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INPUT OF PETROLEUM HYDROCARBONS TO THE OCEAN VIA ATMOSPHERIC TRANSPORT

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ABSTRACT

There are few data available on petroleum hydrocarbons in the marine atmosphere. The only class of organic compounds for which any significant data base exists is n-alkanes, which comprise ~ 30 percent of an average crude oil. Using data on n-alkanes in aerosols, rain, and in the gas phase from Atlantic, Pacific, and Indian Ocean regions, crude estimates of the deposition of n-alkanes to the ocean are made. Deposition of gaseous and particulate n-alkanes by rain scavenging, of particulate n-alkanes by dry deposition, and of gaseous n-alkanes by direct vapor exchange with the ocean are evaluated. Rain scavenging of particulate n-alkanes appears to be the primary transport path to the ocean from the atmosphere. The total input of n-alkanes to the ocean from the atmosphere is estimated to be from 0.03 to 0.3 Tg/yr. The accuracy of these estimates could be evaluated by the analysis of carefully collected rain samples over the Atlantic and Pacific Oceans. More precise estimates of the atmospheric input of petroleum to the ocean will have to await more information on the inputs of the various components of petroleum to the sea surface and further understanding of the reaction products, pathways and rates of transformation of these compounds in the atmosphere.

E-R-R-A-T-A

Page 3, line 10 should read – Atlas and Giam, personal communication, 1981.

Page 4, line 13 should read – Atlas and Giam, personal communication, 1981.

Page 9, line 6 should read – Atlas and Giam, personal communication, 1981.

Page 9, line 7 should read – Atlas and Giam.

Page 19, line 23 should read – Dr. Elliot Atlas and Dr. C.S. Giam.

Page 24, reference 4 should read – Atlas and Giam, personal communication, 1981.

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I. INTRODUCTION

Less is known about the global sources, distribution, and fluxes of organic matter than any other major class of chemical substances in the atmosphere. Aside from methane and certain halocarbons in the vapor phase, very few measurements of gaseous or particulate organic matter are available outside urban areas. Recent reviews by Duce (1978) and Simoneit and Mazurek (1981) have attempted to synthesize the available data and summarize our knowledge. The situation is complicated, of course, by the fact that there are probably thousands of different organic compounds emitted to the atmosphere from natural and pollution sources and many other compounds are produced from atmospheric, particularly photochemically induced, reactions. Each of these substances has its own characteristic chemical and physical properties and associated atmospheric sources, residence times, and sinks.

Our understanding of atmospheric petroleum hydrocarbons (PHC) and their input to the ocean is similarly sketchy. Crude estimates of the input of petroleum hydrocarbons to the ocean from the atmosphere have been made in the past. SCEP (1970) estimated that 9 Tg/yr (1 Tg = 10^{12}g) of PHC entered the ocean from the atmosphere at that time, and suggested this number could double by 1980. NAS (1975) estimated that the atmospheric input of PHC was much lower, about 0.4 Tg/yr. This estimate was not based on any measurements over the ocean, but simply on the total quantity of PHC injected into the atmosphere, its assumed reactivity in the atmosphere, and the general distribution of particles and the patterns of rainfall over the sea and land. The NAS (1975) report pointed out that vehicle emissions are the single most important source of atmospheric hydrocarbons. However, this report suggested that vehicle hydrocarbon emissions in the United States would decrease by 1985 to about one third of the 1968 values as a result of emission control standards. Other important sources of PHC in the atmosphere include refinery losses, evaporation, transfer losses, and solvent use (Robbins and Robinson, 1968).

