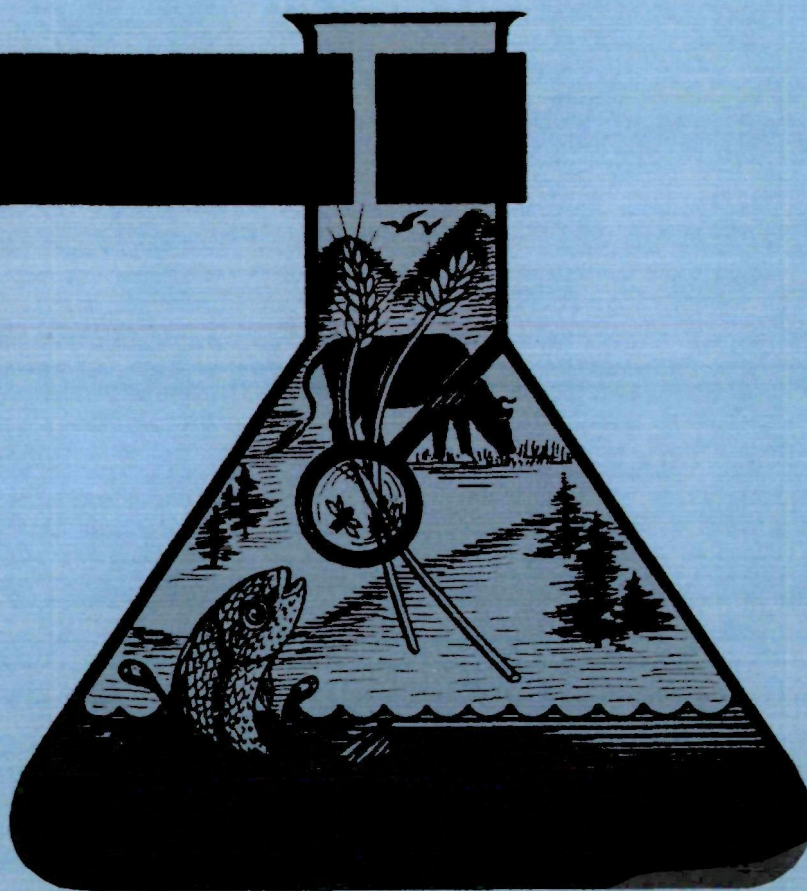# ♻EPA

WET AND DRY DEPOSITION - A
SYNOPSIS CONTAINING ESTIMATES OF
DEPOSITION VELOCITIES FOR SOME
POLLUTANT AND TRACE GASES IN THE
ATMOSPHERE

CERL-037

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by

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Introduction

The initial point at which most air pollutants become of concern to human health, and ecology is when removal from the atmosphere occurs at the earth's surface. Some pollutants such as nitrogen oxides and hydrocarbons undergo chemical reactions while in the atmosphere and are removed in a different form than when they were first emitted. The impact of air pollutants on terrestrial ecosystems, however, is a function of the quantitative and qualitative deposition at the earth's surface. The purpose of this report is to summarize, analyze, and present a synopsis of what is presently known about the rates at which some common pollutants are removed from the atmosphere.

Locally, the concentration of a pollutant in the atmosphere is determined primarily by the rate of horizontal dispersion and is roughly proportional to the inverse of the wind speed. On continental and global scales, the concentration is directly related to removal processes at the surface; thus wet and dry deposition are key factors in the mass budgets of air pollutants on these scales. An analysis of the relative importance of horizontal dispersion and surface deposition is presented in the appendix.

