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SCAVENGING OF GASEOUS
TRITIUM COMPOUNDS
BY RAIN

APRIL 1972

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SCAVENGING OF GASEOUS TRITIUM COMPOUNDS BY RAIN

by

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April, 1972

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TABLE OF NOMENCLATURE

<u>Symbol</u>	<u>Definition</u>
a	drop radius, ℓ
b	height of plume base, ℓ
c	mixed-average concentration in drop, moles/ ℓ^3
D	diffusion coefficient, ℓ^2/t
d	height of plume top, ℓ
E	capture efficiency
F	fractional depletion of plume
H, H'	Henry's-law constant, atm, ℓ^3/mole
h	emission height, ℓ
J	rain rate, ℓ/t
K	overall mass-transfer coefficient, moles/ $\ell^2 t$
k	individual mass-transfer coefficient, moles/ $\ell^2 t$
M	washout rate, moles/ ℓt ; also raindrop mass, m; also molecular weight
m	liquid water content of fog, m/ ℓ^3
N	molar flux through drop surface, moles/ $\ell^2 t$
r	radial position coordinate, ℓ
Re	Reynolds number
Sc	Schmidt number
Sh	Sherwood number
Sn	Heaviside step function constant
t	time, t; also temperature, $^{\circ}\text{C}$
$\bar{u}$	mean wind speed, ℓ/t

<u>Symbol</u>	<u>Definition</u>
v_t	terminal velocity, ℓ/t
W	molar pollutant accumulation rate, moles/t
x	downwind position coordinate, ℓ ; also liquid-phase mole fraction
y	crosswind position coordinate, ℓ ; also gas-phase mole fraction
z	vertical position coordinate, ℓ
ζ	variable defined by Equation (16) $1/\ell$
ξ	variable defined by Equation (17) moles/ ℓ^4
ν	kinematic viscosity, ℓ^2/t
<u>Subscripts</u>	
A	component A
b	bulk
e	equilibrium
o	interfacial or ground-level
x	liquid phase
y	gas phase

SCAVENGING OF GASEOUS TRITIUM COMPOUNDS BY RAIN*

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ABSTRACT

Washout of gaseous tritium compounds from the atmosphere has been investigated theoretically. This analysis is based upon reversible gas-washout theory, and accounts for such factors as desorption and the influence of liquid-phase transport.

General equations are presented which describe pollutant concentrations in single drops as they fall through the atmosphere. Results from these equations may be combined to provide total washout characteristics for natural rain by simple distribution over the drop-size spectra. These general equations are based upon the assumptions of vertical rainfall, spherical noninteracting drops, and linearity of the mass-transport processes, as well as several other less serious stipulations. They should be applicable for washout of all gases depending upon their deviations from this idealized behavior. The compounds of primary interest to this investigation (HT , T_2 , HTO , and T_2O) should satisfy most of these requirements well; satisfaction of others, of course, will depend to a large extent on meteorological conditions.

Sample calculations are presented for a specific rain situation in conjunction with bivariate, normally-distributed plumes containing HT and HTO . Major conclusions from these calculations are given as follows:

- 1) HTO is washed out much more rapidly than HT , this arising from the low solubility of the latter;*

*Work performed under U.S. Atomic Energy Commission Contract No. AT(45-1)-1830.

- 2) *Stack height plays a rather prominent role in affecting washout, especially at distances close to the source; and*
- 3) *Fog formation may be important in affecting HTO washout, but it should be an insignificant influence so far as HT is concerned.*

No data exist for HT or HTO washout which can be used to test these results. Data from experiments with other gases, however, tend to verify this approach, which is recommended as a method for use in estimating washout and dose rates for nuclear plant siting analyses and related considerations.

SCAVENGING OF GASEOUS TRITIUM COMPOUNDS BY RAIN

INTRODUCTION

Dose calculations for the siting of nuclear reactors and reprocessing plants must take cognizance of the amounts of tritium that are carried to the ground via precipitation scavenging. Although significant work has been conducted with regard to the problem of large scale scavenging of tritium and tritium compounds, there exists at present no really adequate analysis of tritium washout from plumes. Such an analysis is needed to provide a generalized method for the engineering calculation of tritium washout rates. The present report is addressed to this task.

The approach taken here is based primarily upon earlier generalized analyses of gas and particulate washout.^(1,2) The methods and equations of this development, therefore, are not restricted solely to the compounds discussed explicitly here; they should be applicable as well to situations involving the scavenging of any gas, vapor or particulate satisfying the ideal behavior exemplified by the substances of present concern.

The following sections of this report describe some of the more important physical properties of tritium gas and tritiated water, and describe the scope of the overall problem to be considered. These sections are followed by a brief description of the microscopic interactions between precipitation elements and their environment which are expected to be fundamental to the overall scavenging process. Subsequent sections deal with applying these concepts macroscopically to the practical problems of estimating scavenging dose rates, and the development of a generalized method to accomplish this objective.