It is very difficult to ascertain the actual atmospheric input of petroleum to the ocean surface for several reasons. Petroleum is a complex mixture of many classes of compounds whose members have different reactivities and solubilities. For example, low molecular weight polynuclear aromatic hydrocarbon (PAH) and n-alkane reactivities with OH radical span five orders of magnitude (Darnell et al., 1976). Chameides and Cicerone (1978) suggested that the photochemical lifetime of atmospheric ethane is ~ 25 days while that of propane, butane, and pentane may be ~ 5 days. Zimmerman (1978) and Hanst et al. (1980) have pointed out the potential importance of the photooxidation of non-methane hydrocarbons as a source for atmospheric CO. Gas to particle conversion also occurs for organic material (Simoneit and Mazurek, 1981 and Duce, 1978). During transport from continents to the sea via the atmosphere, particle fractionation may occur. Hence, if the organic composition is different for various particle size classes, the overall atmospheric particulate organic composition will change as a function of transport distance and time. Thus the organic chemical composition of petroleum derived substances in the remote marine atmosphere may bear very little resemblance to what was emitted into continental air masses several thousand kilometers away. Many individual compounds in petroleum are also produced from other natural sources, such as n-C_{15} and n-C_{17} from marine phytoplankton, pristane from zooplankton and n-C_{27} and n-C_{29} from land plants. In several areas of the ocean such as upwelling zones or downwind of major forests, these compounds may make up a significant portion of the hydrocarbons in the atmosphere. Finally, there is a paucity of data on petroleum organic compounds in rain, vapor and particulate samples from open ocean areas, thus requiring a large number of simplifying assumptions to be made in any estimate of air to sea transport.

Taking into consideration the problems discussed above, we have decided to concentrate on the n-alkane components of petroleum. The n-alkanes constitute approximately 30 percent of petroleum (NAS, 1978) and some data are available, albeit very limited, to undertake estimates of their atmospheric input to the open ocean (Ketseridis and Eichmann, 1978; Eichmann et al., 1979, 1980; Hahn, personal communication, 1981; Gagosian et al., 1981a; Zafiriou and Gagosian, 1981; Atlas, personal communication, 1981). Data for PAH are fewer and not sufficient to estimate their atmospheric input. Aerosol samples from coastal Norway which had an oceanic origin were collected by Bjorseth et al. (1979). The total PAH concentration averaged 1.6 ng/m^3. Hahn (1980) found PAH to be 80 percent of the n-alkane concentration for aerosol samples from the southern North Atlantic. His PAH values averaged 11 ng/m^3. However, no single PAH was detected in > 5 pg/m^3 air concentration for particles at Enewetak Atoll in the Central North Pacific (Gagosian et al., 1981a). No PAH vapor or rain data have been reported from the open ocean.

II. DATA BASE FOR n-ALKANES IN THE ATMOSPHERE

A. General

As stated earlier, many of the n-alkanes produced by marine plankton and land plants are the same as those in petroleum. It is very difficult to subtract out this other "biogenic" component from many of the data sets available without introducing a preconceived bias. Rather than do this for selected samples, we will not do it for any of them. We will thus derive atmospheric inputs to the ocean for n-alkanes as a class of organic substances. The fraction of these n-alkanes which are of petroleum origin is uncertain. Thus the fluxes obtained represent maximum values relative to petroleum n-alkane input to the ocean from the atmosphere.

There are few data for n-alkanes over the ocean, with the data limited basically to that from three research groups. These are at the Max-Planck Institute, Mainz, FRG; Woods Hole Oceanographic Institution; and Texas A and M University. Data from over the open North Atlantic Ocean, from the Irish coast, and from Cape Grim, Tasmania in the Indian Ocean are from the Max-Planck Institute (Ketseridis and Eichmann, 1978; Eichmann et al., 1979, 1980; Hahn, personal communication, 1981). Data from Enewetak Atoll, Marshall Islands, in the tropical North Pacific, have been obtained by the Woods Hole and Texas A and M groups (Gagosian et al., 1981a; Zafiriou and Gagosian, 1981, Atlas, personal communication, 1981). The latter data were obtained as part of the SEAREX (Sea/Air Exchange) Program. Additional data from the SEAREX groups will be available in late 1981 from American Samoa in the tropical South Pacific.

