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THE IMPACT OF THE PROPOSED ATIKOKAN
ELECTRIC GENERATING FACILITY ON THE
WET DEPOSITION OF SULFUR IN THE
BOUNDARY WATERS CANOE AREA

by

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SUMMARY

The major impact of Atikokan on the Boundary Waters Canoe Area (BWCA) during precipitation will be related to the increased deposition of acidic sulfate which has been transformed during transit from the SO_2 source at Atikokan. The BWCA faces an equally serious impact due to the increased washout of SO_2 which, once in the surface waters, is likely to convert to an acidic sulfate.

Both experimental data and theoretical models suggest that the wet deposition of sulfate from Atikokan will be seasonally dependent and will be related to features such as storm type, precipitation rate and concentration of sulfate being drawn into the storms. The concentration of SO_4 being drawn into the storms is dependent upon the rate of SO_2 conversion to sulfate during the transit from the source. Approximately 6 hours will be required for emissions from Atikokan to reach the BWCA. During this time 10% or more of the SO_2 can be converted to SO_4 .

The highest wet deposition of sulfate is expected in the summer and should be related to the frequent occurrence of intense convective activity. These summertime convective showers can remove 20 to 30 times the sulfate mass removed by wintertime snowstorms with the same precipitation intensity and duration. For these convective showers, isolated "hot" spots of sulfate deposition are expected with rainfall pH values of less than 3.5.

During storms when the Atikokan plume intercepts the boundaries of the BWCA, the concentration of sulfate in precipitation is predicted to be higher for periods with light precipitation rates (less than 2 mm/hr) than for periods with heavier precipitation rates. Intermittent precipitation will contain more acidic water than precipitation from continuous rainfalls. The pH during intermittent precipitation, in which unscavenged air is drawn into a precipitating cloud over the BWCA, is expected to be near 4.4. During widespread continuous precipitation, in which upwind scavenging occurs before the Atikokan plume reaches the BWCA, pH values of 4.9 are expected.

Sulfur dioxide removal should also be seasonally dependent, with less being removed in snowstorms than in rainstorms. The deposition rate of SO_2 is strongly dependent upon precipitation pH and is predicted to increase by a factor of ten as the pH increases from 4.4 to 4.9. At pH values of 4.9, the net wet flux of sulfur is determined primarily by the washout of SO_2 , while at pH values of 4.4 and less, sulfate wet removal contributes the bulk of the sulfur deposited on the ground.

The following report documents the procedures for determining wet deposition of both SO_4 and SO_2 . Estimates of the actual wet deposition associated with Atikokan, and predictions of precipitation acidity are presented. A general background discussion also presents the important concepts relating clouds and precipitation to the sulfate deposition at the ground.

The impact of the proposed Atikokan electric generating facility on the wet deposition of sulfur in the Boundary Waters Canoe Area.

1. Introduction

Acid rains, associated with sulfate pollution, are known to be related to structural, agricultural, and ecological damage. Sulfates also contribute to visibility degradation through light scattering by submicron particles and are suspected to be detrimental to human health (EPA, 1975).

The incorporation of sulfate into precipitation gives rise to a major portion of the acidity found in rainwater (Granat, 1977). Thus the electric utility at Atikokan is likely to decrease the pH of local rainfall primarily by emitting SO_2 which is transformed to SO_4 during transit and deposited in precipitation at points downwind. The major question therefore, is by how much will the precipitation acidity change? Procedures for determining the wet deposition of both SO_4 and SO_2 are presented in Section 3. Estimates of the actual wet deposition associated with Atikokan and the predicted precipitation pH using the most recent developments in the art of predicting precipitation scavenging are presented in Section 4. First however, a general background discussion is presented so as to familiarize the reader with the important concepts relating clouds and precipitation to the sulfate deposition at the ground.

2. Background

The concentration of sulfate in precipitation is a consequence of several cumulative processes occurring within and beneath the clouds. Brownian motion, phoretic attachment, inertial impaction, and nucleation all

serve to remove the sulfate aerosol from the air and attach it to the cloud and precipitation elements. However, Brownian and phoretic attachment mechanisms cannot place sufficient SO_4 mass into the cloud water to account for observed concentrations, and inertial impaction of sub-cloud sulfate is of second order importance when compared to other removal mechanisms (Scott, 1978).

Since sulfate particles are generally soluble, and are quite small, with the majority of mass distributed over particles with diameters less than $1.0 \mu\text{m}$ (Harrison et. al., 1976), they should be effective as cloud condensation nuclei. Indeed, if as Weiss, et al. (1977) claim, the major portion of the aerosol with diameters between 0.1 and $1.0 \mu\text{m}$ is sulfate, then the airborne sulfate aerosol could be responsible for nearly all of the cloud droplets appearing in continental clouds.