The information presented in this report allows one to estimate the rate of removal by the earth's surface of a variety of pollutants, both globally and locally, by sea, soil, and vegetation surface types, given the pollutant concentrations in the atmosphere. Figure 1 shows the
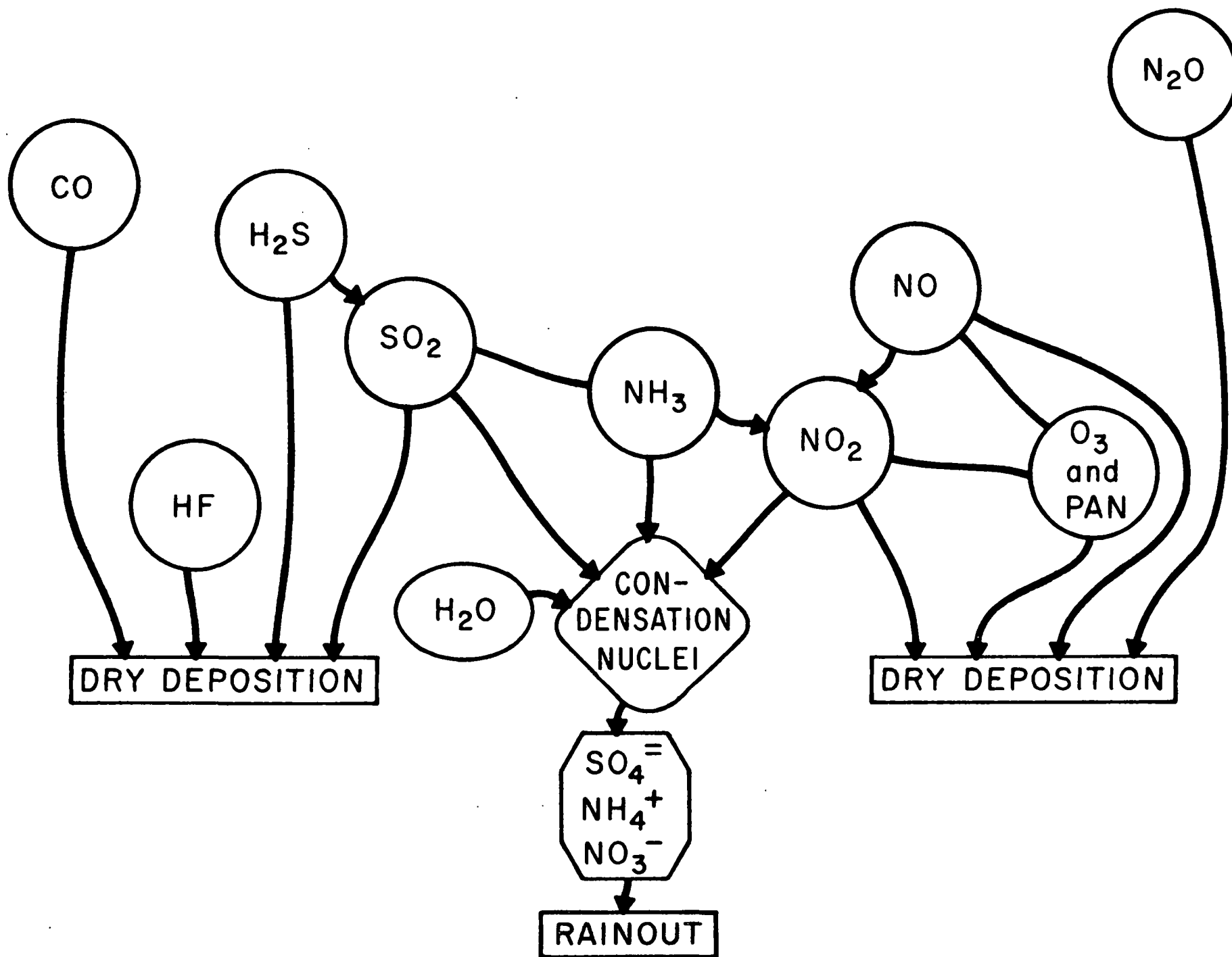
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Figure 1: Removal and interaction of some common pollutant and trace gases in the atmosphere.

removal mechanisms and interactions among some common pollutants and trace gases and Table 1 presents estimates of deposition velocities from which removal rates can be determined given the concentration of these components in the atmosphere.

The report also contains an annotated bibliography of the relevant literature on this subject and which is the source of most of the material contained herein.