SCOPE OF PROBLEM

The problem of interest is shown pictorially in Figure 1, which indicates the processes for removing material from an elevated plume and bringing it to the ground via precipitation scavenging. During their passage to the

Figure 1. Schematic of Precipitation-Plume Interaction

ground the raindrops may pick up pollutant gas or vapor by absorption or condensation; or, if fog is present, some pickup may occur through capture of pollutant-laden droplets. Under appropriate conditions the falling drops may also lose pollutant gas by desorption or evaporation.

The compounds considered directly in this report are the isotopic hydrogen gases, HT and T₂, and the isotopic waters, HTO and T₂O. No distinction between a gas and a condensible vapor shall be necessary in this treatment, hence the isotopic waters will be considered the same as water-soluble gases for the purposes at hand. For purposes of visualization it is convenient also to consider HTO and T₂O as chemical species separate from the H₂O that constitutes the majority of the mass of each raindrop.

Since the transport and thermodynamic properties of HT, T₂, HTO and T₂O differ, they must be treated individually. Total scavenging dose rates, of course, can be computed by summing the contributions of the individual compounds.

PHYSICAL PROPERTIES OF TRITIUM COMPOUNDS

Scavenging rates depend upon both thermodynamic (equilibrium) and transport properties. Some physical properties that will be useful in later calculations are given in Tables I and II.

Vapor-pressure relationships for water-tritiated water solutions follow Raoult's law closely.⁽³⁾ Expressed mathematically Raoult's law is given by:

$$P_A = P_A^\circ x_A, \quad (1)$$

where P_A designates the vapor pressure of pollutant A in equilibrium with the solution of mole fraction x_A , and P_A° is the vapor pressure of pure A. Gas-phase mole fractions may be calculated from P_A using Dalton's law of partial pressures.

Equilibrium relationships for dilute tritium gas solutions in water are expected to follow Henry's law closely.⁽⁴⁾ Mathematically Henry's law is given by:

$$P_A = H x_A \quad (2)$$

where H is the Henry's law constant. Equation [2] is similar to [1], and may be viewed as a generalization of it. Because of the idealities exhibited by these equations, vapor-liquid equilibria may be represented simply in terms of P_A° and H as shown in Table I. This ideal behavior reduces the complexity of scavenging calculations considerably, as will become evident in the following development.

The isotopic effects on the various properties, as indicated in Tables I and II, seldom amount to more than about twenty percent of the values themselves. Since the errors in the washout calculations of this paper are expected to be greater than this, the neglect of such effects would have little consequence on the accuracy of the ultimate results. It is permissible, therefore, to utilize properties of the common compounds if corresponding isotopic properties are unavailable, as in the case of the Henry's-law constant for the isotopic hydrogen gases.

WASHOUT OF GASES AND VAPORS

As discussed in the previous literature⁽²⁾ it is usually convenient to visualize the washout of gases and vapors to occur as a two step process wherein the pollutant molecules first migrate from the bulk gas to the surface of the falling drop, and subsequently mix into the drop interior. Because reversible behavior is not precluded, this process may occur in the opposite direction; that is, under appropriate conditions desorption will take place. The rate and direction of this process depends upon the concentration "driving forces" of the system. This dependency can be expressed by writing equations describing the flux N_{Ao} of material through the interface of a falling drop in terms of concentration changes and mass-transfer coefficients (cf., Bird, et al. [11]). Thus

TABLE I

PARTIAL PRESSURES AND HENRY'S-LAW CONSTANTS FOR TRITIATED
COMPOUNDS IN WATER SOLUTION

t, °C	Partial Pressure, Atm.			Henry's-Law Constant, Atm.
	H ₂ O	HTO	T ₂ O	H ₂ , HT, T ₂
0	.0060	.0053	.0046	62900
5	.0086	.0076	.0068	66200
10	.0121	.0108	.0097	69000
15	.0168	.0151	.0135	71400
20	.0231	.0210	.0190	74100
25	.0313	.0286	.0261	75200
30	.0419	.0385	.0354	76600

TABLE II

DIFFUSION COEFFICIENTS OF TRITIATED COMPOUNDS IN AIR AND IN WATER

t, °C	Diffusion Coefficients, cm ² /sec					
	In Air				In Water	
	HTO	T ₂ O	HT	T ₂	HTO, T ₂ O	HT, T ₂
0	.215	.209	.487	.410	1.21	2.4
5	.222	.216	.502	.423	1.39	2.7
10	.229	.216	.517	.435	1.58	3.2
15	.236	.229	.534	.449	1.82	3.7
20	.243	.236	.549	.462	2.08	4.1
25	.250	.243	.565	.476	2.38	4.8
30	.257	.250	.582	.890	2.73	5.4

NOTES:

1. Isotopic water vapor pressures from data of Jones⁽⁵⁾ and Van Hook⁽⁶⁾.
2. Partial pressures of hydrogen gas from Stephan⁽⁷⁾. Assumption of same partial pressures for HT and T₂ will result in conservatively low estimates.
3. Diffusion coefficients in air calculated from collision integral data using the Wilke-Chaing relationship⁽⁸⁾.
4. Diffusion coefficients in water from data of Ottar⁽⁹⁾ and Vivian and King⁽¹⁰⁾. Assumption of zero isotopic effect has been made.

$$N_{Ao} = -k_y (y_{Ab} - y_{Ao}) \quad (3)$$

and

$$N_{Ao} = -k_x (x_{Ao} - x_{Ab}) \quad (4)$$

correspond to the gas-phase and liquid-phase steps of the process, respectively. k_y and k_x are known as the gas and liquid phase mass-transfer coefficients, and y_{Ab} , y_{Ao} , x_{Ao} , and x_{Ab} respectively refer to the mole fractions in the bulk gas, the interfacial gas, the interfacial liquid and the bulk of the drop. Sign convention is such that fluxes away from the drop are positive.

Equations (3) and (4) reflect the two-step visualization of the gas-scavenging process. It is usually more practical to combine these steps into a single equation of the form

$$N_{Ao} = -K_y (y_{Ab} - y_{Ae}) \quad (5)$$

where y_{Ae} is the mole fraction of A in the vapor phase that would exist in equilibrium with dissolved A of mole fraction x_{Ab} . K_y is obtained from k_x , k_y , and equilibrium characteristics; it is known as the "overall mass-transfer coefficient based on the gas driving force."

For systems that obey Henry's law the overall mass-transfer coefficient can be related to the individual coefficients as follows:*

$$\frac{1}{K_y} = \frac{H}{k_x} + \frac{1}{k_y} \quad , \quad (6)$$

(cf., [11]). Furthermore, Equation (5) can be applied to any spherical droplet of radius a to obtain the following differential equation describing the change of pollutant concentration in the drop as it falls;

$$\frac{dc}{dz} = \frac{3 K_y}{v_t a} (y_{Ab} - H' c) \quad . \quad (7)$$

Here $H' = H M_w / \rho_w$ where M_w and ρ_w pertain to the molecular weight and density of water: v_t is the terminal velocity of the droplet, dz/dt , and y_{Ab} is the (variable) gas-phase concentration of A that it experiences at any point z , and c is the mixed average concentration in the drop.

The overall mass-transfer coefficient, K_y , must be known before (7) can be evaluated. Values of K_y have been the subject of much conjecture, and depend in a complex way upon fluid-mixing properties of the falling drop.⁽²⁾ It is sufficient for the present development, however, to examine two limiting cases which should bracket the behavior to be expected in nature. These limiting cases are stated as follows:

1. Rapid mixing inside drop (gas-phase limiting situation).
2. Mixing in drop by molecular diffusion only (stagnant drop conditions).

For the first case $k_x = \infty$ and $K_y = k_y$ (cf., Eq. [6]). k_y may be estimated by the Froessling equation,⁽²⁾

*One should note that for normally encountered conditions where the total pressure is in the neighborhood of one atmosphere, the gas-phase mole fraction of pollutant is very nearly equal to its partial pressure in atmospheres.

$$\text{Sh} = 2 + 0.6 \text{Re}^{1/2} \text{Sc}^{1/3} \quad , \quad (8)$$

where

$$\text{Sh} = \frac{2 k_y a}{D_{Ay} c_y} = \text{Sherwood number}$$

$$\text{Re} = \frac{2 a v_t}{\nu} = \text{Reynolds number}$$

$$\text{Sc} = \frac{\nu}{D_{Ay}} = \text{Schmidt number.}$$

Here c_y denotes total gas concentration, D_{Ay} is the diffusion coefficient in the gas, v_t is the terminal velocity of the drop (<0) and ν is the kinematic viscosity of air. An important aspect of Equation (8) is its indication that k_y should be independent of time and concentration.

K_y for the second limiting case may be calculated by solving the equation of continuity for pollutant as it migrates through the drop's interior. For this case the appropriate form is given by

$$\frac{\partial c}{\partial t} = D_{Ax} \left(\frac{\partial^2 c}{\partial r^2} + \frac{2}{r} \frac{\partial c}{\partial r} \right) \quad (9)$$

with the initial and boundary conditions

$$c = 0 \quad \text{at} \quad t = 0 \quad \text{for all} \quad r \quad (\text{for an initially clean drop}) \quad (9a)$$

and

$$\frac{\partial c}{\partial r} = \frac{k_y}{D_{Ax}} (y_{Ab} - H' c) \quad \text{at} \quad r = a \quad . \quad (9b)$$

Here D_{Ax} denotes diffusivity of pollutant in the drop, and a and r denote drop radius and the radial position coordinate, respectively.