The observed concentrations of particulate and vapor phase n-alkanes in the marine atmosphere are presented in Tables 1 and 2. Data from three North Atlantic sites are presented. Loophead is on a peninsula on the west coast of Ireland at about 52° 30'N, 9° 50'W. Samples were collected from a cliff about 70 m above sea level. Only samples collected when the wind was from the ocean are reported here. Samples were also collected from a ship at the JASIN (Joint Air/Sea Interaction) site, which is located between Iceland and Scotland (60°N, 13°W). The tropical North Atlantic samples were also collected from a ship, in this case operating in the North Atlantic tradewind regime at ~ 15°N between Africa and the Caribbean Sea. The German data from Cape Grim, Tasmania were obtained from the Australian Baseline Atmospheric

Monitoring Station located on the northwest tip of Tasmania (40°41'S, 144°40'E). Samples were collected on a cliff 90 meters above sea level. The samples obtained by the Woods Hole and Texas A and M groups were collected from a 20 meter tower located on the windward coast of Bokandretok Island, Enewetak Atoll, Marshall Islands (11°20'N, 162°20'E). Sample collection on Enewetak was controlled automatically by wind speed and direction as well as total atmospheric particle counts to avoid local island contamination. Efforts were made in all studies to avoid local contamination.

It is not our intent to go into detail here on the analytical methodology of measuring hydrocarbons in atmospheric samples. A recent review by Simoneit and Mazurek (1981) and reports by Ketseridis et al. (1976), and Gagosian et al. (1981a), discuss the necessity of ultraclean samplers and sampling conditions. The need to separate the hydrocarbon classes from other organic compound classes (usually by liquid chromatography) before gas chromatography (GC) and GC/mass spectrometry for quantitative analyses and structural determination is stressed in the latter report. We feel the use of high resolution glass capillary GC for analysis is a necessity. It should be emphasized that it is critical that these hydrocarbon measurements be made in conjunction with micro-meteorological studies of the sampling site and long range transport studies to ascertain more completely the sources and transport pathways involved. Clearly, it is also desirable to have data on other anthropogenic compounds such as chlorinated hydrocarbons, phthalate esters and trace metals along with source marker information such as ^{210}Pb and $\delta^{13}C$ to more fully interpret the hydrocarbon data.

Table 1 lists the particulate n-alkane data from C_{15}-C_{30} and Table 2 presents the vapor phase n-alkane data for C_{10}-C_{30}. Particulate n-alkane data for C_{10}-C_{14} was not presented since these compounds cannot be quantitatively recovered during the extraction of the filter with organic solvent, the solvent evaporation, and the liquid chromatography steps in the analytical scheme (Mackay and Wolkoff, 1973).

B. Particulate n-Alkanes

As might be expected for such different oceanic regions, the measured concentrations of particulate and vapor phase n-alkanes were quite different at several of these locations. Data for particulate n-alkanes (Table 1) from the Ireland, JASIN, and Cape Grim sites are all rather similar, generally a few tenths of one ng/m^3. All are much lower, however, than the data from the tropical North Atlantic. The reason for this difference is unclear. The latter sampling area is in the region of the Sahara dust plume, which carries large quantities of sand and soil derived materials to the tropical North Atlantic in the northeast tradewinds. However, the west coast of Africa would not be expected to be a significant source of petroleum derived atmospheric n-alkanes, even though there is extensive tanker traffic along that coast. Viewed in the context of the other data presented in Table 1 we have tentatively concluded that the tropical North Atlantic data reported are not representative of that region. Clearly additional measurements to evaluate these data are needed. We feel the JASIN, Ireland and Cape Grim data are most representative of concentrations over the North Atlantic and in the coastal regions of the other oceans.

Particulate n-alkane concentrations from Enewetak Atoll are considerably lower than over the North Atlantic or at Cape Grim. These data are probably more representative of mid-North Pacific Ocean, South Pacific Ocean, South Atlantic Ocean, and Indian Ocean regions far from continental influences.