Deposition Velocity

It has been found that the rate of pollutant removal from the atmosphere by the surface is roughly proportional to the concentration of the pollutant in the atmosphere near the surface, i.e.:

$$F = v\chi \tag{1}$$

(typical units)

where F is the removal rate (flux) $(g\ cm^{-2}\ sec^{-1})$

χ is a characteristic concentration $(g\ cm^{-3})$

and v is a constant of proportionality $(cm\ sec^{-1})$

The proportionality constant, v, has units of velocity and for this reason it is called a deposition velocity since it relates the rate of deposition or removal to the concentration. Rearranging (1) we can define the deposition velocity as:

$$v = \frac{F}{\chi} \tag{2}$$

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TABLE 1

WET AND DRY DEPOSITION

GAS	GLOBAL				LOCAL			
		(1)		(2)				
	** $\bar{V_d}$ cm/sec	$\bar{V_w}$ cm/sec	$\bar{\chi}$ µg/m³	τ yr	V_d cm/sec sea	soil	flora	W_r
MORE REACTIVE COMPOUNDS								
SO$_2$	10^0_0	10^0_0	10^0_0	10^{-2}	*	*	*	10^5 Water Soluble
NO$_2$	10	10	10_0	10^{-2}	*	*	*	10^5
NH$_3$	10^{-1}	10^{-1}	10	10^{-1}	10^{-1}	*	*	10^5
H$_2$S	?	?	10^{-1}	?	?	?	?	10^{-2}
O$_3$	10^0_0	10^{-6}	10^0	10^{-2}	*	*	*	10^0
HF	10	0	10^{-1}	10^{-2}	*	*	*	0
PAN	10	?	?	10^{-2}	?	?		?
C$_2$H$_6$	10^{-1}	?	10^0_0	10^{-1}	?	?	?	?
NO	$<10^{-1}$	10^{-7}	10^0	10^{-1}	$<10^{-1}$	10^{-1}	10^{-1}	10^{-1}
LESS REACTIVE COMPOUNDS								
CO	10^{-2}	10^{-7}	10^2	10^0	10^{-2}	10^{-1}	0	10^{-2}
CH$_4$	10^{-2}	10^{-7}	10^3	10^0_0	10^{-2}	?	?	10^{-2}_0
N$_2$O	10^{-2}	10^{-6}	10^2	10_0	10^-	$<10^{-2}$	$<10^{-2}$	10_0
CCl$_4$	10^{-3}	10^{-6}	?	10_0	10^{-3}	?	?	10
CCl$_3$F	10^{-3}	?	?	10_0	?	?	?	$?_0$
MeI	10^{-3}	10^{-5}	?	10_0	10^{-3}	?	?	10_0
(Me$_2$)S	10^{-3}	10^{-5}	?	10	10^{-3}	?	?	10

(1) Wet deposition velocity computed assuming 100 cm/yr precipitation.

(2) Residence time computed assuming effective mean troposphere depth of 5 km.

* Dry deposition limited by atmospheric turbulent-transport which varies from about 0.1 cm/sec for stable conditions to about 10 cm/sec for highly turbulent conditions. Rough surfaces such as forests are more efficient removers of pollutants than smoother surfaces such as the sea and cropland.

** $\bar{V_d}$ globally averaged dry deposition velocity

$\bar{V_w}$ globally average wet deposition velocity

$\bar{\chi}$ global mean concentration

V_d local dry deposition velocity over sea, soil, and flora

W_r washout ratio

For a given pollutant, surface, and level of atmospheric turbulence, U , is often relatively constant over a wide range of concentrations while the removal rate, F , is not. It is thus useful for estimating the removal rate when the concentration is known. Because the assumption of proportionality between removal rate and concentrations is usually a crude approximation there is sometimes considerable variability in the values of the deposition velocity determined experimentally. Moreover because of the great variability in environmental factors, the deposition velocity should be expected to be somewhat dependent on the particular situation in which it is determined. For these reasons the deposition velocities reported here are presented only to within a factor of ten, although for a particular well-defined situation it is possible to determine a more precise relationship between the removal rate and the concentration. In general, however, one can only expect to estimate removal rates to within about one order of magnitude. With the deposition velocities presented in Table 1, using equation (1), removal rates can be estimated for any given concentration of each of several common pollutant gases under a variety of conditions.

Dry Deposition

Pollutants are removed from the atmosphere by contacting the earth's surface. Their transport to the surface is a result of air turbulence and in the case of particulate pollutants or particles to which gaseous pollutants have been sorbed, gravitational setting. They can also be removed by rainfall; this process is called wet deposition or rainout. In the absence of precipitation, the pollutant is said to be dry deposited on the surface if the pollutant, upon reaching the

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surface, is sorbed by the materials of the surface, i.e., the sea, soil, and vegetation.