A general solution to Equations (9) shows that unlike the gas-phase coefficient, k_x depends upon the concentration history of the drop except under specialized circumstances. One such set of circumstances is that corresponding to a drop experiencing a gas concentration that increases linearly over long periods of time. Under these conditions the overall mass transfer coefficient for a stagnant drop is given by⁽²⁾

$$K_y = \frac{5 k_y}{\frac{a H' k_y}{D_{Ax}} + 5} \quad . \quad (10)$$

Attempts to apply (10) to describe washout in situations wherein the drops do not experience linear changes in concentration constitute "linearization" approximations to true behavior. They should give conservatively low estimates of K_y which should be reasonably valid for situations wherein the gas-phase concentrations change in a reasonably well-behaved manner.

Overall mass-transfer coefficients for the gas-phase controlled and stagnant drop situations are shown for HTO and HT at 20°C in Table III. It is noted from this table that the difference between values for the limiting situations is far more significant for HT than for HTO. This behavior is in accordance with the well-known observation that highly soluble substances tend to exhibit gas-phase controlled behavior, while liquid-phase controlled behavior usually predominates for slightly soluble materials. These values will be utilized in conjunction with Equation (7) to evaluate macroscopic washout behavior upon first considering the consequences of scavenging via the additional mechanism of fog-droplet capture by the falling raindrops.

PARTICULATE SCAVENGING AND RAINOUT

Situations involving raindrop passage through natural clouds or condensing plumes require additionally the consideration of particulate scavenging. Washout of droplets in clouds has been described traditionally in terms of a washout efficiency, E .⁽¹⁾ Accordingly one may write

$$\frac{d\dot{M}}{dz} = \int_0^{\infty} -\pi a^2 E(a,m) f(m) dm \quad (11)$$

Choosing an appropriate intermediate value of E to represent collection of the distributed system of fog droplets, the molar rate of pollutant accumulation may be given approximately by the form

$$\frac{dW_A}{dz} = -\frac{\pi a^2}{M_w} E(a) x_{Ac} m \quad , \quad (12)$$

TABLE III

LIMITING OVERALL MASS-TRANSFER COEFFICIENTS FOR SPHERICAL RAINDROPS, $t = 20^{\circ}\text{C}$

Drop Diameter cm	Overall Mass-Transfer Coefficients, moles/cm ² sec			
	Gas-Phase Limited		Stagnant Drop	
	HT	HTO	HT	HTO
.075	.00203	.00110	4.14×10^{-9}	9.54×10^{-4}
.095	.00193	.00106	3.27×10^{-9}	8.93×10^{-4}
.103	.00190	.00104	3.02×10^{-9}	8.73×10^{-4}
.110	.00188	.00103	2.82×10^{-9}	8.56×10^{-4}
.115	.00186	.00102	2.70×10^{-9}	8.44×10^{-4}
.120	.00184	.00102	2.59×10^{-9}	8.33×10^{-4}
.126	.00182	.00101	2.47×10^{-9}	8.19×10^{-4}
.135	.00179	.00099	2.30×10^{-9}	8.00×10^{-4}
.150	.00174	.00097	2.07×10^{-9}	7.67×10^{-4}

where x_{Ac} is the mole fraction of pollutant A in the suspended cloud droplets, M_w is the molecular weight of water, and W_A denotes the total number of moles of A in the raindrop. If it is assumed that the mass of water collected is much less than M , then the equation can be expressed in terms of concentration as

$$\frac{dc}{dz} = - \frac{3 E (a)}{4 a M_w} m x_{Ac} , \quad (13)$$

which can be viewed as a counterpart to Equation (7).

E depends in a complex fashion on the distribution of cloud-droplet sizes, the raindrop size, and other physical characteristics. Extensive discussions of these relationships have been published elsewhere.⁽¹²⁾ From these it appears that in the ranges of raindrop and cloud droplet sizes of importance E should vary from about 0.6 to about 1.0. Table IV shows some estimated efficiencies as a function of drop and droplet size for comparison. From this one should note that the value of E employed in the present paper is intended to be a mean entity taken from a distribution over the range of cloud-droplet sizes. It should be noted as well that droplet sizes in natural fogs normally are expected to fall in the approximate range of 2 - 50 microns with mean diameters ranging from about 10 microns to 30 microns.⁽¹⁾

Because of their small sizes and slow terminal velocities, it is valid under most circumstances to consider the pollutant in the fine, suspended cloud droplets to be at equilibrium with the pollutant in the gas phase: hence x_{Ac} in Equation (13) can be replaced by the Raoult's-law, or Henry's law expressions ([1] or [2]), depending upon whether the pollutant of concern is a gas or a condensible vapor. Accordingly, rainout from a condensing plume may be considered as droplets which fall from the plume, beginning