C. Vapor Phase n-Alkanes

Vapor phase n-alkane concentrations are presented in Table 2. Again the Loophead, JASIN, and Cape Grim data are quite similar but they are considerably higher than the Enewetak data, generally by a factor of 50 to 100. Note that there is, in general, good agreement between the Woods Hole and Texas A and M data at Enewetak for n-C_{24} to n-C_{29} alkanes. There are no vapor phase n-alkane data available from the tropical North Atlantic region. Again, the Loophead, JASIN, and Cape Grim data appear to be most representative of concentrations over the North Atlantic Ocean and in coastal regions while the Enewetak data may be more representative of concentrations over the Indian, South Atlantic, South Pacific, and mid-North Pacific Oceans.

III. MODEL CALCULATIONS FOR THE ATMOSPHERIC INPUT OF n-ALKANES TO THE OCEAN

A. Assumed Atmospheric Concentrations

1. Geographical Regions

As can be seen from the data presented in Tables 1 and 2, the geographical coverage for atmospheric n-alkanes is very sparse. From this limited data we have derived mean atmospheric particulate and vapor phase n-alkane concentrations over the world ocean. Obviously the data do not warrant a detailed breakdown into concentration zones. For simplicity we will assume the marine atmosphere can be divided into two geographical regions, relative to the concentrations of n-alkanes. These regions, and the concentrations and deposition derived for them, will be referred to as Case A and Case B.

Case A will include the atmosphere over all of the North Atlantic Ocean north of 20°N, the atmosphere over 25 percent of the North Pacific Ocean, and the atmosphere over 10 percent of the rest of the world ocean. These figures reflect the expected higher n-alkane concentrations over the North Atlantic and parts of the North Pacific Oceans as a result of petroleum related use in North America, Asia, and Europe. They also reflect the possibly higher atmospheric concentrations in general found in coastal regions. The oceanic area covered by Case A is 8 x 10^{17} cm^2 (Baumgartner and Reichel, 1975).

Case B will include the atmosphere over the rest of the world ocean. The oceanic area covered by Case B is 28 x 10^{17} cm^2.

2. Particulate Atmospheric n-Alkane Concentrations

Case A - The assumed atmospheric particulate n-alkane concentrations for Case A were determined by taking the mean of the Cape Grim and JASIN area data. The Ireland and JASIN data are quite similar and appear to be rather representative of the North Atlantic. The JASIN data were used since they are from a more open ocean region. The assumed concentrations so obtained are given in Table 3. Concentrations for n-C_{29} and n-C_{30} were extrapolated based on the average concentrations for n-C_{21} to n-C_{28}. The extrapolated concentrations were not determined from Case B n-C_{29} and n-C_{30} concentrations because n-C_{29} in Case B has a clear land plant input (Gagosian et al., 1981a). Extrapolating this factor of 5 concentration increase for n-C_{29} relative to n-C_{28} in Case B to Case A would unduly bias the German group's data.

Case B - The assumed atmospheric particulate concentrations for Case B were obtained by taking the data of Gagosian et al. (1981) and Zafiriou and Gagosian (1981). These data were extrapolated to obtain n-C_{15} to n-C_{20} concentrations by assuming the relative concentrations changed in a manner similar to the Case A data for n-C_{15} to n-C_{20}. The assumed concentrations are presented in Table 3.

3. Atmospheric Vapor Phase n-Alkane Concentrations

Case A - The assumed atmospheric vapor phase n-alkane concentrations were again obtained by taking the mean of the JASIN and Cape Grim data, with an extrapolation of the data to n-C_{29} and n-C_{30} by assuming the relative concentrations changed in a manner similar to the Case B data. The assumed concentrations are given in Table 4.

Case B - The assumed atmospheric vapor phase n-alkane concentrations were obtained for n-C_{13} to n-C_{23} by using the data of Atlas (personal communication, 1981), for n-C_{24} to n-C_{29} by using the mean of the data of Atlas (personal communication, 1981 and Zafiriou and Gagosian (1981)), and for n-C_{30} by using the data of Zafiriou and Gagosian (1981). The data of Atlas were extrapolated to obtain n-C_{10} to n-C_{12} concentrations by assuming the relative concentrations changed in a manner similar to the Case A data. The assumed concentrations are given in Table 4.