Sulfate may be generated within the cloud and precipitation water through the oxidation of absorbed SO_2 . The oxidation processes appear to be temperature dependent and often appear to rely on the presence of metal catalysts. Laboratory and theoretical work also suggests that oxidants such as O_2 , O_3 and H_2O_2 are capable of producing substantial quantities of sulfate in cloud water (see e.g., Levy et. al (1976) for an extensive literature survey). However, direct evidence of actual liquid phase oxidation has not been observed in the atmosphere.

Both the oxygen and ozone transformation mechanisms are pH dependent and begin to decrease substantially in importance as the pH decreases to less than 6 for O_2 reactions and 4.5 for O_3 reactions. The hydrogen peroxide mechanism is relatively insensitive to acidity, but no measurements of tropospheric H_2O_2 exist to determine the contribution to SO_4 by this oxidant. Ammonia can also play an important role in aqueous phase SO_2 oxidation by buffering the solutions and keeping the acidity low. However, recent solubility measurements by

Drewes and Hales (1978) imply that oxidation mechanisms based upon the presence of ammonia proceed more slowly than previously thought.

Fortunately some evidence is beginning to accumulate suggesting that it is not necessary to consider in-cloud conversion of SO_2 to SO_4 in order to predict the sulfate concentration in precipitation. Recent observations by Scott and Laulainen (1978), and modeling efforts by Scott (1978) have suggested that for certain precipitation events, the sulfate concentration in precipitation is determined largely by the sulfate concentration in the air flowing into the storm system. Scott suggests that the sulfate concentration in precipitation is inversely proportional to the precipitation rate and strongly dependent upon the type of storm system producing the precipitation.

The removal of soluble, submicron, pollutant aerosol from clouds appears to be accomplished primarily by large collector particles, such as snowflakes or raindrops, sweeping downward through the cloud and capturing the small cloud droplets containing high concentrations of the aerosol. The final concentration in the precipitation reaching the ground is dependent upon two features; first, the initial concentration in the collector particles as they start their descent through the region of the cloud where accretion of cloud droplets is the primary growth mechanism, and secondly, the concentration of pollutant in the cloud water accreted by the collector particles.

The solubility of sulfate particles makes them extremely effective as cloud condensation nuclei. The sulfate concentration in the collected cloud droplets depends upon the amount of cloud water condensed about each activated sulfate particle which, in turn, depends upon the number of available aerosol,

their size, and the intensity of the updraft velocity within the cloud.

The model of sulfate removal by Scott (1978), considers the three basic precipitation systems illustrated in Fig. 1. In the first case (Figure 1a), the Bergeron or ice growth process is primarily responsible for precipitation development. Ice crystals nucleate in the upper portions of the cloud, grow rapidly to precipitation sized particles, aggregate with each other, and accrete tiny cloud droplets. Even if melting should occur before the ice particles reach cloud base, the hydrometeors are large enough so that accretion of small cloud droplets continues to be the primary growth mechanism.* The sulfate incorporated into the precipitation is assumed to be predominantly that advected through the cloud base. This first case represents a situation where the collector particle (snow) is relatively pollutant free when it begins to accumulate liquid water. The ice nucleation is in an environment subsaturated with respect to water and upon nuclei with lattice structures similar to ice, such as silicas and clays (McDonald, 1964). Sulfate aerosol are not activated as cloud condensation nuclei in the upper portions of the cloud, and are not initially incorporated into the hydrometeor water. Sulfate pickup comes primarily through incorporation of the dirty cloud water in the lower portions of the cloud. Surface precipitation from this type of cloud may be snow or rain.

* Hydrometeors refer to ice or water particles large enough to fall from the cloud to the surface.

The Bergeron or cold cloud is felt to be responsible for the majority of precipitation falling from layer type clouds over the continents (Mason, 1971). The precipitation from continuous rain or snow storms over northern Minnesota almost certainly relies upon a Bergeron process for its development.

In the second situation (Figure 1b), the ice growth process is assumed to be ineffective in initiating precipitation. Rain develops entirely through warm phase mechanisms. Gentle uplift ($0.1 - 0.5 \text{ m s}^{-1}$) is implied and long times are available for precipitation sized drops to develop by condensation and coalescence. A major fraction of the moisture and pollutants are assumed to be transported through the sides of the storm. For this second case, sulfate aerosol flowing into the storm at the higher levels are activated in environs saturated with respect to water. The collector particles therefore have an initial sulfate concentration when they begin their descent through the lower portions of the cloud. Net sulfate pick up is equal to the sum of the sulfate material activated in the collector particles at their formation altitude, plus the sulfate accumulated by accretion of the dirty cloud droplets near cloud base. Thus, this warm cloud is capable of removing more sulfate than the cold cloud.