TABLE IV

COLLISION (TARGET) EFFICIENCIES FOR RAIN DROPS COLLIDING
WITH DROPLETS AT 0°C AND 900 mb*

Drop Diameter mm	Droplet Diameter, microns							
	2	3	4	6	8	10	15	20
0.03	0.03	0.05						
0.05	0.01	0.02	0.05	0.23				
0.08	0.004	0.01	0.04	0.29	0.55			
0.14	0.02	0.03	0.11	0.40	0.65	0.83	1.12	
0.2	0.03	0.07	0.18	0.47	0.67	0.83	1.08	1.26
0.3	0.07	0.14	0.28	0.55	0.72	0.84	1.04	1.16
0.4	0.10	0.21	0.35	0.61	0.76	0.86	1.01	1.11
0.6	0.15	0.31	0.45	0.68	0.80	0.89	1.00	1.06
0.8	0.17	0.37	0.51	0.72	0.84	0.91	1.00	1.06
1.2	0.17	0.40	0.54	0.74	0.85	0.91	0.99	1.02
2.0	0.15	0.37	0.52	0.74	0.83	0.90	0.97	1.00
2.8	0.11	0.34	0.49	0.71	0.83	0.89	0.96	0.96
3.6	0.08	0.29	0.45	0.68	0.80	0.86	0.98	0.95
4.8	0.04	0.22	0.39	0.62	0.75	0.83	0.93	0.97
6.0	0.02	0.16	0.33	0.55	0.71	0.81	0.91	0.95

*Table prepared from report of Engelmann⁽¹⁾.

their journey to the ground at a concentration which is saturated with respect to ambient plume conditions.

COMBINED GAS AND PARTICULATE SCAVENGING

In condensing plumes, where both gas and particulate scavenging occur, total removal will be some function of these two individual mechanisms. As a first approximation it seems appropriate to assume that they are additive, thus

$$\frac{dc}{dz} \cong - \frac{3 E (a) m y_{Ab}}{4 a H' \rho_w} + \frac{3K_y}{v_t a} (y_{Ab} - H'c) \quad (14)$$

Here the entity x_{Ac} has been replaced with $y_{Ab} M_w/H' \rho_w$ in accordance with the equilibrium assumption discussed earlier.

CALCULATION OF SCAVENGING RATES

Equations (7), (13) and (14) pertain to microscopic analyses of individual drops. Washout rates can be calculated from these equations by defining plume geometries, integrating over the vertical fall, and distributing over the size spectrum of the rain. A variety of simplifying assumptions can be employed to aid in accomplishing this end; for present purposes the following assumptions will be used:

1. the rain falls through essentially vertical trajectories;
2. growth of the precipitation elements during their fall is negligible, furthermore no interactions of elements occur that will perturb the mass transfer process;
3. particulate scavenging and gas washout, as implied by (14), are additive;
4. geometry of the plume, under precipitation conditions, is known,

5. fog, if present, exists at the same density and size distribution at all elevations.

The assumption of linearity will also be employed; that is, K_y and H (or H') will be assumed independent of concentration or concentration history of the falling drops. From the preceeding discussion it is seen that this requirement is satisfied well for all cases except, possibly, for that of the stagnant drop situation described by Equations (9). The linearized expression (10) will be utilized for estimates of actual behavior in the present analysis.

As discussed in previous work⁽²⁾ the calculation of precipitation scavenging entails the solution of two coupled conservation equations; one of these is for pollutant conservation in the gas phase and the other pertains to conservation of pollutant in the rain. Assumption (4) implies that the solution to the gas-phase equation is already known, hence the liquid-phase equation may be solved without considering the complications of feedback. This results in an enormous simplification to the solutions; errors from this assumption, of course, will depend upon the plume description utilized and upon physical circumstances.

Assumption (5) seems quite reasonable for conditions wherein the plume is emitted into a foggy atmosphere. It is expected to be a reasonable first approximation to the behavior of a condensing plume in a clear atmosphere as well. This is based upon the fact that the entity of prime interest here is the product $m y_{Ab}$. Toward the edges of the condensing plume y_{Ab} will probably be reduced well below its centerline value, and moderate variations in m will have little effect on the net result.

Integration of (14) subject to these assumptions gives the following expression for the concentration of pollutant in an initially clean drop at any point in an arbitrary plume:

$$c = \xi e^{-\zeta z} \int_{\infty}^z e^{\zeta z'} y_{Ab} dz' \quad (15)$$

where

$$\zeta = \frac{3 K_y H'}{v_t a} \quad (16)$$

and

$$\xi = -\frac{3 E m}{4 a H' \rho_w} + \frac{3 K_y}{v_t a} \quad (17)$$

By letting z equal zero in Equation (15) one obtains the expression for concentration of pollutant in the rain at ground level;

$$c_{Ao} = \xi \int_{\infty}^0 e^{\zeta z'} y_{Ab} dz' \quad (18)$$

As indicated above, the definition of the plume in Equation (15) is arbitrary. It seems a reasonable first approximation, however, to assume the plume to follow bivariate-normal behavior. For reflection of pollutant at the ground the corresponding plume description is given by⁽¹³⁾

$$y_{Ab}(x,y,z) = \frac{Q}{2\pi \sigma_y \sigma_z \bar{u}} \exp \left[-1/2 \left(\frac{y}{\sigma_y} \right)^2 \right] \quad (19)$$

$$\left\{ \exp \left[-1/2 \left(\frac{z-h}{\sigma_z} \right)^2 \right] + \exp \left[-1/2 \left(\frac{z+h}{\sigma_z} \right)^2 \right] \right\}$$