B. Deposition Calculations

Deposition of n-alkanes to the ocean will be calculated for Case A and Case B for particulate and vapor phase n-alkanes. For particulate n-alkanes, we will estimate the input via precipitation and via dry deposition. For vapor phase n-alkanes, we will estimate the input via precipitation and direct gas exchange.

1. Input of Atmospheric Particulate n-Alkanes to the Ocean

a. Precipitation Removal

Estimates of wet (rain) removal of atmospheric particles or material present on particles can be made by utilizing the washout factor or scavenging ratio, W, where:

$$W = C_R D / C_A \tag{1}$$

and C_R = concentration of material in rain (ug/Kg)

C_A = concentration of material in air (ug/m^3)

D = density of air (~ 1.2 Kg/m^3 at 20°C, 1 atm)

W is dimensionless. Values for W generally range from about one hundred to a few thousand for particles in the atmosphere. A value for W of 1000 roughly means that 1 gram (or 1 cm^3) of rain scavenges about 1 m^3 of air. W is, of course, dependent upon a number of factors, including particle size, chemical composition, vertical concentration distribution of the particles, vertical extent of the precipitating cloud, etc. Eisenreich et al. (1981) report values for W for organic substances which range from ~ 10 to 350. Experimental values of W for particulate n-alkanes have only been measured at Enewetak Atoll. At that site W ranged from about 700 to 2000 for heavier n-alkanes (n-C_{27} to n-C_{31}). We will assume a value for W of 100 to 1000 for particulate n-alkanes. These values are typical of washout factors for trace metals found on particles with radii < 1 μm (Duce et al., 1981). Higher washout factors are often found for substances present on larger particles.

Using W values of 100 to 1000 and the assumed particulate n-alkane concentrations in Table 3, the predicted n-alkane concentrations in rain for both Case A and Case B conditions can be calculated. These concentrations are presented in Table 5. The rainfall quantities over the ocean in the areas covered by Case A and Case B were obtained from Baumgartner and Reichel (1975) and are also presented in Table 5, as are the total n-C_{15} to n-C_{30} particulate n-alkane fluxes by rain removal. As seen in Table 5, the range of the calculated values for particulate n-alkane wet deposition in the Case A area is about a factor of twenty higher than that calculated for Case B, even though the total rainfall is higher in the Case B area.

b. Dry Deposition

Dry deposition of atmospheric particulate matter or material present on atmospheric particles, is often estimated using the deposition velocity, v_d, where:

$$v_d = F/M \qquad (2)$$

and M = mass of aerosol in the atmosphere (or material on aerosol)(ug/cm^3)
F = flux of atmospheric particles to the surface (ug/cm^{2}sec)
v_d = deposition velocity (cm/sec).

v_d for particles can be estimated from theoretical considerations or it can be measured in laboratory or field situations. No direct measurements of v_d for n-alkanes on atmospheric particles have been made. In a laboratory wind tunnel experiment Sehmel and Sutter (1974) investigated aerosol deposition velocity over a water surface as a function of wind speed and particle size. Their results are presented in Figure 1. They found v_d was very dependent upon particle size. For example, for wind speeds of 7-14 m/sec they find deposition velocities ranging from 0.02 to 1 cm/sec for 0.3 to 2 μm radius particles respectively. Slinn and Slinn (1980) developed a theoretical two layer model for the prediction of particle dry deposition to natural water surfaces. They pointed out that if particle growth by water vapor condensation occurs in the humid regions near an air/water interface, the deposition velocity of certain types of particles, e.g., $(NH_4)_2SO_4$, with dry radii near 1 μm is nearly independent of particle size and can be approximated by $v_d = 1.3 \times 10^{-3}\ \bar{u}$, where $\bar{u}$ is the mean wind speed in cm/sec. At wind speeds of 5-10 m/sec (~ 10-20 kts) this results in an aerosol v_d of ~ 1 cm/sec (see Figure 2). As Figure 2 shows, v_d is very dependent upon particle size except for the region around 1 μm dry radius.