The third case (Figure 1c) considers precipitation development in convective storms. Here strong updrafts produce large supersaturations and large liquid water contents which enable combined condensation and coalescence to produce precipitation size drops faster than they can be removed by hydrometeors falling from above. The mass flux of moisture and pollutants is assumed to be largely through the cloud base. In the convective cloud, both the ice capture mechanism of the cold cloud and the conden-

sation, coalescence growth of the warm cloud are effective in removing sulfate from the atmosphere. The removal potential exceeds that of either the individual warm or cold clouds primarily because those droplets which grow into collector particles have grown by coalescence in the lower portions of the cloud where the cloud water contains high concentrations of sulfate. Showery, summertime precipitation in Minnesota should exhibit removal characteristics of the convective cloud; that is, extremely high concentrations of sulfate should be associated with convective showers affecting a small (approximately 1-10% of the total area) area at any one time.

These qualitative results can be expressed explicitly in terms of a washout ratio defined as the ratio of sulfate concentration in the precipitation water ($g_{\text{sulfate}}/g_{\text{water}}$) to the sulfate concentration in air below the cloud base ($g_{\text{sulfate}}/g_{\text{air}}$). Figure 2, from Scott (1978), illustrates the predicted variation in washout ratio as a function of precipitation rate, J , for the cold cloud (curve 3), the warm cloud (curve 2), and the convective cloud (curve 1). For a fixed concentration of airborne sulfate and for a given precipitation rate, Fig. 2 predicts the lowest sulfate concentrations in precipitation originating as snow. Factor of 2 and 3 increases are predicted when precipitation develops by warm phase mechanisms in stratiform clouds. The greatest sulfate concentrations are predicted to occur in precipitation from convective clouds. The convective and warm cloud mechanisms would be most prevalent during the summer months while the ice growth mechanism would naturally occur during the winter.

If the precipitation is in the form of snow or originated as snow in the upper portions of the clouds (curve 3), then the surface sulfate

concentration in precipitation is roughly proportional to $J^{-0.3}$ over the interval from $J = 0.2$ to 2.0 mm h^{-1} . If the precipitation sized drops develop independently of an ice stage, then the surface sulfate concentration becomes more strongly dependent upon rainfall rate and upon the airborne sulfate concentration at the inflow levels of the storm. If the precipitation forms without the benefit of an initial ice growth stage, then for light precipitation rates ($J < 0.2 \text{ mm h}^{-1}$), the sulfate concentrations in precipitation water can increase by a factor of 70 or more over the ice-dependent predictions. At more moderate precipitation rates ($J \sim 1 \text{ mm h}^{-1}$), the precipitation originating as snow is predicted to have about 1/3 to 1/2 the sulfate concentration of that originating on water droplets. At heavy precipitation rates ($J > 7 \text{ mm h}^{-1}$), the sulfate concentration is nearly independent of the precipitation formation mechanisms.

The curves of Fig. 2 provide a clue which might help to explain natural seasonal variations in sulfate concentration detected in the northeast U.S. Fig. 3 illustrates the variability observed in the MAP3S precipitation chemistry network (MAP3S, 1977). Although there is considerable scatter to this precipitation chemistry data, there seems to be a definite decline in winter concentrations of sulfate followed by an increase during the warmer seasons. High concentrations in the summer may be related to removal by convective storms, while winter time removal of sulfate is likely associated with cold rain and snow storms. Similar seasonal variations in sulfate removal are also expected in northern Minnesota.

In summary, both experimental and theoretical data are beginning to accumulate suggesting that sulfate deposition is seasonally dependent and

related to such features as storm type, precipitation rate, and concentration of pollutant being drawn into the storms. Of the three storm situations discussed above, the sulfate concentration in the precipitation falling on the Boundary Waters Canoe Area (BWCA) should be best predicted by using the cold cloud model, except for situations when the precipitation is clearly from convective clouds.

The concentration of SO_4 being drawn into the storm systems is dependent upon the rate of SO_2 conversion to sulfate during the transit from the source. Approximately 6 hours will be required for emissions for Atikokan to reach the BWCA. During this time 10% or more of the SO_2 can be converted to SO_4 .

The BWCA faces an additional impact due to the washout of SO_2 which once in the surface waters is likely to convert to SO_4 . This conversion of SO_2 surface waters may or may not present problems for the environment depending upon its concentration and acidity.

The derivation of SO_2 and SO_4 wet removal rates requires similar concepts. The procedures used to define and calculate wet removal by precipitating systems are discussed in the next section.

3. Wet removal rates for SO_2 gas and SO_4 aerosol

In most models describing pollutant transport, transformation, and removal, one typically finds an equation of the form

$$\frac{dn}{dt} = -\lambda n + S \quad (1)$$

where n represents the mass concentration of pollutant, and λ represents a rainout or washout coefficient. The symbol S denotes all other pollutant sources and sinks such as photochemical production, chemical conversions,

and dry deposition. Neglecting these additional source-sink terms and considering only the wet removal processes, the solution to (1) becomes

$$n = n_0 \exp (-\lambda t) \quad (2)$$

where n_0 represents the initial concentration of pollutant. When used as a description for wet removal of pollutants, (2) is generally applied over some vertical depth of the atmosphere such as the mixing layer, the cloud layer, or the troposphere.

