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Application of Gas-Aerosol Adsorption Data to the Selection of Air Quality Standards

A quantitative approach is presented for selecting air quality standards which take into account pollutant gas-aerosol synergistic effects. These synergistic health effects have been postulated to be due to the adsorption or absorption of the pollutant gas by the aerosol particles. The approach presented in this paper assumes that the synergistic toxic agent is the adsorbed pollutant gas. Therefore, limiting the concentration of the adsorbed pollutant gas limits the magnitude of the synergistic effects. The concentration of the adsorbed pollutant gas is related to the concentrations of the gaseous phase pollutant gas and the atmospheric aerosol using the Langmuir adsorption isotherm. An example is presented of the selection of air quality standards for sulfur dioxide and the atmospheric aerosol using concentration data for these two pollutants along with health effect data.

The presently established air quality standards do not take into account the synergistic health effects of mixtures of a pollutant gas with an aerosol. The observed synergistic health effects of gas-aerosol mixtures have been postulated to be due to the adsorption of the pollutant gas onto the surface of solid aerosol particles or the absorption of the gas into liquid aerosol droplets. This phenomenon has been postulated so often, that it is reported in recent nontechnical literature as an established fact.

Dautrebande (1939) reported that the toxicity of mustard gas was markedly increased by the presence of an inert aerosol, and that (1950) irritant effects on humans subjected to various gases were increased by the presence of aerosols. LaBelle (1955) reported that the presence of inert aerosols increased the toxicity of formaldehyde, had no effect on acrolein, and decreased the toxicity of nitric acid fumes. Goetz and Tsuneishi (1959) reported that the presence of aerosols had profound effects on the toxicity of automobile exhaust and formaldehyde on bacteria. Amdur (1959) showed that sulfur dioxide or formaldehyde mixed with a sodium chloride aerosol caused greater changes in the respiratory mechanics of guinea pigs than did either gas without the aerosol. However, on healthy adults, Amdur (1964) reported no difference between the effects of sulfur dioxide and a mixture of sulfur dioxide with a sodium chloride aerosol. Dalhamn and Reid (1967) reported that the ciliary activity of rats exposed to a mixture of ammonia and a carbon aerosol was significantly impaired and showed a high frequency of severe mucosal damage compared to exposure either to the carbon or ammonia alone.

Relationship of Concentrations of Adsorbed Pollutant, Gaseous Pollutant, and Aerosol Mass

General Mathematical Relationship

Experimental observations support the hypothesis that the synergistic effects of gas-aerosol mixtures are due to the formation of an irritant aerosol. Assume that the concentration of the irritant aerosol is a function of the amount of pollutant gas adsorbed onto the surface of inert solid aerosol particles (absorption into liquid droplets will not be considered here). An equation to calculate the concentration of the adsorbed irritant or pollutant gas as a function of the gaseous pollutant concentration and the aerosol concentration can be derived. The number of adsorbed molecules per volume (cm^3) of air is given by the following equation:

$$N_{\text{Adsorbed}} = \frac{A(V/V_m)}{\sigma} \quad \frac{\text{(No. adsorbed molecules)}}{\text{cm}^3} \qquad (1)$$

where:

A = aerosol surface area per volume of air (cm^2/cm^3)
V/V_m = fraction of aerosol surface area covered with adsorbed pollutant gas
σ = area of adsorption site for one pollutant molecule

The concentration of adsorbed pollutant gas in parts per million is given by the following equation:

$$C_{\text{Adsorbed}} = \frac{A(V/V_m)RT}{6.023 \times 10^{17}\sigma P} \quad \text{(ppm)} \qquad (2)$$

where

R = universal gas constant
T = temperature
P = pressure

For monolayer adsorption, which is the usual case for p/p_0 much less than unity, V/V_m can be described by the Langmuir adsorption isotherm.

$$\frac{V}{V_m} = \frac{c(p/p_0)}{1 + c(p/p_0)} \qquad (3)$$

where

c = adsorption constant
p = vapor pressure of pollutant gas
p_0 = vapor pressure of pollutant gas at saturation

$$C_{\text{Adsorbed}} = \frac{1.66 \times 10^{-18} ARTc(p/p_0)}{\sigma P[1 + c(p/p_0)]} \qquad (4)$$