We have little information on the particle size distribuion of n-alkanes in the marine atmosphere. Ketseridis and Eichmann (1978) found roughly equal concentrations of n-alkanes on particles with radii greater than 1 μm and on particles with radii less than 1 μm at Mace Head on the west coast of Ireland. Hoffman and Duce (1977) and Chesselet et al (1981) find about 80 percent of the mass of total organic carbon is present on marine atmospheric particles with radii less than 1 μm. From this information and from Figures 1 and 2, it appears that a reasonable range of v_d applicable to particulate n-alkanes over the ocean would be roughly 0.05 to 0.5 cm/sec. It must be recognized, however, that v_d apparently increases very rapidly with increasing radius above a few micrometers, as shown by both Figures 1 and 2. For example, a 20 μm particle has a v_d of ~ 10 cm/sec at wind speeds of 5 - 10 m/sec. Thus a relatively small concentration of n-alkanes on these very large particles could contribute significantly to the n-alkane flux. Unfortunately, however, there are not sufficient data available to evaluate this possibility.

Using values of v_d from 0.05 to 0.5 cm/sec and applying them to the assumed atmospheric particulate n-alkane concentrations in Table 3 results in the dry deposition values reported in Table 6. Note that the range of the calculated values for the particulate n-alkane dry deposition in the Case A area is about a factor of 20 higher than that calculated for Case B, even though the total oceanic area covered by Case B is three times that of Case A.

3. Input of Vapor Phase n-Alkanes to the Ocean

a. Precipitation Removal

Precipitation scavenges trace gases as well as particles from the atmosphere. To estimate the contribution of scavenging of vapor phase n-alkanes by precipitation we will assume that the precipitation is all rain and that the dissolved n-alkane concentrations in rain are in equilibrium with the assumed vapor phase concentrations of n-alkanes. Slinn et al. (1978) have estimated that vapor phase - rain equilibrium should be attained rapidly, probably within a 10 meter fall distance of the raindrop. The partitioning of a vapor phase organic substance between the gas and liquid phase is described by Henry's Law. If the Henry's Law constant, H, is known, then the concentration of a trace organic substance in the liquid phase, e.g., rain, can be determined. However, this assumes the organic substance, in our case n-alkanes, remains dissolved and unassociated with other dissolved substances (Galloway et al., 1981).

The Henry's Law constants for n-alkanes can be determined if the saturation vapor pressure, p_0, and the aqueous solubility, s_0, are known at the same temperature.

$$H = p_0/s_0 \qquad (3)$$

Where H = Henry's Law constant (atm m^3/g)
p_0 = Saturation vapor pressure at 25°C (atm)
s_0 = Solubility at 25°C (g/m^3)

The saturation vapor pressure, p_0, can be calculated for n-alkanes up to n-C_{20} at 25°C by use of the Antoine Equation and appropriate constants found in Lange (1961). p_0 values for n-C_{21} to n-C_{30} alkanes can be obtained by extrapolation of the n-C_1 to n-C_{20} regression line. The p_0 values so obtained are presented in Table 7. The solubilities of n-C_1 to n-C_{36} alkanes in distilled water have been summarized by McAuliffe (1980) and are shown in Figure 3. Note that there is a break in the solubility curve at about n-C_{12}, with the apparent solubility decreasing much slower after n-C_{12} relative to n-C_1 to n-C_{12}. This break could signify the point where the chain length for n-alkanes allows for the commencement of micellar layer formation. Basically a monomolecular layer of these compounds may dissolve themselves. However, it is also possible that colloids begin to be formed at this concentration and the compounds of interest are not truly dissolved (McAuliffe, 1969; Sutton and Calder, 1974). Hence, higher solubilities would be erroneously inferred. This would also be true if the higher molecular weight solid hydrocarbons do not completely dissolve. Until more data are available it is difficult to decide on the correct solubility values for n-alkanes greater than n-C_{12}, i.e., those shown in Figure 3 or those obtained by extrapolating the n-C_1 to n-C_{12} solubilities in Figure 3 to n-C_{30}. As a first approximation, we will use n-C_{13} to n-C_{30} solubility values calculated by extrapolating the regression line for n-C_1 to n-C_{12} n-alkanes. Table 7 gives these solubilities and the corresponding Henry's Law constants for each n-alkane.