Although wet removal is generally considered to be described by first order expressions such as (1), it is not intuitively obvious that it should be, or can be described in such a manner. Indeed, we will show that the first order assumption is not strictly correct. However, a first order expression can be approximated after considering basic principles. The following derivation will clearly illustrate the conditions under which the application of (1) is appropriate and will determine the form of λ for the wet removal of SO_2 gas and SO_4 aerosol.

(3a) wet removal of pollutants

An exact description of the local time variation of pollutant concentration results from applying the basic continuity equation; i.e.,

$$\frac{\partial n}{\partial t} = -\vec{\nabla} \cdot n\vec{V} \quad (3)$$

Here $\vec{V}$ represents the three dimensional wind vector with the vertical component described by

$$V_3 = W - V_f, \quad (4)$$

where w is the vertical wind speed and v_f (positive) is the fall speed of precipitation particles. Application of (3) for the description of wet removal, implies that pollutant is carried to and from the volume of interest only by the wind and falling precipitation. Assuming that boundary layer flow in the atmosphere is nondivergent and rearranging (3) in terms of a substantial derivative, results in a form analogous to (1);

$$\frac{dn}{dt} = \frac{\partial n v_f}{\partial z} \quad (5)$$

Integration over height, z , provides the desired expression for describing the wet removal of pollutants from the atmosphere;

$$\frac{d\bar{n}}{dt} = \frac{(nv_f)_z - (nv_f)_{z_0}}{z - z_0} \quad (6)$$

where $\bar{n}$ represents the vertical average over a column extending from z_0 to z . Therefore instead of finding that pollutant removal is directly proportional to the pollutant concentration as in (1), we find that removal is actually determined by the vertical flux divergence of pollutant in the column under consideration. The rate of mass (concentration) removal is a consequence of the mass flux of pollutant into the top of a volume minus the mass flux of pollutant out the bottom.

For wet removal, the mass flux of pollutant past a particular level can be represented by the precipitation rate, j , multiplied by the pollutant concentration of the precipitation water, C , where j has the units of a water flux, and C has units of mass of pollutant per mass of water. Thus, the flux divergence can be represented by

$$\frac{d\bar{n}}{dt} = \frac{(jC)_z - (jC)_{z_0}}{z - z_0} \quad (7)$$

A major difficulty in describing the wet removal of pollutants is determination of the vertical extent of the region being scavenged. Modelers often wish to determine pollutant removal for a layer of fixed thickness and generally apply (1) to a surface layer of air. However, unless the surface layer encompasses the entire vertical extent of the region being cleansed by precipitation, such an approach will produce only a crude approximation to the true removal. As (7) illustrates, both the flux into and out of the surface layer must be considered. Without the assistance of detailed vertical profiles of precipitation rates and pollutant concentration, the flux into the top of a surface layer will be indeterminate. Currently detailed vertical profiles of precipitation and pollutant concentration are unavailable. Thus we find our first restriction to applying (7) or (1); the layer under consideration must extend to heights where the wet, downward flux of pollutant is near zero.

(i) wet removal of sulfate aerosol

Figure (4) represents the simplest case for wet removal. Sulfate aerosol removal is considered, and the removal model described by Scott (1978) is employed. Briefly, the model assumes that in the portion of the figure above cloud base, cloud droplets are nucleated on sulfate condensation nuclei. Large collector particles (snowflakes) then enter the box from above and, as they descend, grow to larger sizes primarily by accretion of the cloud droplets. The process envisioned here is one of precipitation development in a cold cloud by the Bergeron process. The sweeping out of a dirty layer of cloud water above the cloud base by relatively pure collector particles is the

major removal mechanism. The region of the cloud where precipitation growth is primarily by accretion of cloud droplets is designated as the riming zone. Since the snowflakes are assumed to be relatively sulfate free when they enter the riming zone, the wet, downward pollutant flux at the top of the riming zone is zero. The model described here has been illustrated in Fig. 1a.

The thickness of the riming zone can be estimated from the fall speed of a typical collector particle and from the time required for the particles to grow to raindrop sizes. By utilizing the work of Kessler (1969), the fall speed of the median volume drop can be expressed in terms of the precipitation rate as

$$v_f = 3.89 J^{0.105} \quad (\text{m/s}) \quad , \quad (8)$$

where here, J represents the precipitation rate in mm h^{-1} . In continuous rainfalls, precipitation rates generally average between 0.5 and 1.0 mm h^{-1} . For such rainfall rates, the median volume drop diameter is roughly between 0.7 and 1.0 mm. Millimeter sized ice particles can be produced by riming in 5 to 13 minutes in mixed phase clouds with water concentrations near 1 g m^{-3} (Hindman and Johnson, 1972; Scott, 1976). Therefore, a time of 9 minutes is felt to be an appropriate estimate for the time collector particles remain in the riming zone while growing to precipitation sizes.

