Response of ECC and Brewer-Mast Sondes to Tropospheric Ozone

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Abstract. The ECC ozonesonde has been used at Canadian stations since 1980, while the Brewer-Mast (BM) sonde was used during the earlier period, and continues to be used at some European stations. Balloon intercomparison campaigns conducted during the last fifteen years have shown large, and not always consistent, differences in the sensitivity of the two sonde types to tropospheric ozone. The variation in reported sensitivity is sufficient to significantly affect the validity of reported trends in tropospheric ozone derived from ozonesonde measurements. We are fortunate to have on hand a number of examples of both old and new ECC and BM sondes.

Sondes were compared in their response to ozone at laboratory temperature and pressure with a NIST-traceable calibrated Dasibi ozone analyzer. Neither sonde shows clear evidence of a change, between older and more recent instruments, in sensitivity to tropospheric ozone. However, sonde response, particularly in the BM type, is strongly dependent on the details of the pre-flight preparation procedures employed.

We conclude that our previously published trends in tropospheric ozone measured by ECC sondes [*Tarasick et al.*, 1995] have not been affected by secular changes in sonde response. These trends may therefore be regarded with increased confidence. However, the possibility that apparently minor changes in pre-flight preparation may have introduced systematic changes in sonde response in the troposphere should be considered in future analyses of trends derived from BM ozone sounding data.

1. Introduction

Both sondes employ the well-known reaction of potassium iodide with ozone:

$$2\mathrm{KI} + \mathrm{O_3} + \mathrm{H_2O} \rightarrow 2\mathrm{KOH} + \mathrm{I_2} + \mathrm{O_2} \qquad (1)$$

followed by

$$\mathrm{I_2} + 2e^- \rightarrow 2\mathrm{I}^-. \qquad (2)$$

However, the BM sonde is a galvanic cell consisting of a platinum cathode and a silver anode in 0.1% KI solution, while the ECC sonde is a concentration cell consisting of a platinum cathode in 1% KI solution and a platinum anode in saturated KI solution, in separate chambers connected electrically by an ion bridge. The BM sonde requires an external applied potential of 0.41 volts to balance its internal e.m.f., while the ECC requires none; the ECC sonde is constructed of non-reactive Teflon while the BM sonde is made of acrylic. The electronics of the BM sonde must also be calibrated before the sonde is used. This is done by at the factory by exposing the sonde electronics to a known current source. A sonde calibration curve derived from this is supplied with the sonde.

Preparation procedures for the sondes are quite different, and in the case of the BM sonde two commonly used sets of preparation procedures exist [*Mueller*, 1976; *Claude et al.*, 1987] which differ in their prescriptions for preflight calibration and exposure to sensing solution. Significant differences are that *Mueller* recommends using the calibration curve supplied by the manufacturer, while *Claude et al.* recommend calibration of the entire sonde, via exposure to a known ozone source, by the operator before launch. *Mueller* also suggests that, once prepared, the sonde may be flown immediately or left for a few hours. For both types of sonde actual preparation procedures at individual stations may vary somewhat from these recommended procedures, and may also have changed over the period of the station sounding record.

Both sondes produce a background current in the absence of ozone, which must be subtracted from the raw ozone measurement. The origin of this current is not well understood. In the BM sonde the background correction is constant, while for the ECC sonde, standard practice is to use a correction that is proportional to atmospheric pressure, on the assumption [*Komhyr*, 1969] that the background current is due to reaction (1) with oxygen rather than ozone. Previous laboratory work [*Thornton and Niazy*, 1982; 1983] has indicated that the background current in the ECC sonde is probably due to residual tri-iodide in solution and should therefore be constant in the troposphere. Background current is recorded prior to sonde release at all Canadian sites. Preliminary analysis of these data, for the ECC record, indicates that at several stations there are significant trends in background current, some of which are large enough to affect derived ozone trends in the upper troposphere, if the background current were in fact constant with altitude. This possible source of error has not been considered in trend studies [*Logan*, 1994; *Tarasick et al.*, 1995].