Here Q is the source strength expressed as volume of pollutant release per unit time measured at ambient conditions. σ_y and σ_z are plume-spread parameters and h is the effective height of release. x , y and z denote distances from the stack base and plume centerline.

It should be noted here that Equation (19) is intended to describe a time-averaged concentration whereas the y_{Ab} employed earlier was depicted as the instantaneous value experienced by a falling drop along its own particular trajectory to the ground. Since all plumes fluctuate with time in a complex manner, there is no guarantee that the instantaneous gas concentration experienced by a given drop should resemble the time-averaged value at all. It has been shown elsewhere, however, that the use of time-averaged concentrations in (18) will result in the calculation of the mean concentration of the ensemble of drops that have fallen to the ground, provided that the scavenging process is linear. Fortunately, because of the strict obedience of Raoult's and/or Henry's laws, (and also because of the assumption of invariant K_y), the systems of interest here satisfy this condition of linearity, simplifying enormously the assessment of scavenging behavior.

Substitution of (19) into (18) and integration gives

$$c_{Ao}(a) = - \frac{Q F \xi}{2 \sqrt{2\pi} \sigma_y \bar{u}} \exp \left(- \frac{y^2}{2\sigma_y^2} + \frac{\sigma_z^2 \zeta^2}{2} \right) \left\{ \exp(\zeta h) \left[1 - \operatorname{erf} \left(\frac{-\sigma_z^2 \zeta - h}{\sigma_z \sqrt{2}} \right) \right] + \exp(-\zeta h) \left[1 - \operatorname{erf} \left(\frac{-\sigma_z^2 \zeta + h}{\sigma_z \sqrt{2}} \right) \right] \right\}, \quad (20)$$

which provides a means for calculating the ground level pollutant concentration in any a-radius drop. Here the dimensionless variable F represents the fractional depletion of the plume at the downwind distance of interest. For the physical situations described in this report F is close to unity. F will be defined in terms of overall washout in the following development. It is emphasized here that Equation (20) pertains to a drop of given size. If average rain concentration is required, Equation (20) must be solved for a number of drop sizes and the results must be averaged according to the rain spectrum.

Computations for large distances from the source may be accomplished somewhat more conveniently using the following asymptotic approximation to (20);

$$c_{Ao}(a) = \frac{-Q \sigma_z F \xi}{2\pi \sigma_y \bar{u}} \exp \left(-\frac{y^2}{2\sigma_y^2} - \frac{h^2}{2\sigma_z^2} \right)$$

$$\left\{ \frac{1}{-\sigma_z^2 \zeta - h} \left[1 - \left(\frac{\sigma_z}{-\sigma_z^2 \zeta - h} \right)^2 \right] \right\} +$$

$$\frac{1}{-\sigma_z^2 \zeta + h} \left[1 - \left(\frac{\sigma_z}{-\sigma_z^2 \zeta + h} \right)^2 \right] \left\{ + O \left(\frac{\sqrt{2} \sigma_z}{\sigma_z^2 \zeta - h} \right)^4 \right\} . \quad (21)$$

The final term in (21) is a truncation-error estimate, O denoting "order of". Downwind washout rate, defined as the amount of material washout per unit time per unit downwind distance can be calculated with the use of (20) or (21) by integrating over the crosswind distance and then distributing according to the rain spectrum. Thus the downwind washout rate is given by

$$M = \frac{\int_0^\infty a^3 c_{cross}(a) v_t(a) f(a) da}{\int_0^\infty a^3 v_t(a) f(a) da} , \quad (22)$$

where J denotes rainfall rate and c_{cross} , defined by

$$c_{\text{cross}} = \int_{-\infty}^{\infty} c_{\text{Ao}}(a) dy \quad , \quad (23)$$

is obtained by formal integration of (20) or (21); thus

$$c_{\text{cross}} = \frac{-Q F_{\xi}}{2 \bar{u}} \exp \left(\frac{\sigma_z^2 \zeta^2}{2} \right) \left\{ \exp(\zeta h) \left[1 - \operatorname{erf} \left(\frac{-\sigma_z^2 \zeta - h}{\sigma_z \sqrt{2}} \right) \right] + \exp(-\zeta h) \left[1 - \operatorname{erf} \left(\frac{-\sigma_z^2 \zeta + h}{\sigma_z \sqrt{2}} \right) \right] \right\} \quad (24)$$