Taking the height of the riming zone to be defined by collector particle velocity (8), and multiplying by the time of collector particle growth in the riming zone gives the riming zone thickness, Δz , as

$$\Delta z = 2100 J^{0.105} \quad (\text{m}) \quad . \quad (9)$$

Thus, the thickness of the riming zone is generally near 2000 m and weakly depends upon precipitation rate.

The distance from the ground to cloud base in a precipitating cloud is typically small compared to 2000 m. Therefore, Δz can be considered to represent the distance from the ground to the top of the riming zone. Since $z - z_0 \approx \Delta z$, the flux divergence over the entire column extending from the ground to the top of the riming zone can then be evaluated by computing only the pollutant flux at the surface.

The concentration of sulfate in the precipitation water reaching the surface can be parameterized in terms of the sulfate concentration of the air being drawn into the cloud base. Fitting curve 3 of Fig. 2 in Scott (1978) with a least square curve for $0.13 < J < 2.5$ gives the surface water concentration of sulfate (grams of sulfate per gram of water) as

$$C = 0.46 x_g(SO_4) J^{-0.27} \quad (10)$$

where $x_g(SO_4)$ is the clear air concentration of sulfate (grams of sulfate per m^3 of air) being drawn into the cloud at cloud base. Generally, the subcloud air is well mixed and the sulfate concentration should be fairly uniform between the ground and cloud base. Therefore we approximate x_g with the surface air concentration of sulfate.

Combining (7), (9), and (10), the wet removal rate for sulfate can be expressed as

$$\frac{d\bar{x}(SO_4)}{dt} = - 0.22 x_g(SO_4) J^{0.625} \quad (11)$$

where $\bar{x}(SO_4)$ represents the average SO_4 aerosol concentration (grams of sulfate per m^3 of air) in the layer extending from the ground to the top of the riming zone.

(ii) removal of SO_2 by snow

Much of the preceding material can be used to describe the wet removal of SO_2 . For the simplest case, that of SO_2 scavenging by snow, a direct analogy follows. Here we assume that the bulk of SO_2 picked up by frozen collector particles occurs as these particles capture cloud droplets in the riming zone. The dissolved SO_2 in these cloud droplets is assumed to be in equilibrium with the environment, which, if the SO_2 air concentration decreases monotonically with height, implies that the droplets at the upper portions of the riming zone will contain less SO_2 than those droplets near cloud base. As the snowflakes collect cloud droplets, the droplets will freeze rapidly, and will have no opportunity to adjust to new equilibrium values as they are carried to lower levels in the cloud.

Since the wet, downward, flux of SO_2 through the upper boundary of the riming zone is negligible, the SO_2 removal rate by snow is determined by evaluating the pollutant flux at the ground. Written in terms of a flux divergence over the riming zone, the wet SO_2 removal rate is given by

$$\left. \frac{d\bar{x}(SO_2)}{dt} \right|_{\text{snow}} = - \frac{JC}{\Delta z}$$

$$= -0.48 J^{0.9} C \quad (12)$$

where C represents the dissolved SO_2 concentration in the snowflakes arriving at the

ground.

From Scott (1978), the final concentration of pollutant in a collector particle passing through the riming zone is given by

$$C = \bar{C} [1 - \exp(-2\bar{m})] \quad (13)$$

where $\bar{C}$ is the vertical average of the SO_2 water concentration in the riming zone, and $\bar{m}$ is the vertical average of the cloud water concentration. Then, taking $\bar{C}$ to equal the arithmetic average of the equilibrium concentration at the ground, C_g , and at the top of the riming zone, and setting the upper level concentration equal to zero results in

$$\frac{d\bar{x}(SO_2)}{dt} \text{ snow} = - 0.24 C_g J^{0.9} (1 - \exp(-2\bar{m})) \quad (14)$$

Furthermore, Scott (1978) has presented an expression relating precipitation rate to cloud water concentration;

$$\bar{m} = 1.56 + 0.44 \ln J \quad (15)$$

Equation (15) was intended to generalize all precipitation events. However no liquid water need to be present in snow clouds. Caution should be exercised when applying it to snowfalls, particularly when precipitation rates are very light.

Values of C_g can be obtained from Fig. 5 which presents equilibrium concentrations of SO_2 as a function of pH and SO_2 air concentration. The

curves of Figure 5 result from the simultaneous solution of three equilibrium equations describing the dissociation of SO_2 in water (e.g., See Appendix A, Easter and Hobbs, 1974).