2. Method and Results

Experiments were conducted at laboratory temperature and pressure, using either a NIST-traceable calibrated Dasibi ozone analyzer (Model #1008-PS). The air output from the ozone source was allowed to flow through Teflon tubing which vented to the laboratory, while the analyzer and sondes sampled air from the tube. In this way it was assured that both the sondes and the analyzer sampled the same airstream, while maintaining that airstream at laboratory pressure. Sondes were prepared according to standard procedures [*Mueller*, 1976; *Komhyr*, 1986]; however, in order to compare only the sonde sensors, the associated electronics (which differ considerably between the BM and ECC, and even between different ECC models) were not used. Output from the ECC sensors was passed through a 1 k-ohm resistor and the voltage drop was recorded with a Campbell 21X data logger. Sensor current was then calculated from the measured voltage. For the BM sondes an operational amplifier circuit was used to convert current to voltage. After subtraction of the background current, these measurements were converted to ozone partial pressure values in nanobars via the well-known relation [*Komhyr*, 1986]

$$P_{O_3} = 0.004307\, i\, T_B\, t, \qquad (3)$$

where i is current in microamperes, T_B is sonde box temperature in Kelvins, and t is the time in seconds to pump 100 ml of air. Partial pressures were converted to mixing ratio by dividing by the measured atmospheric pressure.

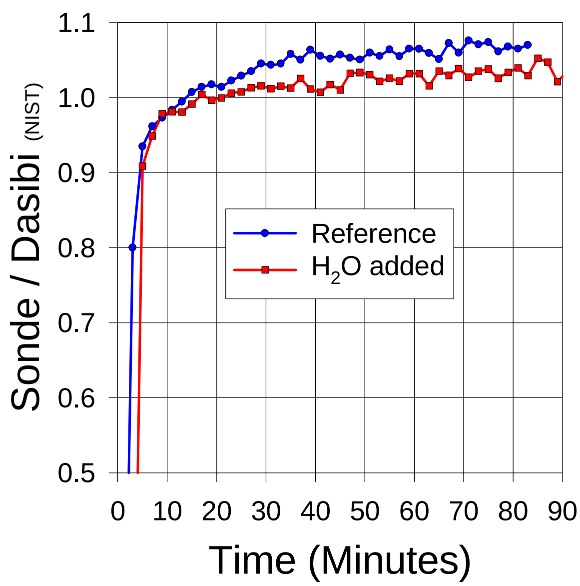

Figure 1. Relative response of ECC sonde 5A15323 for a constant ozone input. The lower curve is the result of an experiment where distilled water was added to keep the sensing solution concentration approximately constant.

Our initial comparisons showed that both types of sonde tend to show a slow but relatively steady increase in response when exposed to a constant ozone source. An experiment (Figure 1), in which distilled water was added to compensate for that lost by solution evaporation, indicates that this increase in response is only partly due to increase of solution concentration. In addition, the BM sondes indicated 0–30% lower ozone than the true value of the source, while ECC sondes give values much closer to the actual value (generally ±5% in our experiments). This is consistent with the expectation that the lower KI concentration in the BM sensing solution allows a certain percentage of ozone to escape without reacting, and/or that there are losses to the walls of the pump and sensor.

New BM sondes, however, consistently showed a significant (~15%) increase in sensitivity between successive experiments. No such effect was observed with previously flown sondes. The effect appears to be related to exposure to sensing solution, and suggests that the performance of new BM sondes might be improved if charged with sensing solution several days before flight, like ECC sondes.

Recent work at the Swiss Meteorological Service has shown that BM sondes that are subjected to meticulous cleaning and then calibrated repeatedly, with fresh sensing solution on each occasion, show a continual increase in response, approaching 100% after several such calibrations [B. Hoegger, private communication, 1996]. A similar effect has been noted in the literature for the KI method in glass apparatus [Bergshoeff *et al.*, 1980].

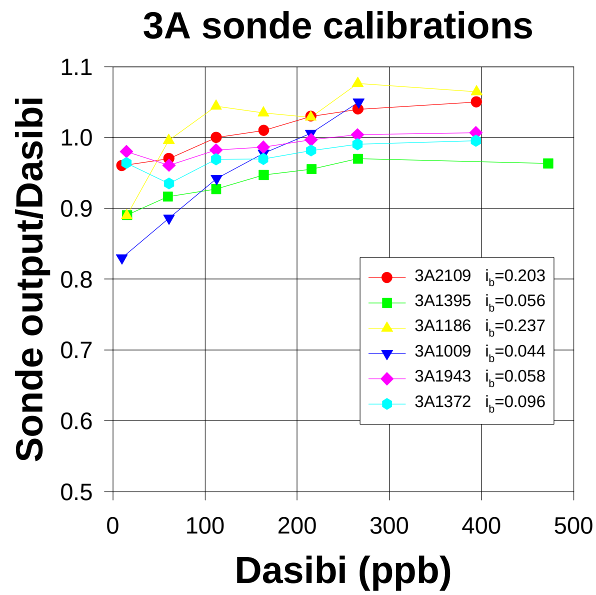

Figure 2. Results of calibration experiments on ECC 3A sondes. This type was flown at Canadian stations from 1980 to about 1985. All were reconditioned instruments. Background current is given in microamperes.

