Influence of Chlorine Emissions on Ozone Levels in the Troposphere

Golam Sarwar[1], Ravi Joseph[2], Rohit Mathur[1]

[1]United States Environmental Protection Agency, [2]Austin Energy, Texas

Abstract Chlorine emissions from cooling towers are emitted mainly as hypochlorus acid, not as molecular chlorine. Chlorine emissions from cooling towers in electric utilities in the U.S. are estimated to be 4,400 tons per year. On a molar basis, molecular chlorine results in a greater increase in tropospheric ozone than hypochlorus acid. However, hypochlorus acid produces more ozone than molecular chlorine when an equal amount of chlorine is present on a mass basis.

1. Introduction

Recent studies suggest that chlorine chemistry can increase ozone (O_3) in the troposphere in some areas of the U.S. (Chang *et al.*, 2002; Knipping and Dabdub, 2003; Chang and Allen, 2006; Sarwar and Bhave, 2007). While these studies suggest that chlorine may affect O_3 concentrations in the troposphere, information about chlorine emissions is sparse. Molecular chlorine (Cl_2) is a hazardous air pollutant; thus, the National Emissions Inventory (NEI) for hazardous air pollutants includes estimates of anthropogenic Cl_2 emissions in the U.S. However, both Cl_2 and hypochlorus acid (HOCl) can undergo photolysis to produce chlorine radical (Cl) which can enhance chemical production of O_3. Thus, emissions inventories for air quality study need to include estimates of both Cl_2 and HOCl emissions. This study develops an estimate of chlorine emissions from cooling towers in electric utilities and evaluates the relative impact of Cl_2 and HOCl on tropospheric O_3 formation.

2. Method

Chlorine is used as a biocide to control the growth of microorganism in cooling water. When Cl_2 is added to cooling tower, following reactions can occur in water:

$$Cl_2 + H_2O \leftrightarrow HOCl + H^+ + Cl^- \quad (1)$$
$$HOCl \leftrightarrow H^+ + OCl^- \quad (2)$$
$$NH_3 + H_2O \rightarrow NH_4^+ + OH^- \quad (3)$$
$$HOCl + NH_3 \rightarrow NH_2Cl + H_2O \quad (4)$$
$$H_2O \rightarrow H^+ + OH^- \quad (5)$$

where, NH_3 is ammonia, H_2O is water, and NH_2Cl is monochloramine (H^+, Cl^-, NH_4^+, and OCl^- are ions). Concentrations of these species are dependent on pH and temperature. Other competing reactions such as formation of other chloramines and reactions with metals, hydrogen sulfide were not accounted for in this study. In order to calculate the concentration of various chlorine species in water, mass balance based on the equilibrium constants was solved. Calculated distribution of chlorine compounds in water is shown in Table 1. Cooling towers are operated at a pH of 7.0 and greater. At such conditions, the amount of Cl_2 in water is negligible. The fraction of HOCl depends on pH. Thus, chlorine emissions from cooling tower can be emitted in the form of HOCl, not as Cl_2 and only a fraction of chlorine that is added to water is available for striping into the atmosphere.

Table 1. Percent distribution of chlorine compounds (as Cl) in cooling water

pH	Cl^-	Cl_2	NH_2Cl	HOCl	OCl^-
7.0	50.0	Negligible	0.1	38.7	11.2
7.5	50.0	Negligible	0.5	25.9	23.7
8.0	50.0	Negligible	1.4	12.5	36.2

Holzworth et al. (1984a) conducted experiments at a refinery cooling tower with a circulation rate of 60,000 gallon per minute that used 184,000 gm of Cl_2 per day. HOCl emissions for this cooling tower are estimated as follows:

$$\text{HOCl emissions (gm/day)} = 1.48 * TCl_2 * P_{HOCl} * F / 100$$

The factor of 1.48 is the ratio of the molecular weight of HOCl to Cl, TCl_2 is the total Cl_2 added to the cooling tower (gm/day), P_{HOCl} is the percent of total chlorine present as HOCl in water (%), and F is the flash-off factor for HOCl (-).

While the average pH of water at this cooling tower was 8.2, other cooling towers can be operated at lower or higher pH. For this study, a pH of 7.5 is used to estimate emissions. At this pH, only 25.9% of the total chlorine is present as HOCl in water. Flash-off factor determines the fraction of chlorine that can be stripped from the cooling tower into the atmosphere. Holzwarth et al. (1984b) determined flash-off factors for HOCl in laboratory. The highest flash-off factor was 0.1 which is used in this study to estimate the maximum possible emissions. Using these values, estimated HOCl emissions from this cooling tower are about 7,000 gm/day. Chlorine emissions of cooling towers in electric utilities are estimated by multiplying this value to the ratios of water circulating rates. Cooling tower data

for electric utility were obtained from the Environmental Directory of U.S. Power Plants (Bergesen and Hull, 1996). More than 600 cooling towers are operated in electric utilities in the U.S. To our knowledge, chlorine emissions from these cooling towers have not been estimated before.

3. Results and Discussion

Annual HOCl emissions from cooling towers in electric utilities are estimated to be 4,400 tons. This estimate is only a fraction of the 33,000 tons of Cl_2 emissions in the 1999 NEI for hazardous air pollutants. The top five ranked states are: Pennsylvania, Texas, Georgia, Arizona, and Ohio.