(66) removal of SO_2 by rain

To extend these concepts to SO_2 removal by rain scavenging, consider the features illustrated in Figure 6. Again the riming zone is represented by the distance $(z-z_0)$, while the freezing level height is designated by (z_f-z_0) . For this model, snowflakes, as before, are assumed to accrete cloud droplets containing dissolved SO_2 and then to melt to raindrops after falling through the freezing level. In applying the flux divergence concept, the vertical fluxes in and out of each of the two boxes in Figure 6 must be considered. In the upper box, the only change in SO_2 concentration results from a downward flux through the freezing level. As in the purely snow case, the amount removed is

$$\left. \frac{dx(\text{SO}_2)}{dt} \right)_{\text{ice}} = - \frac{j(z_f) C(z_f)}{(z-z_f)} \quad (16)$$

where both the precipitation rate, and the SO_2 concentration in the snow are evaluated at the freezing level. Below the freezing level, the removal due to rain is

$$\left. \frac{dx(\text{SO}_2)}{dt} \right)_{\text{liquid}} = \frac{j(z_f) C(z_f) - j(z_0) C(z_0)}{(z_f-z_0)} \quad (17)$$

where $jC(z_0)$ and $C(z_0)$ are ground values. Below the freezing level, the SO_2 concentration in the drops is assumed to be determined solely by establishing an equilibrium concentration between the dissolved and airborne SO_2 .

In order to derive a removal rate that is analogous to the previous removal rates and applies over the entire region being scavenged (the top of the riming zone to the ground) a weighted average over both boxes is performed;

$$\frac{d\bar{x}(SO_2)}{dt} \Big|_{\text{rain}} = \frac{(z-z_f) \frac{d\bar{x}(SO_2)}{dt} \Big|_{\text{ice}} + (z_f-z_0) \frac{d\bar{x}(SO_2)}{dt} \Big|_{\text{liquid}}}{(z-z_0)} \quad (18)$$

Substituting (16) and (17) into (18) results in the desired expression for SO_2 removal by rain;

$$\frac{d\bar{x}(SO_2)}{dt} \Big|_{\text{rain}} = - 0.48 J^{0.9} C_g \quad (19)$$

Comparison between (14) and (19) illustrates that the rain removal rate of SO_2 can exceed the snow removal rate by a factor of two or more at equivalent precipitation rates. In particular, as the cloud water concentration goes to zero, the wet removal of SO_2 by the snow riming mechanism postulated above becomes negligible.

For both (14) and (19), the ground level concentration of dissolved SO_2 is related through the curves of Fig. 5 to the ground level SO_2 air concentration, $x(SO_2)$. That is,

$$C_g = \beta x(SO_2) \quad (20)$$

Thus, the expressions describing wet removal of SO_2 and SO_4 (Equations 11, 14, 19) can be generalized to

$$\frac{d\bar{x}}{dt} = - K x_g J^a \quad (21)$$

Notice that (21) is not an exact first order expression, as was assumed a-priori in (1). The average wet removal of SO_2 and SO_4 for a layer depends

not on the average pollutant concentration in the layer, but upon the surface level concentration in the layer. If the surface level concentration, x_g , can be expressed in terms of a layer average, then the first order relationship of (1) will result. For example, suppose the surface level concentrations of SO_2 and SO_4 decrease linearly to zero at the top of the riming zone. Then $x_g = 2\bar{x}$ and

$$\left. \begin{aligned} \frac{d\bar{x}(SO_4)}{dt} &= -0.44 \bar{x}(SO_4) J^{0.625} \\ \frac{d\bar{x}(SO_2)}{dt} \Big|_{\text{snow}} &= -0.48 \beta \bar{x}(SO_2) J^{0.9} (1 - \exp(-2\bar{m})) \\ \frac{d\bar{x}(SO_2)}{dt} \Big|_{\text{rain}} &= -0.96 \beta \bar{x}(SO_2) J^{0.9} \end{aligned} \right\} \quad (22)$$

Another common situation is to assume a Gaussian profile for a plume. Then

$$\left. \begin{aligned} x_g &= \bar{x} \Delta z / [1.25 \sigma_z \operatorname{erf}(\Delta z / (1.41 \sigma_z))] \\ &= \gamma \bar{x} \end{aligned} \right\} \quad (23)$$

Substitution of (23) into 11, 14 and 19 gives

$$\left. \begin{aligned} \frac{d\bar{x}(SO_4)}{dt} &= -0.22 \gamma \bar{x}(SO_4) J^{0.625} \\ \frac{d\bar{x}(SO_2)}{dt} \Big|_{\text{snow}} &= -0.24 \beta \gamma \bar{x}(SO_2) J^{0.9} (1 - \exp(2\bar{m})) \\ \frac{d\bar{x}(SO_2)}{dt} \Big|_{\text{rain}} &= -0.48 \beta \gamma \bar{x}(SO_2) J^{0.9} \end{aligned} \right\} \quad (24)$$