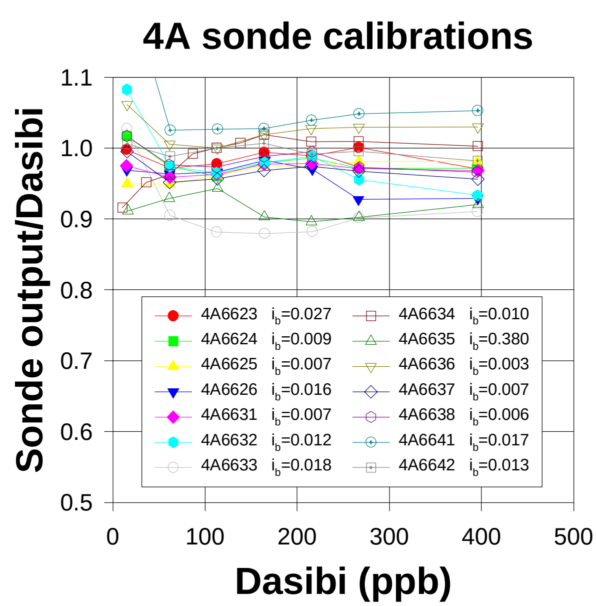

Figure 3. Results of calibration experiments on ECC 4A sondes. All were new instruments.

Figures 2, 3 and 4 show the results of calibrations performed on ECC 3A, 4A and 5A sondes respectively. The duration of each sonde calibration was approximately 70 minutes. Sonde response to varying amounts of ozone, for the 4A's and 5A's is quite linear in all cases, and the average response is close to 1. (Note that the first point on each curve, at 10ppb, is more variable than the others since the measurement error is at least 1ppb). Half of the 3A sondes show some degree of nonlinearity; this is surprising since the essential difference between the 3A and 4A sonde is a change of pump design, and this should have little effect at laboratory pressure. However, these were reconditioned sondes, rather than new instruments. It is difficult therefore to conclude whether or not any systematic difference in sonde response is apparent. A change of this type would imply larger negative trends in the troposphere than in our previous analysis [Tarasick *et al.*, 1995]. However, reanalyses of ozone trends for several Canadian stations, in which the linear trend model includes an additional parameter to allow for a difference in mean response between 3A and 4A sondes, show no significant differences in tropospheric response between the two types.

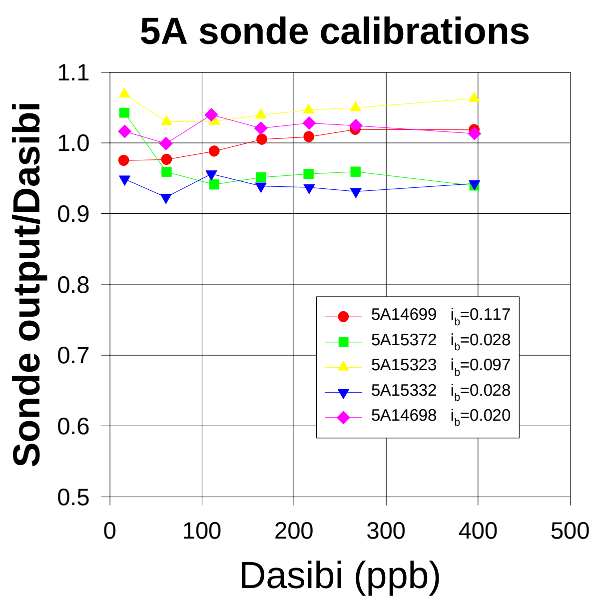

Figure 4. Results of calibration experiments on ECC 5A sondes. All were new instruments.

Figure 5 shows the results of calibrations performed on BM sondes of pre-1980 vintage. All were reconditioned sondes. Response to varying amounts of ozone is nonlinear in all cases; the variance in absolute response is also large. New sondes, in Figure 6, show similar nonlinear behaviour. This change of response appears to occur quite independently of the response achieved by the sonde at higher ozone input values, and after one hour (when it would, in flight, have reached the lower stratosphere). It will therefore have the effect of producing tropospheric readings that are too low, relatively independently of the total ozone correction factor, as this factor is controlled primarily by the much larger stratospheric ozone amounts.

Some of the variation in the final response exhibited by each sonde in Figures 5 and 6 is apparently due to differences in previous exposure to sensing solution and/or ozone, as discussed earlier. In Figure 6, the three sondes that had been used previously in our initial experiments show higher response than the six newer sondes. The sonde-to-sonde variability for sondes with a similar history and similar pre-flight preparation is probably therefore better than would appear at first to be indicated by these figures.