is the expression for c_{cross} corresponding to (21) and

$$c_{\text{cross}} = \frac{-\sigma_z Q F \xi}{\sqrt{2\pi} \bar{u}} \exp\left(\frac{-h^2}{2\sigma_z^2}\right)$$

$$\left\{ \frac{1}{-\sigma_z^2 \zeta - h} \left[1 - \left(\frac{\sigma_z}{-\sigma_z^2 \zeta - h} \right)^2 \right] + \frac{1}{-\sigma_z^2 \zeta + h} \left[1 - \left(\frac{\sigma_z}{-\sigma_z^2 \zeta + h} \right)^2 \right] \right\} . \quad (25)$$

is that corresponding to (22).

In the event that there is appreciable depletion of the plume by washout F may be calculated from the expression

$$F = 1 - \frac{1}{Q c_y} \int_0^x M dx , \quad (26)$$

c_y denoting the total molar gas concentration at ambient conditions of temperature and pressure. Depending upon how the raindrop statistics are treated the previous equations may reduce to explicit forms upon incorporating (26), or they may be implicit in nature, necessitating iterative or numerical approximations to their solutions.

Although the bulk of effort in this report is devoted to normally distributed plumes, the general applicability of Equations (15) and (18) should be emphasized. For example a "top hat" distribution, characterized by

$$\begin{aligned} y_{Ab} &= 0 \text{ for } z > d, \\ y_{Ab} &= S_n \text{ for } d < z < b, \text{ (} S_n \text{ a constant)} \\ y_{Ab} &= 0 \text{ for } z < d \end{aligned} \quad (27)$$

can be substituted into Equation (18) to provide the following expression for ground-level drop concentration;

$$c_{Ao} = S_n \frac{\xi}{\zeta} F(e^{\zeta b} - e^{\zeta d}) \quad (28)$$

Similarly, general descriptions of plumes from line sources, area sources, puff releases, et cetera can be employed to provide corresponding results.

EXAMPLE CALCULATIONS

The equations described in the preceeding sections were solved for conditions corresponding to HT and HTO releases in nonfogging plumes for a variety of conditions. Physical-properties data were obtained from Tables I and II. Atmospheric mixing was assumed to follow Pasquill "type C" behavior.⁽¹³⁾ Conditions for the test calculations are summarized in Table IV; the lumped rain spectrum chosen for these calculations is given in Table V.

TABLE V

CONDITIONS CHOSEN FOR SAMPLE CALCULATIONS

Downwind Distances: 100, 200, 400, 800, and 1600 m
Source Heights: 30 and 100 m
Wind Speed: 5 m/sec
Source Strength: 1 mole/sec
Pressure: 1 atm
Temperature: 20°C
Rain Rate: .0001 cm/sec

TABLE VI*

LUMPED RAIN SPECTRUM USED IN WASHOUT CALCULATIONS

<u>Drop Diameter, cm</u>	<u>Fraction of Drops In Size Interval</u>
0.075	0.10
0.095	0.10
0.103	0.10
0.107	0.10
0.110	0.10
0.115	0.10
0.120	0.10
0.126	0.10
0.135	0.10
0.150	0.10

*Based on data presented by Engelmann⁽¹⁾.

Washout rates predicted by Equations (22) and (24) for the stipulated conditions are given in Table VI. Under some circumstances these rates vary considerably with emission height and with distance from the source; other circumstances however, for example stagnant-drop calculations for HTO, show considerably less variation. Comparison of the results in Table VI indicates that HT should be washed out much more slowly than HTO. This, of course, should be expected, owing to the lower solubility of the former in water.

Figures 2-7 are plots of washout concentration as a function of crosswind distance. These were calculated by employing Equation (20) for each drop size listed in Table V, and then distributing accordingly. These figures again show the tendency for lower washout from higher plumes exhibited by the results in Table VI. They also indicate the extent of uncertainty between the limiting solutions.

The concentrations of pollutant in rain that correspond to diffusional equilibrium with ground-level gas-phase concentrations are also given in Figures 2-7. Shown as circular dots, these values indicate that an equilibrium washout situation - that is, one where the washout concentrations approach ground-level equilibrium values - is approached as downwind distances become large. This should be expected, since at such distances the plumes become sufficiently dispersed in the vertical to allow ample time for the drops to approach equilibrium during their fall. A simple, conservative criterion for equilibrium washout conditions has been derived earlier.⁽²⁾ For normally-distributed plumes this is

$$\frac{-3 K_y H' \sigma_z e^{1/2}}{v_t a \exp(h^2/2\sigma_z^2)} \gg 1 \quad (29)$$

