to mean zero passes, or simply an arbitrary number of passes after the light intensity has begun to decay from the cavity? In either case, there appears to be some duplication or lack of clarity over the "0" subscripts on either the intensities or the pass numbers that make the figure and the equations difficult to understand. It would be helpful if the authors could clarify these points.

Also, what does the "+" sign mean in equation (15) ?

Answer: In equation 15 (old numbering) we just want to point out that the result is positive. We removed the +-sign, since the referee apparently found it confusing. The Index 0 is clarified, we changed n0 to n=0, etc..

Page 488, equations 17-18: The quantity DCE is not well defined. Presumably, this is the observable quantity, and is intended to mean the logarithm of observed ratio of background intensity (no absorber) to signal intensity (absorber present) outside of the optical cavity. This is not explicitly stated. It is given either after n traverses or as the integral of an intensity decay. The latter would seem to be correct (equation 18), though not equivalent to the intensity ratio at a given point on a decay (equation 17). The two definitions for DCE seem to be inconsistent, so that the definition of which DCE is actually used later in the paper should be clarified. In either case, the intensity is taken as one that only decays from the cavity, rather than as one that has both a source term and a decay term, as in a real CEAS experiment (see comment

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above). It appears that equation 18 is actually what is used beyond this point, which I have taken to mean the logarithm of the observed intensity ratio without and with the absorber. In this case, equation 18 is given as an equality between two logarithms, i.e., $ln(I_0/I) = ln[(rho_0+tau_0)/rho_0)]$ There should be an explanation at this point as to why the logarithms are needed. The equality between the arguments of these logarithms is identical to the treatment of cavity enhanced spectroscopy already in the literature (see for example, Fiedler references cited herein). One could arrive at equation 18 simply by taking the logarithm of both sides of equations already derived in the literature, assuming that my interpretation of the meaning of the integrals given in equation 18 is correct.

Answer: We rearranged and clarified the derivation of the equations mentioned above (Eq. 26 in the revised version of the manuscript). We now explicitly state that DCE is the observed optical density seen at the detector. We also added a comment after equation 37) that an equivalent relationship between D and intensities of empty/filled cavity was also derived by Fiedler et al [2007].

Page 488-489, limits of DCE. I was not able to reproduce the first limit given here. A plot of DCE against tau for realistic values of rho_0 and tau would perhaps be useful to demonstrate where this limit is actually achieved. Using, for example, rho_0 = 10-6 and tau = 10-4 for case 1, DCE = 4.62, not close to the limiting value of 2 given here. Increasing tau does not bring the limit any closer to 2 and does not result in a constant value. If indeed this limit is not correct, the statement on page 489 (and later) that high mirror reflectivity is problematic is not well justified.

Answer: We used a wrong simplification in Equation 19 (old numbering). The correct results are now given in Eq. 27 and Eq. 28. In particular we state that for high mirror reflectivities the differential optical density only grows with the logarithm of the trace gas concentration, which is a pretty weak dependency. We trust that the difficulties associated with high mirror reflectivities (in the sence that rho << tau) are now presented in a straightforward manner.

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Page 489, equation 21: This is a different expression for DCE that does not seem to be justified by the equations leading to this point. It states that the logarithm of the intensity ratio (i.e., DCE) is directly proportional to the product of the average path length and the optical extinction coefficient, i.e. $DCE = ln(I_0/I) = L^*c^*sigma = L^*epsilon$ Where here L is the average path length defined in the paper (L bar) and c the average concentration (c bar). Using the previously given expressions for average path length (i.e., equation 13), and the previous definition for DCE (equation 18), I am not able to reproduce the expression in 21 (also used again, for example, in 23). If the equation is correct, its meaning needs to be clarified. Perhaps, for example, this equation is not intended to relate the average path length in (13) to the definition of DCE in (18), or perhaps this DCE is different than that given in (18). Either way, this equation needs clarification.

Answer: Equation 21 give the general DOAS approach to treating trace gas absorptions, i.e. splitting the absorption cross section into a portion strongly varying with wavelength and a quasi "continuous" portion. The discussion of the DOAS approach was moved to the beginning of the revised manuscript (Equations 1 to 7). From there we develop the CE-DOAS approach. We trust that we clarified the point raised by the reviewer.

Page 491, equation 26: This equation is based on the above relationship, and follows directly if equation 21 and 23 are indeed correct. If so, this would seem to be the end point of this paper, since it gives an analytical expression for the desired quantity, the trace gas concentration. Identical expression using the ratio of DCE/(1-DCE) are then given by other methods in the following pages, which seems redundant. Some condensation of this material seems possible?

Answer: We agree and summarised the points discussed in section 3 (original version of the manuscript) into section 4 (revised manuscript) thereby shortening the text from two pages to one page.

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Pages 495- 497, section 5: The direct comparison of CEAS to DOAS here is useful in the sense that background intensity, I0, is not necessarily easily determined in an open path CEAS configuration, just as it is not determined in DOAS, but rather fit as a slowly varying component with wavelength. Solutions 1 and 5 addresses this issue, whereas solutions 2-4 address the important, but separate issue of determining total cavity loss. These discussions should be distinguished.

Answer: We kept and expanded this discussion (now section No. 6) in the revised version. In particular we added text explaining the (different) consequences of different reasons (see enumeration a) … c)) for changes in the intensity reaching the detector.

Summary: The paper suggests the substitution of the linear relationship commonly used in CEAS to derive trace gas concentrations from measured changes in intensity outside of an optical cavity with a logarithmic relationship that more closely resembles Beer's law. Though the substitution would be useful if it would allow applications of DOAS conventions to CEAS, the development is difficult to follow and requires either clarification or revision. The literature expression for the intensity change given in various references (e.g., Fiedler and coworkers) is, using the notation of this paper:

$(I_0-I)/I = [(1-rho)/d_0] c sigma$

It is true that replacement of this relationship with a logarithmic one results in a nonlinear relationship between the "optical density", In(Io/I), and the trace gas concentration, c. The advantage in surrendering the linear relationship is not clear from this paper but could perhaps be made clearer from a more explicit comparison to the above equation. Lastly, it is noteworthy that nowhere in the above equation is there an explicit need for a path length. Only the cavity loss due to mirror loss, Rayleigh scattering (and Mie scattering, if particles are present) needs to be known. While there is no question that the effective path length associated with these cavity losses is variable and would change as the absorber concentration changes, it is not necessary to know, or to correct for,

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this variation to derive a concentration. Again, it would seem some further justification on the explicit use of path length to derive concentration where is it not otherwise required should be given.

Answer: Of course using the mirror reflectivity and other cavity losses or length of light path should be equivalent in principle. However in our opinion our approach does give more insight, for instance it allowed us to derive the distortion of trace gas absorption bands. Ultimately, the exact approach for the evaluation of CEAS measurements should be the choice of the scientists involved. We just want to point out here that the frequently heard argument (e.g. in the comment made by D. Venables "Background extinction and concentration retrieval", see http://www.cosis.net/copernicus/EGU/acpd/8/S5154/acpd-8-S5154_p.pdf) that the ring down time should be used instead of the light path is really only a matter of taste. After all the light path is given by (speed of light) * (ring down time).

Interactive comment on Atmos. Meas. Tech. Discuss., 1, 481, 2008.

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