A box model containing gas-phase chemical reactions was used to assess the relative impact of Cl_2 and HOCl on O_3. The 2005 version of the Carbon Bond (CB05) chemical mechanism was combined with chlorine chemistry and was used in the box model (Yarwood et al., 2005). While both Cl_2 and HOCl photolyze to produce Cl, photolysis rate of Cl_2 is about 8 times faster than that of HOCl (9.0 hr^{-1} for Cl_2 vs. 1.1 hr^{-1} for HOCl at typical summer noon). The box model run was performed with prescribed initial conditions for urban conditions based on Gao et al. (1996). Model calculations were performed without and with initial chlorine. Three sets of initial chlorine were examined: 300 pptv of Cl_2, 300 pptv of HOCl, and 600 pptv of HOCl. The difference in predicted O_3 with and without chlorine is presented in Figure 1.

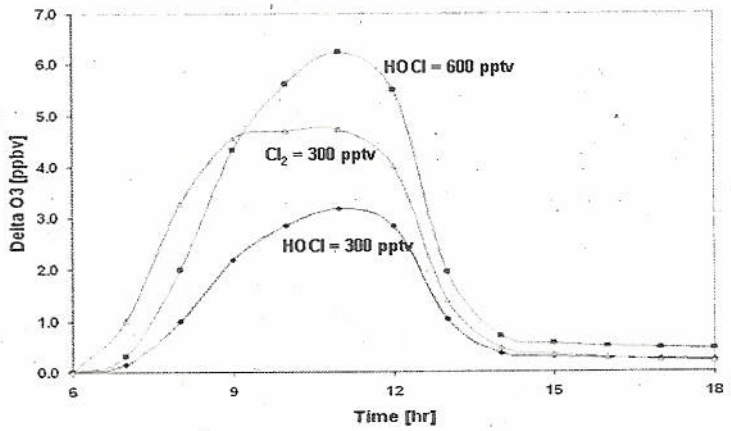

Figure 1: The relative impact of Cl_2 and HOCl on O_3 in the troposphere

When an equal amount of Cl_2 and HOCl is present on a mole basis (300 pptv), the increases in O_3 with Cl_2 are greater than those with HOCl. The rate of increase of O_3 with Cl_2 is also greater than that with HOCl. When an equal amount of chlorine is present on a mass basis (300 pptv of Cl_2 vs. 600 pptv of HOCl), then the largest increase in O_3 obtained with HOCl is greater than that with Cl_2. However, the initial rate of increase of O_3 with Cl_2 is still greater than that with HOCl. Similar results were also obtained for rural conditions described in Gao et al. (1996).

4. Summary

These findings have important implications. First, it suggests that only a fraction of chlorine that is added to cooling tower water can be emitted into the atmosphere. Second, chlorine emissions from cooling towers are primarily emitted as HOCl, not as Cl_2. The chemical form of chlorine emissions is important since it affect O_3 differently. We plan to combine these estimates with other available estimates of chlorine emissions and evaluate their impacts on O_3 in the U.S. by using the Community Multiscale Air Quality (CMAQ) model (Byun and Schere, 2006).

Disclaimer: Although this paper has been reviewed by EPA and approved for publication, it does not necessarily reflect EPA's policies or views.

References

Bergessen, C.A.E. and Hull, V., 1996. Environmental Directory of US Power Plants, Edison Electric Institute, Washington DC.

Byun, D., and Schere, K.L, 2006. Review of the governing equations, computational algorithms, and other components of the Models-3 Community Multiscale Air Quality (CMAQ) modeling system, *Applied Mechanics Reviews,* 59, 51–77.

Chang, S., McDonald-Buller, E.C., Kimura, Y., Yarwood, G., Neece, J., Russel, M., Tanaka, P., and Allen, D., 2002. Sensitivity of urban ozone formation to chlorine emission estimates, *Atmospheric Environment,* 36, 4991-5003.

Chang, S. and Allen, D. T., 2006. Atmospheric chlorine chemistry in Southeast Texas: Impacts on ozone formation and control, *Environmental Science & Technology,* 40, 251-262.

Gao, D., Stockwell, W. R., Milford, J. B., 1996. Global uncertainty analysis of a regional-scale gas-phase chemical mechanism, *Journal of Geophysical Research*, 101, C4, 9107-9119.

Holzwarth, G., Balmer, R. G. and Soni, L., 1984a. The fate of chlorine in recirculating in cooling towers. *Water Research,* 18, 1429-1435.

Holzwarth, G., Balmer, R.G. and Soni, L., 1984b. The fate of chlorine and chloramines in cooling towers. *Water Research,* 18, 1421-1427.

Knipping, E.M. and Dabdub, D., 2003. Impact of chlorine emissions from sea-salt aerosol on coastal urban ozone, *Environmental Science & Technology,* 37, 275-284.

Sarwar, G. and Bhave, P., 2007. Modeling the effect of chlorine emissions on atmospheric ozone across the eastern United States, Journal of Applied Meteorology and Climatology, 46, 1009-1019.

Yarwood, G., Rao, S., Yocke, M., and Whitten, G., 2005. Updates to the Carbon Bond Chemical Mechanism: CB05, Final Report to the US EPA, RT-0400675, Available at http://www.camx.com/publ/pdfs/CB05_Final_Report_120805.pdf.