TABLE VII

SUMMARY OF CALCULATED WASHOUT RATES

HTO Washout Rates				
Washout Rate, Fraction of Plume Removed Per Meter of Downwind Distance				
Distance From Source, m	h = 30 m		h = 100 m	
	GPC*	SD*	GPC*	SD*
100	4.68×10^{-3}	1.10×10^{-3}	3.39×10^{-3}	1.02×10^{-3}
200	4.63×10^{-3}	1.10×10^{-3}	3.37×10^{-3}	1.02×10^{-3}
410	4.51×10^{-3}	1.09×10^{-3}	3.36×10^{-3}	1.02×10^{-3}
800	4.19×10^{-3}	1.07×10^{-3}	3.36×10^{-3}	1.01×10^{-3}
1600	3.56×10^{-3}	1.02×10^{-3}	3.22×10^{-3}	1.00×10^{-3}

HT Washout Rates				
Washout Rate, Fraction of Plume Removed Per Meter of Downwind Distance				
Distance From Source, m	h = 30 m		h = 100 m	
	GPC*	SD*	GPC*	SD*
100	1.06×10^{-11}	7.52×10^{-10}	0.00	6.20×10^{-10}
200	2.62×10^{-9}	7.52×10^{-10}	4.33×10^{-18}	6.21×10^{-10}
400	5.88×10^{-9}	7.44×10^{-10}	3.75×10^{-11}	6.23×10^{-10}
800	4.68×10^{-9}	7.18×10^{-10}	9.15×10^{-10}	6.25×10^{-10}
1600	2.80×10^{-9}	6.61×10^{-10}	1.76×10^{-9}	6.10×10^{-10}

* GPC and SD refer, respectively, to gas phase controlled and stagnant drop mass-transfer conditions.

Figure 2. Calculated Concentrations of HTO in Rain, 100 m Downwind From Source

Figure 3. Calculated Concentrations of HT in Rain, 100 m Downwind From Source

Figure 4. Calculated Concentrations of HTO in Rain, 400 m Downwind From Source

Figure 5. Calculated Concentrations of HT in Rain, 400 m Downwind From Source

Figure 6. Calculated Concentrations of HTO in Rain, 1600 m Downwind From Source

Figure 7. Calculated Concentrations of HT in Rain, 1600 m Downwind From Source

The results described up to the present pertain to nonfogging conditions. Because of the linear character of Equation (15) (or Equation [20]), however, washout concentrations for fogging conditions can be calculated simply by multiplying the results of Equation (20) by the factor

$$\frac{-\frac{3 E m}{4 a H' \rho_w} + \frac{3 K_y}{v_t a}}{\frac{3 K_y}{v_t a}} ;$$

(cf., Equation [17]).

Since the first term of Equation (17) pertains to the fog-capture mechanism and the second to simple gas washout, one can reasonably expect conditions for negligible washout by fog capture to exist whenever

$$-\frac{3 K_y}{v_t a} \gg \frac{3 E m}{4 a H' \rho_w} ,$$

or, in more compact form,

$$\frac{4 K_y H' \rho_w}{E m v_t} \gg 1 . \quad (30)$$

This criterion for neglect of the fog-capture mechanism has been given earlier.⁽²⁾ The dimensionless group in inequality (30) can be viewed as a ratio of washout rates from simple gas absorption and from the fog-scavenging mechanism.

For an example, consider a .15 cm diameter drop falling through a 3 gm/m³ fog at 20°C. From the results tabulated earlier the ratio in inequality (30) (assuming stagnant-drop behavior and $E=1$) is found to be 0.71 for HTO and 6.7 for HT. Since the conditions chosen for this example favor the fog-capture mechanism these results suggest that this mechanism should never be very important so far as HT washout is concerned. It may, however, be of some consequence in HTO removal depending upon physical circumstances.

Unfortunately there are no experimental data available to test these results directly. Data for other gases, particularly sulfur dioxide⁽¹⁴⁾ however, indicate that satisfactory agreement between these equations and theory may be expected, at least for release heights up to 100 ft and limited downwind distances. Obviously there is a need for experimental confirmation before complete confidence can be placed in this model.

It is emphasized that the equations derived in this report pertain to removal by washout only. Any removal by "dry" deposition from the atmosphere must be factored in to the analysis as an additional consideration. In addition, the "nonfeedback" assumption of this linear model may give rise to errors if significant redistribution of the plume via the absorption-desorption process occurs. This effect should be inconsequential at short downwind distances, but conceivably could become significant if these distances become large.

In a final analysis the model presented in this report is suggested as a tentative means for washout estimation involving HT, T₂, HTO and T₂O (as well as other simple gases). This recommendation is based partly upon the encouraging results obtained from previous washout studies with other

gases, partly because of the apparent inadequacy of the conventional washout-coefficient approach for gas-scavenging calculations, and finally, partly because of the fact that no reasonable alternative procedure for accomplishing this end exists at the present time. This model should be tested directly with experimental data, however, before any large degree of confidence is placed in its predictive capabilities.

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