For gases, dry deposition takes place upon sorption by the surface (in the case of re-emission of the gas by the surface, dry deposition will be considered as the net deposition, the sorption minus the re-emission). For particles, dry deposition does not take place until the pollutant material in the particle is taken up by the surface. This is often the rate-limiting process for the dry deposition of particles. For although the particles may be carried or fall out of the atmosphere rather rapidly, the actual transfer and sorption of the pollutant from the particle to the surface can be rather slow, slower than the dry deposition rate of many gases. Prior to sorption or incorporation the particle is subject to resuspension by the wind.

Dry deposition can be rate-limited by atmospheric or surface processes. The transport of a pollutant gas to the ground from the atmosphere is determined by the level of turbulence in the atmosphere. On a windy, sunny day the atmosphere is highly turbulent while on calm, clear nights turbulence may be nonexistent. Over a forest or other very rough surface the deposition velocity under highly turbulent conditions can be 10 cm/sec or more while under nonturbulent (or stable) conditions the deposition velocity may be less than 0.1 cm/sec.

Once the pollutant has reached the surface, the rate of uptake is a complex function of the type of pollutant, biological and chemical state of the surface, dryness of the surface, etc. These factors themselves

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are complex functions of climate, season, weather, time of day, soil structure, ecostructure and a host of other variables. For very reactive pollutants such as sulfur dioxide, nitrogen dioxide, ammonia, ozone, and hydrogen fluoride, the surface sorbs the pollutants essentially as rapidly as the atmosphere can deliver them, i. e. the deposition velocities of highly reactive pollutants are rate-limited by atmospheric turbulence. Thus the deposition velocities for these pollutants vary between about 0.1 cm/sec to 10 cm/sec, typically about 1 cm/sec.

For less reactive pollutants, the surface cannot remove the pollutant as fast as it is delivered, and therefore the deposition velocities for these materials are rate-limited by the surface. Deposition velocities determined by surface processes vary widely and cannot be easily generalized. For instance, the noble gases such as argon essentially do not react at all with the surface and thus have deposition velocities which are practically zero while other relatively slowly reacting pollutants such as carbon monoxide have deposition velocities approaching 0.1 cm/sec.

Table 1 gives estimates of dry deposition velocities for various pollutant and trace gases. These estimates are based on reports of actual measurements and modelling estimates found in the literature (see annotated bibliography). Dry deposition velocities over sea, soil, and vegetation as well as a global average deposition velocity for each compound are presented.

Wet Deposition or Rainout

Certain pollutant gases, notably sulfur dioxide, nitrogen dioxide, and ammonia which are readily water soluble, are taken up in the process of raindrop formation and deposited on the surface by the rain (or snow). The wet deposition velocity, V_w, is related to a quantity, W_r, called the washout ratio[66] by

$$V_w = W_r \, P \qquad (3)$$

where P is the precipitation rate.

Table 1 presents values of the washout ratio for various gases. The global average wet deposition velocity for a precipitation rate of 100 cm/year is also given. A comparison of the global average wet and dry deposition velocities for SO_2, NO_2, and NH_3 shows that wet and dry deposition are on the average of about equal importance in removing these gases from the atmosphere. However, locally large quantities of these gases can be removed during a rain storm; wet deposition during rainy weather can be far more important than dry deposition.

Residence time

The typical time that a pollutant remains in the troposphere is determined by the rate of removal or emission, the concentration, and the depth through which it is mixed. An effective tropospheric mixing depth for estimating residence time in the lower atmosphere is about 5 km[65]. The relation between removal rate and concentration is contained

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in the deposition velocity. The residence time, τ, can be estimated by:

$$\tau = \frac{h}{v}$$

(4)

where h is the tropospheric mixing depth. It is seen that the residence time is inversely proportional to the deposition velocity, i.e. pollutants which are removed at a relatively slow rate remain in the atmosphere a long time while those which are removed at a rapid rate have short residence times. Thus, for a reactive gas such as sulfur dioxide, the residence time is only a few days while a less reactive gas such as carbon monoxide can remain in the atmosphere for months.

Table 1 presents estimated global average tropospheric residence times for various pollutants. Pollutants which manage to be carried into the stratosphere can remain much longer because the mixing between stratosphere and the troposphere is quite slow relative to the mixing in the troposphere itself.

