

Response to J. Fritsche concerning his comments on our Mercury Paper [ACP-2009-162]

Although separate calibration checks (standard additions) might have been desirable, this was not possible with the equipment at our disposal at the time the TGM measurements were made at Cape Point. Nonetheless, we still think that the DEs we have been observing are not due to instrumental artefacts but are real for the following reasons:

- 1) A de-activation of the gold traps is a well known phenomenon – see e.g. Tekran manual. The de-activated gold traps are usually regenerated by heating in air stream or by a procedure consisting of a cleaning in HNO₃ solution, drying, and heating. A spontaneous regeneration has not been reported so far.
- 2) DEs at Cape Point often showed sudden recoveries within a matter of about two hours and are not always linked to changing wind directions. If gold tube de-activation would have taken place as a result of VOCs, it is unlikely that “re-activation” could take place so fast, especially in polluted air. A simultaneous de-activation and re-activation of the two different gold traps by the same amount is thus unlikely, although, based on the procedure used at Cape Point, it could not be ruled out.
- 3) The well-pronounced diurnal cycle (maxima between 12:00 and 19:00) implies that there is in fact a chemical control mechanism behind the DEs. The cycle suggests that the DE process is also driven by solar radiation. If VOCs play a central role in de-activating the gold tubes, random behaviour would be expected due to the irregular nature of our wind flow patterns and different air compositions (ranging from ‘clean’ to ‘dirty’).
- 4) Data that has come to our attention recently show that DEs have also been observed by other researchers in non-polar regions and in polar region in summer:
 - a. TGM measurements made during the Polarstern cruise in 2008 has shown several DEs between 37 °N and 20 °N falling within similar diurnal time slots (noon till afternoon) as seen at Cape Point.
 - b. Likewise, TGM measurements made during the Polarstern cruise in 2009 has shown DEs on seven consecutive days between 37 °S and 26 °S and between 37°N and 20°N. These were not total depletions. But then again the Cape Point DEs do also not always constitute total depletions, but comprise a whole range from partial to complete DEs.
 - c. A summer depletion event in Antarctica has been reported by Temme et al. (Environ. Sci. Technol., 37, 22-31, 2003). Measurements of total gaseous mercury and gaseous elemental mercury by two simultaneously run Tekran instruments suggest transformation of gaseous mercury to mercury attached to particles.
- 5) DEs have been seen in air of different composition: clean marine, local pollution, continental air and air of a mixed nature. While VOCs might be present in air with a continental and/or anthropogenic signature, it is unlikely that background marine air contains high enough VOC

levels to be able to cause gold tube de-activation. We also had an incidence where air descending from aloft (NOAA-ESRL trajectory information show 2000 m altitude arrival height), contained steady background levels of CO and O₃ with a corresponding major TGM DE. It is highly unlikely that this air mass contained substantial amounts of VOCs.

In summary, we cannot altogether rule out the possibility of an artifact, but based on the above arguments and the experience accumulated by the operators of the Tekran and similar instruments over more than a decade of continuous measurements, we believe it very unlikely. Nonetheless, we propose to insert a small paragraph into our document stating exactly that, i.e. that analytical artefacts do constitute a small possibility.