The ratio of the gaseous phase pollutant concentration to the concentration at saturation C/C_0, can be substi-

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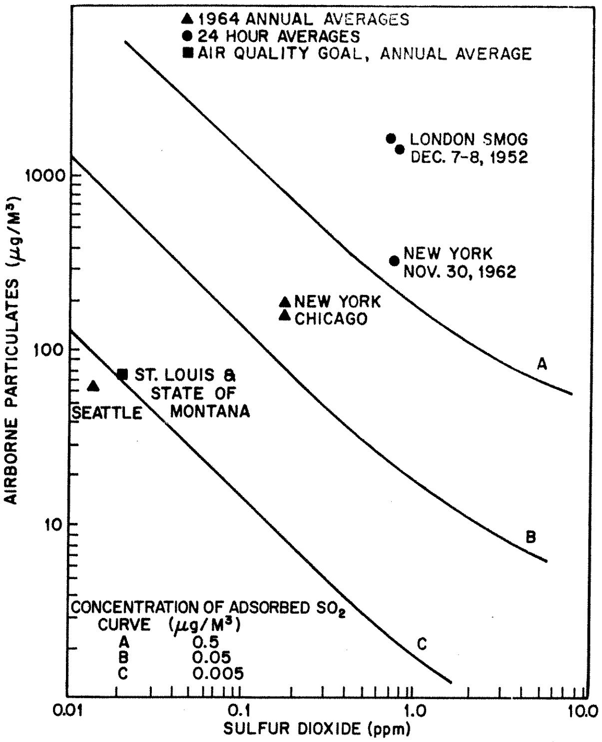

Figure 1. Graph relating concentrations of gaseous sulphur dioxide and suspended particulates at constant concentrations of adsorbed sulphur dioxide.

tuted for the ratio of the vapor pressure to the vapor pressure at saturation, p/p_0.

$$C_{\text{Adsorbed}} = \frac{1.66 \times 10^{-18} ARTc(C/C_0)}{\sigma P[1 + c(C/C_0)]} \quad (5)$$

Substituting 293°K for T, 82.05 (cc-atm/mole °K) for R, and 1 atm for P gives:

$$C_{\text{Adsorbed}} = \frac{3.99 \times 10^{-14} AcC}{\sigma(C_0 + cC)} \quad (6)$$

Relationship for Adsorbed SO₂, Gaseous SO₂, and Aerosol Mass

The concentration of adsorbed sulfur dioxide is a function of the aerosol surface area, the concentration of gaseous sulfur dioxide in the air and at saturation, the adsorption constant, and the adsorption site area. The concentration of the atmospheric aerosol is most frequently reported in mass concentration units. The aerosol surface can be calculated from the aerosol mass using an average aerosol surface area of 5.4 × 10⁴ cm²/cm³ particulates as reported by Noll (1966) and an average particle density of 2.0 g./cm³.

$$A = 2.72 \times 10^{-8} W \quad (\text{cm}^2/\text{cm}^3 \text{ air}) \quad (7)$$

where:

W = aerosol mass concentration (micrograms/cubic meter)

Assuming an adsorption site area σ of 20 A² and substituting Equation (7) into Equation (6) gives:

$$C_{\text{Adsorbed}} = \frac{5.42 \times 10^{-7}\, cCW}{C_0 + cC} \text{ (ppm)} \quad (8)$$

This equation relates the three variables, concentration of adsorbed gas (C_{Adsorbed}), concentration of gaseous pollutant (C), and the aerosol mass concentration (W).

The concentration of adsorbed sulfur dioxide in micrograms per cubic meter ($\mu g/m^3$) is given by the following equation:

$$C_{\text{Ad.SO}_2} = \frac{1.55 \times 10^{-3} cCW}{C_0 + cC} \quad (\mu g/M^3) \quad (9)$$

Substituting into Equation (9) a c of 10^6 and C_0 (saturation concentration) of 3.2×10^6 ppm for sulfur dioxide at 20°C gives:

$$C_{\text{Ad.SO}_2} = \frac{1.55 \times 10^3\, CW}{3.2 \times 10^6 + 10^6 C} \quad (\mu g/M^3) \quad (10)$$

