Atmos. Chem. Phys. Discuss., 14, C6029–C6031, 2014
www.atmos-chem-phys-discuss.net/14/C6029/2014/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Gas adsorption and desorption effects on cylinders and their importance for long-term gas records" *by* M. C. Leuenberger et al.

Anonymous Referee #2

Received and published: 19 August 2014

The manuscript by Leuenberger et al. from the Climate and Environmental Physics department in Bern presents results from experiments designed to characterize the dependence of gas concentrations upon emptying high pressure cylinders. The problem of changing concentrations during withdrawal of air from such cylinders is well known and is of particular importance for the long term cylinders characterizing the respective international trace gas scales. Experience teaches that below a certain threshold the concentrations become unreliable. However, the threshold varies from laboratory to laboratory and largely depends on the treatment of the cylinders. Systematic studies of the corresponding effects are scarce and details need to be characterized in a more

quantitative fashion in order to avoid artifacts in the high-precision measurements of atmospheric trace gases. The experiments by Leuenberger et al. are an important step in this direction.

The major factors causing concentration changes are thermal fractionation during gas withdrawal, the type of cylinder (aluminium, stainless steel), surface treatment before filling, adsorption of trace gases on cylinder walls, reactions with the wall material, residual moisture, diffusion through cylinder or valve gaskets and more. According to Keeling et al. (Tellus 59B, 3, 2007), the largest effects are thermal fractionation, corrosion and leakage. Desorption effects account for less than 5 % of the total uncertainty. Other laboratories have reported much larger effects, which mainly have been attributed to cylinder handling (cylinders kept horizontally or standing upright, with consequences for the temperature distribution).

The manuscript by Leuenberger et al. concentrates on adsorption effects. The experiments are described quickly: High-pressure cylinders filled with ambient air are emptied using a continuous bleed with a variety of flows, thereby monitoring gas concentrations (CO2, CO, CH4 and H2O). Seven cylinders were studied, some were aluminium, some stainless steel tanks. The temperature was changed between -10 and +50 °C. The CO2 concentrations change considerably with temperature, with a large scatter of the data for the steel tanks. The aluminium tanks show a much smaller dependence. It would have been nice to read a discussion of the possible causes (like heat conductance of the materials), which has not been made.

All experiments are interpreted mainly in terms of adsorption / desorption. The flow rates are rather high (up to 5 L / min). Some important information is not provided: - position of the cylinders before and during the experiments (horizontal or vertical) - temperature gradient - surface roughness and treatment prior to filling - CO2 adsorption as a function of moisture.

The sometimes artificial distinction between physisorption and chemisorption is rather

ACPD
14, C6029–C6031, 2014

simplistic and not discussed specifically for the different species involved. CH4 could be expected to have little chemical activity and therefore be described using physisorption only. H2O in contrast will exhibit mainly chemisorption, thereby providing a liquid surface where gases like CO2 might dissolve in at varying degrees depending on the local pH. These effects are not discussed in the manuscript at all.

The surface area is given as a geometric term only. However, untreated surfaces often are a lot larger than the pure geometry might suggest. Hence, before calculating the number of adsorbed layers, the surface area must be known with some accuracy.

The reported adsorbed CO2 amounts (up to 9 ppm for a steel tank) seem very high and need to be confirmed independently. A simple experiment would be to fill a tank and measure the corresponding air concentrations simultaneously. The adsorbed gas would decrease the gas concentrations in the cylinder. Hence, there should be a difference of 9 ppm between the gas measured during filling and the gas withdrawn from the (steel) cylinder afterwards. I expect a missing amount of no more than 0.2 ppm, but I may be wrong.

Overall, the line between temperature related diffusion and adsorption / desorption effects is difficult to draw given the set of experiments. Some of the effects are unusually large. The effect of water adsorbed to the surfaces needs closer inspection.

The manuscript may be published, but only after paying close attention to effects that may be caused by temperature inhomogeneities and associated (very slow) diffusion and effects that can clearly be attributed to surface phenomena. The latter also requires a minute characterization of the surfaces involved.

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 19293, 2014.