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APPENDIX

A Note Concerning the Relative Importance
of Deposition versus Transport
in Affecting Air Pollutant Concentrations
in an Industrial Area

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*On assignment from the National Oceanic
and Atmospheric Administration

This note will help clarify the roles played by deposition (wet and dry), and by transport by the mean wind in the removal of pollutants from the air in an industrial region. It explains why some results reported in recent literature, for example Davies (1976), should not have been unexpected. (Davies attempted to relate the wet deposition of sulfur dioxide in Sheffield, England, to "ground-level atmospheric SO_2 concentrations and to various meteorological parameters" but observed that the washout of pollutants by rainfall had only a minor effect on the concentration when compared with effects caused by variations in wind speed.) A simple, heuristic box model indicating factors affecting spatial-mean pollutant concentrations in industrial air will illustrate this point.

Consider an industrialized region with a spatial-mean source flux of pollutants, $\overline{Q}$ (mass per unit time per unit area), and a uniform wind blowing through it (with a mean speed of u). For simplicity, assume that the region and flow are homogeneous in the crosswind direction so that we can use a two-dimensional model. Figure 1 illustrates the situation and the model.

It can be shown that the relative rate of change with time of the local spatial-mean pollutant concentration is described by the following equation:

$$\frac{1}{\overline{\chi}} \frac{\partial \overline{\chi}}{\partial t} = \frac{\overline{Q}}{\overline{\chi} h} - \frac{2u}{\ell}\left(1 - \frac{\chi_o}{\overline{\chi}}\right) - \frac{\sigma}{h} \tag{1}$$
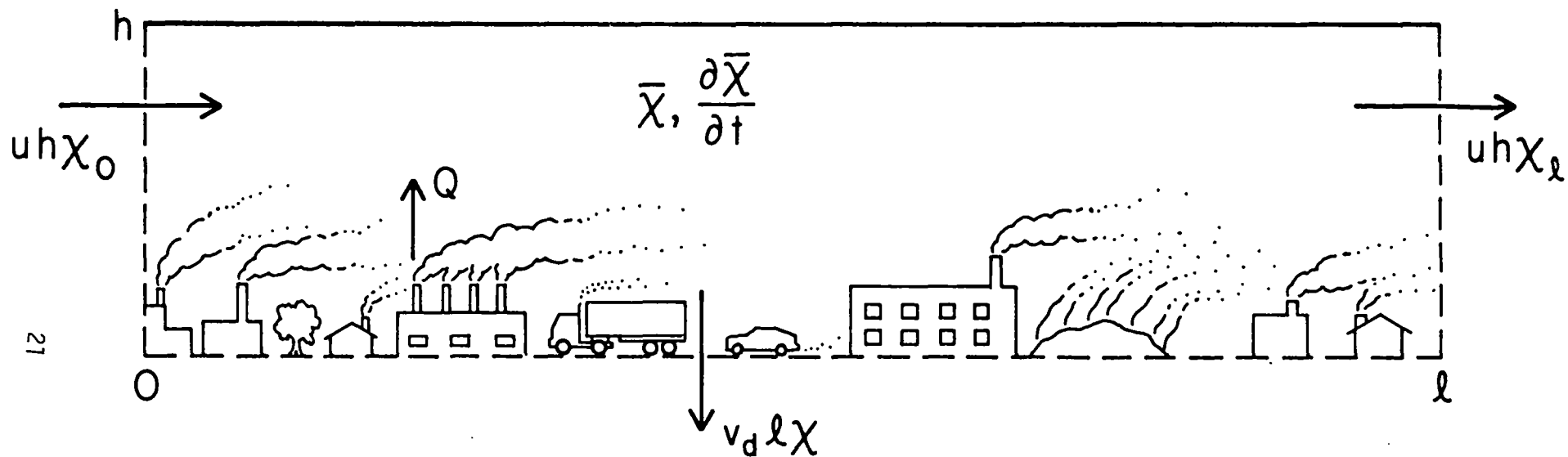
Figure 1: Diagram of an isolated industrial region illustrating the components of a simple box model for air pollutant concentration (see text for definitions). . .

where

$\overline{\chi}$ is the spatial-mean concentration of pollutants in the area,

h the depth through which the pollutants are assumed to be thoroughly mixed,

ℓ is the length of the region,

χ_0 is the pollutant concentration at the upwind edge of the area,

and U is the pollutant deposition velocity (assumed uniform).