Use of Gas-Aerosol Adsorption Data in the Selection of Air Quality Standards

Air quality standards should be established which take into account the synergistic effects of gas-aerosol combinations. The presentation of an example will illustrate how gas-aerosol adsorption data might aid in the selection of standards. In this case it is assumed that it is desired to limit the concentration of sulfur dioxide adsorbed on the atmospheric aerosol (to prevent SO₂-aerosol synergistic effects), the concentration of gaseous sulfur dioxide, and the concentration of airborne particulates. The relationship of these three variables (adsorbed SO₂, gaseous SO₂, and aerosol mass), based on the Langmuir adsorption isotherm in the form of Equation (10) is shown in Figure 1. In this figure constant adsorbed sulfur dioxide concentration lines are plotted on a graph of aerosol mass concentration versus gaseous sulfur dioxide concentrations.

Also included in this figure are points of the pollutant concentrations recorded during the 1952 London smog, the 1962 New York episode, the average pollutant concentrations for various cities, and the air quality standards for the St. Louis Interstate Area and the State

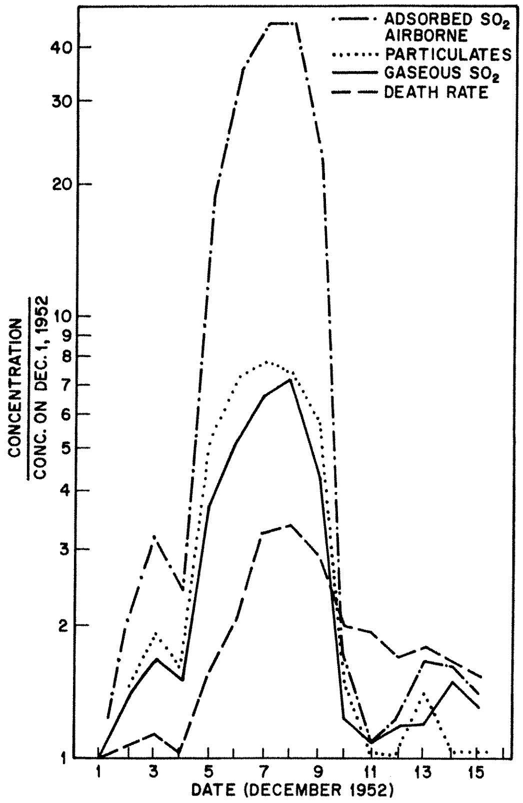

Figure 2. Relative increase in pollutant concentration and death rate during 1952 London smog.

of Montana (annual averages). Actually this graph should be three-dimensional so that the time parameter could be included.

Recognizing that the London and New York episodes produced undesirable effects, let the maximum allowable 24-hour average adsorbed sulfur dioxide concentration be set at curve *B* in Figure 1 (concentration of 0.05 $\mu g/M^3$ adsorbed SO_2 for the assumed absorption constant of 10^6). Note that the concentrations of adsorbed sulfur dioxide are calculated based in Equation (10) (no measurements of the amount of pollutant gases adsorbed on the atmospheric aerosol have ever been made). Let the maximum allowable gaseous sulfur dioxide concentration (24-hr average) be set at 0.1 ppm which is about twice the concentration recommended by the U. S. Public Health Service and one-half the concentration set by the State of Pennsylvania. By referring to curve *B* of Figure 1 it can be seen that, at the two selected sulfur dioxide concentrations (adsorbed and gaseous), the maximum allowable 24-hr airborne particulate concentration is about 140 $\mu g/m^3$

Similarly the toxic effect data reported for animals exposed to various concentrations of aerosol-pollutant gas combinations can be graphed to show the safe concentration levels of aerosol-pollutant gas mixtures.

A significant factor to note concerning the adsorption of a gaseous pollutant onto the aerosol surface area is that the concentration of the adsorbed gas is a function of the multiplication product of the gaseous pollutant concentration times the aerosol mass concentration. This multiplying effect is illustrated in Figure 2 which shows that during the December 1952 London smog the concentration of adsorbed sulfur dioxide (calculated) increased 4300% compared to 610 and 680% increases in the measured concentrations of gaseous sulfur dioxide and airborne particulates, respectively.

Conclusion

The establishment of air quality standards which take into account the effects of gas-aerosol adsorption combinations may be aided by the use of classic adsorption equations, such as the Langmuir adsorption isotherm, and presently available pollutant concentration and effect data.

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