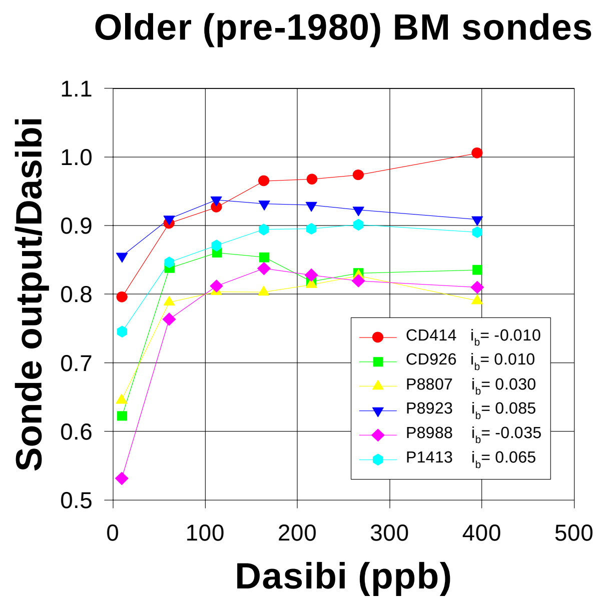

Figure 5. Results of calibration experiments on older BM sondes. These sondes were purchased prior to 1980 and are from stock remaining when the Canadian ozone sounding program switched to ECC sondes. All were reconditioned instruments.

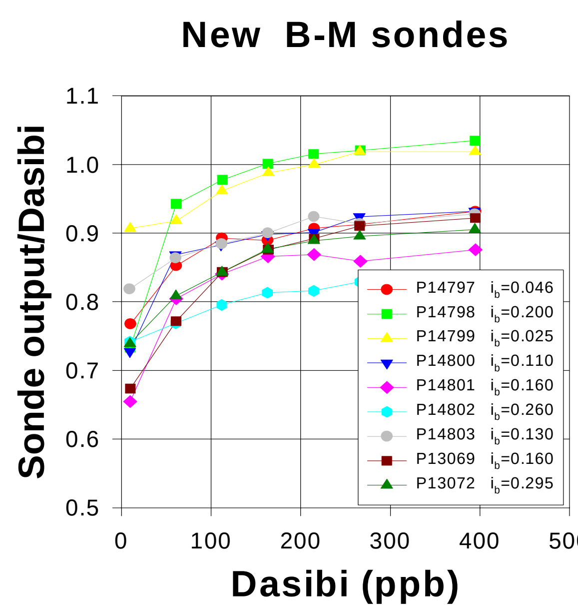

Figure 6. Results of calibration experiments on new BM sondes. All were recently purchased.

3. Conclusions

The existing literature on the laboratory characterization of ozonesonde behaviour is surprisingly small, given that these instruments have been used extensively for more than thirty years. The origin of the background current is still not well understood. The large increase in sensitivity of new BM sondes that we have noted is apparently related to exposure to KI solution but the mechanism is not known. The additional increase in absolute response for both types of sensor that we have observed is also not understood. From our preliminary work, it seems likely that BM sondes would perform better if charged with sensing solution several days to one week or more before use, like ECC sondes. While the response of ECC sondes is generally linear with ozone input, that of BM sondes is nonlinear, so that soundings with these devices will produce tropospheric values that are biased low.

Field intercomparisons of sonde types and of preparation procedures may produce ambiguous results unless these effects are properly understood. For example, such apparently unimportant (and generally unrecorded) factors as the length of time between filling the sonde with solution and launch, or between calibration and launch, may seriously affect the final results.

While we find some suggestion of a change in linearity of response between older and new ECC sondes, the sense of the change (if real) would be such as to cause spurious positive trends in the troposphere. Since preparation procedures have not changed in any way at Canadian stations over the period for which ECC sondes have been in use, we draw the conservative conclusion that our previously published trends in tropospheric ozone [*Tarasick et al.*, 1995], which were predominantly negative, have not apparently been affected by any secular changes in sonde response. These trends may therefore be regarded with increased confidence.

No systematic differences in either construction or performance were found between older and new BM sondes. However, response in the BM sonde is strongly dependent on the details of the pre-flight preparation procedures employed. It seems likely that apparently minor changes or improvements in pre-flight preparation at BM stations may have introduced systematic changes in sonde response in the troposphere. The potential biases that may result from such recent improvements, or others in the past, should be considered in future analyses of trends derived from BM ozone sounding data.

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