The first term on the right side of Equation (1) is the rate of pollutant input into the region from local sources, scaled by the local spatial-mean concentration and mixing depth. Its value is high for heavily industrialized regions and low where there are few sources of pollutants. The second term represents the removal rate of pollutants by wind transport out of the region; the last term represents the removal rate by deposition onto the ground.

Obviously, if the pollutant concentration remains nearly constant, the source term must be of the same order of magnitude as at least one of the removal terms, i.e. the rate of input must nearly equal the rate of removal. We will therefore concern ourselves with the relative magnitudes of the last two terms. The ratio of the deposition term to the transport term is:

$$\frac{v\ell}{2uh\left(1 - \frac{\chi_0}{\overline{\chi}}\right)}$$

(2)

When this ratio is 0 [10] or larger, deposition is the key removal

process and changes in deposition velocity will noticeably affect the

pollutant concentration; if the ratio is 0 [10^1] or less, transport is

the main removal mechanism and changes in wind speed, not deposition

velocity, will create the greater effect on concentration.

First, consider the significance of the factor $\left(1-\frac{\chi_0}{\overline{\chi}}\right)$. If the

industrial region is isolated, i.e. the air entering the region is

relatively fresh so that χ_0 is small when compared to $\overline{\chi}$, then the

value of the factor is nearly unity and the removal of pollutants by

transport could be important. However, if the air entering the region

is itself polluted, i.e. χ_0 is of the same order of magnitude as $\overline{\chi}$,

then the wind brings pollutants into the region as well as removing them

so that its net effect as a removal mechanism is diminished. In this

case deposition becomes the dominant means of removal, the wind moving

the pollutants through the region but not contributing to concentration

reduction. For an isolated industrial region the relevant ratio is

thus:

$$\frac{v\ell}{2u h} \tag{3}$$

For the atmosphere, the mixing height, h, is generally of order 1

kilometer. For very light winds (order 0.5 m/sec or 1 knot), Table 1

gives the value of Ratio (3) for various values of deposition velocity

and size of the industrial area.

Linear Dimension of Industrial Region

λ (km)

		1	10	100
	1	0.01	0.1	1
Deposition Velocity	10	0.1	1	10
U (cm/sec)	100	1	10	100

Table 1. Ratio of deposition removal to transport removal for very light winds.

A deposition velocity of 1 cm/sec is representative of dry deposition of SO_2 (whose dry deposition rate is higher than that of most other pollutants) while a deposition velocity of 100 cm/sec is representative of wet deposition of sulfates for rainfall of somewhat more than 10 mm/hr (see e.g. McMahon, Denison and Fleming, 1976). As Table 1 shows, removal by deposition is more important than removal by transport only for very large industrial regions and rather high dry deposition rates or for moderately large industrial areas in rainy weather, and this only for exceedingly light winds. Table 2 shows the same ratio of deposition removal to transport removal for moderate winds (order 5m/sec or 10 knots).

Linear Dimension of Industrial Region

λ (km)

		1	10	100
	1	0.001	0.01	0.1
Deposition Velocity	10	0.01	0.1	1
U (cm/sec)	100	0.1	1	10

Table 2. Ratio of deposition removal to transport removal for moderate winds.

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As Table 2 shows, only during rainy weather in very large industrialized areas is deposition more important than transport in the removal of pollutants, if the winds are moderate or greater.

These arguments demonstrate that in most industrial regions one should expect that the winds are a more important factor in the removal of air pollutants than is deposition on to the ground. Therefore variation in wind speed will usually have a greater effect on pollutant concentration than variations in deposition velocity. Removal of pollutants by deposition becomes comparable in magnitude to transport only when considering large regions (greater than 100 kilometer in extent). Thus the results reported by Davies (1976) could have been anticipated.

References

1. Davis, T. D. (1976) Precipitation scavenging of sulphur dioxide in an industrial area. _Atmospheric Environment_, 10, 879-890.

2. McMahon, T. A., P. J. Denison, and R. Fleming. (1976) A long-distance air pollution transportation model incorporating washout and dry deposition components. _Atmospheric Environment_, 10, 751-761.