(3b) Wet flux of sulfur and precipitation pH

Having developed procedures for computing removal rates of SO_2 and SO_4 by precipitation, calculations to determine sulfur deposition and rainwater acidity follow directly. In fact, the flux of SO_2 or SO_4 is obtained by multiplying (21) by the region being scavenged, Δz , which is defined by (9). As for pH, the major portion of acidity found in rainwater can be attributed to the incorporation of sulfate (Granat, 1977). Indeed, as Fig. 7 illustrates, a good approximation to rainwater pH results from assuming two hydrogen ions for every sulfate ion (Dana, 1978). The figure presents precipitation chemistry data collected from the MAP3S precipitation chemistry network and suggests that during the summer months when nitrate concentrations in precipitation water are the lowest, the two hydrogen to one sulfate ion is regularly observed. During the winter months when nitrates play a greater role in determining rainfall acidity, there is an excess of hydrogen ions; resulting in the molar ratio of hydrogen to sulfate being greater than 2. Still, at pH values less than 4.3, the assumption of $[\text{H}]/[\text{SO}_4] = 2$ is quite good. Thus, determination of the sulfate concentration in precipitation water should provide accurate estimates of rainfall pH.

4. Impact of Atikokan on precipitation acidity

As illustrated by (10), the sulfate concentration in precipitation is directly proportional to the sub-cloud concentration of airborne sulfate. To approximate what this concentration might be in the pollutant plume originating at Atikokan, a simple box model is applied where the emitted SO_2 is dispersed into a volume determined by the height of a boundary layer, the width of the plume, and the distance of Atikokan from the BWCA. Fig. 8

illustrates the assumed configuration. The concentration of SO_2 within the box of Fig. 8 is dependent upon the flux of SO_2 into the box at the power plant source, and the flux of SO_2 out of the box at the downwind boundary. Therefore, concentration is dependent upon emission rate of SO_2 and the wind velocity.

The depth of the well mixed atmospheric boundary layer is taken to represent the height of the box, and the width is selected by assuming horizontal plume dispersion in a neutral atmosphere 100 km downwind from the source. Typical values for box height and width are 1 km and 15 km respectively, where the width represents $3\sigma_y$. A wind speed of 5 m s^{-1} is selected and represents a travel time of 5.5 hours from Atikokan's stack to the BWCA 100 km downwind. The source strength for SO_2 is taken to be 44,500 tons/yr. Conversion of SO_2 to SO_4 is assumed to occur by a first order process with a conversion rate of $2\% \text{ h}^{-1}$. Such conversion rates are typical for power plant plumes in clean atmospheres (Alkezweeny, 1976).

If conversion to SO_4 were neglected, the average SO_2 concentration in the box would be about $28 \mu\text{g}/\text{m}^3$. However, at a conversion rate of $2\% \text{ h}^{-1}$, approximately 10% of the SO_2 would be converted to SO_4 by the time the plume arrived at the BWCA. Thus, the SO_2 and SO_4 air concentrations over the BWCA are expected to be near 25 and $4 \mu\text{g}/\text{m}^3$ respectively, when the Atikokan plume is overhead.

For typical rainfall rates of 1 mm h^{-1} in continuous rainfalls, (10) yields a concentration of 1.9 mg/l for the sulfate in precipitation water. By assuming 2 hydrogen moles for every sulfate mole, this sulfate concentration converts to a rainfall pH of 4.4.

Having computed the pH, the SO_2 concentration in rainwater, C_g , can be obtained from Fig. 5. For an SO_2 air concentration of $25 \mu\text{g}/\text{m}^3$ and for a rainfall pH of 4.4, C_g equals 0.6 mg/l.

Comparing the wet removal rates for SO_2 and SO_4 for the above air concentrations and pH, we have from (11)

$$\frac{d\text{SO}_4}{dt} = - 9 \times 10^{-7} J^{0.625} \quad (25)$$

and from (19)

$$\frac{d\text{SO}_2}{dt} = - 3 \times 10^{-7} J^{0.9} \quad (26)$$

Equation (25) clearly illustrates, that for the above conditions of air concentrations and conversion rates, the wet flux of sulfate to the ground is about three times the SO_2 flux. Even if all of the SO_2 was converted to sulfate shortly after coming in contact with the ground, the SO_2 would account for less than one third of the total sulfate mass deposited in light rains ($J \approx 1.0 \text{ mm h}^{-1}$), and less than one half the total sulfur mass in moderate rains ($J \approx 10 \text{ mm h}^{-1}$).

The above discussion is representative of wet removal in an intermittent shower situation. That is, the above model neglects any upstream removal processes and assumes washout only for the situation when the pollutant plume is drawn into a precipitating cloud directly over BWCA. If, for example, continuous precipitation was occurring over a widespread area, upstream removal of SO_2 and SO_4 would have to be considered in calculating rainwater pH, and sulfur fluxes at the BWCA. Such a problem is only slightly

more complex, but it requires a solution to a coupled set of first order differential equations describing the transformation and removal processes for SO_2 and SO_4 . Dimensions of the plume must also be specified.

Only a crude solution has been attempted at this time. The results indicate that continuous precipitation will remove considerable SO_2 and SO_4 from the Atikokan plume before it arrives at the BWCA. Because sulfate is efficiently removed by any continuous precipitation upwind of the BWCA, less acidic rainfall will result than for the previous case of washout only over the BWCA. Higher rainwater pH's will increase the solubility of SO_2 and will greatly enhance the SO_2 flux to the surface. Factor of 10 increases in SO_2 flux are predicted with the net sulfur flux being enhanced by a factor of four over the previous case.

A sample calculation reveals that for an average SO_2 air concentration of $14 \mu\text{g}/\text{m}^3$ in the riming zone ($\sim 2\text{km}$ thick), and for 5.5 hours of transit through a storm with an average precipitation rate of 1 mm h^{-1} , the rainfall pH would be near 4.9 if airborne SO_2 was converted to SO_4 at $2\% \text{ h}^{-1}$.

5. Conclusions

It is not yet clear whether the precipitation associated with northerly winds at the BWCA is of the light, steady type or of the brief, showery type. However, the impact of Atikokan on the BWCA during precipitation is related to the deposition of sulfate which has been transformed during transit from the SO_2 source at Atikokan. Intermittent precipitation will contain more acidic water than precipitation from continuous rainfalls. The pH of intermittent precipitation is expected to be near 4.4 while for continuous precipitation, pH's of near 4.9 are expected.

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For typical rainfall rates of 1 mm h^{-1} in continuous rainfalls, (10) yields a concentration of $1.9 \text{ mg}/\text{l}$ for the sulfate in precipitation water. By assuming 2 hydrogen moles for every sulfate mole, this sulfate concentration converts to a rainfall pH of 4.4.

The curves of Fig. 2 predict a strong dependence on storm type for determining washout of sulfate. The summertime convective showers can remove 20 to 30 times the sulfate mass removed by a wintertime snowstorm with the same precipitation intensity. For these isolated showers, local "hot" spots of sulfate deposition can occur where pH's are less than 3.5. Sulfur dioxide removal should also be seasonally dependent, with less being removed in snowstorms than in rainstorms. Thus the summer time deposition of sulfur and acidic precipitation should exceed that deposited in the winter - assuming that at least an equivalent amount of precipitation falls during northerly wind regions in the summer as falls during the winter.

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Figure Captions

Figure 1: Qualitative description of synoptic situations envisioned for the model. The symbols represent: *, ice particles; ⊗, melting ice particles; 0, liquid drops; o, cloud droplets; →, trajectory of air flowing into the storm (solid lines); - - →, motion of hydrometeors relative to the storm (dashed lines). The vertical scale represents typical cloud depths.

Figure 2: Washout ratio as a function of precipitation rate. Curve 1 represents predictions for intense convective storms or from clouds whose tops are warmer than 0°C; Curve 2 represents predictions for storms where rain develops without the assistance of an ice growth stage; Curve 3 is for storms where the ice growth process is necessary for initiating precipitation.

Figure 3: Sulfate concentrations in surface precipitation at Penn State University, Sept. 1976 through Jan, 1978. The curve is an eyeball fit to individual data points.

Figure 4: The volume considered for sulfate removal. The symbols represent: *, ice particles; 0, liquid drops; o, cloud droplets; →, the direction of the sulfate flux at the upper and lower boundaries of the volume.

Figure 5: Curves of C_g/x_g as a function of pH. The labels for the curves represent SO_2 air concentrations ($\mu g/m^3$). The units of C_g and x_g are grams of dissolved SO_2 per gram of water and grams of airborne SO_2 per cubic meter of air, respectively.

Figure 6: The volume considered for wet SO_2 removal by snow and rain. The ground is at z_0 and the top of the riming zone is at z . The freezing level is at z_f . The air concentration of SO_2 is assumed to decrease with height.

Figure 7: Observed relationships between the ion concentrations of H and SO_4 for (a); summer, 1977, and (b), winter, 1977-78. The solid line represents two hydrogen moles for every sulfate mole, while the circles represent data points.

Figure 8: The geometry of the volume considered in the box model. The Atikokan stack is located at the vertex on the left, while the mean wind blows pollutants from left to right.

(a) BERGERON CLOUD

(b) WARM OR MARITIME CLOUD

(c) CONVECTIVE CLOUD