Since we are interested in the total mass of a number of n-alkanes of different molecular weight, H is derived in units of atm m^3/g rather than the more common atm m^3/mole. Note that for the case of the extrapolated slope solubilities, H changes by a factor of about 100 from n-C_{10} to n-C_{30}.

Table 8 presents the n-alkane rain concentrations calculated using the H values in Table 7 and the assumption that the vapor phase n-alkanes (Table 4) are in equilibrium with the dissolved n-alkanes in rain. The concentration in rain, C_R, is calculated from:

$$C_R = C_A/H \qquad (4)$$

Where C_R = n-alkane concentration in rain (g/m^3 or mg/Kg)

C_A = n-alkane concentration in air (atm)

H = Henry's Law Constant (atm m^3/g)

As can be seen by comparison of Table 5 and Table 8, the equilibrium concentrations and total deposition from gas phase rain scavenging are extremely low compared with expected rain concentrations from rain scavenging of particulate n-alkanes. The total n-alkane rain deposition from gas phase scavenging is roughly a factor of 10^6 lower than the rain deposition from particulate scavenging.

It must be pointed out, however, that if the true solubility curve for n-alkanes in water does show a sharp break at n-C_{12} with only a very slowly decreasing solubility for higher n-alkanes, a different conclusion would be reached for the rain scavenging of vapor phase n-alkanes. Much smaller values for H than reported in Table 7 would result from the use of these greater solubilities. This in turn would result in much larger values for the equilibrium concentration of vapor phase n-alkanes incorporated in rain than reported in Table 8. The calculated total n-alkane concentration in rain at 25°C using H values calculated from Figure 3 solubilities and assuming Case B conditions would be ~ 0.006 μg/Kg. For Case A conditions this value would be ~ 0.4 μg/Kg. These concentrations are a factor of 10^6 higher than the calculated concentrations for Case A and Case B reported in Table 8. Most of the mass of the scavenged vapor phase n-alkanes in the rain in this latter case (i.e., H calculated from Figure 3 solubilities) would be in the n-C_{27} to n-C_{30} range. Actual concentrations of n-C_{21} to n-C_{30} alkanes in rain at Enewetak Atoll, a Case B location, are around 0.07 μg/Kg, with the highest concentrations at n-C_{25}. The concentration of n-C_{29} and n-C_{30} alkanes at Enewetak are ~ 0.004 μg/kg each, close to the calculated n-alkane concentrations using H values obtained from Figure 3 (Gagosian et al., 1981b).

Note that if the higher predicted rain concentrations are correct, the total quantity of n-C_{10} to n-C_{30} vapor phase alkanes scavenged by rain and delivered to the ocean would be ~ 0.03 Tg/yr for Case A and 0.002 Tg/yr for Case B. These values are at the low end of the ranges calculated for the particulate n-alkanes scavenged by rain for both cases. The true solubilities of the higher n-alkanes must be determined before more accurate estimates can be made.

It is important to note that the rain scavenging of vapor phase n-alkanes is temperature dependent. For example, at 5°C, p_0 for n-C_{10} to n-C_{20} alkanes is a factor of 2 to 20 times lower than at 25°C. This results in H values which are also lower, resulting in higher equilibrium concentrations of n-alkanes in the rain. A total deposition of scavenged vapor phase n-alkanes at 5°C can be calculated by using these lower H values and the solubilities (s_0) in Table 7. This value is about seven times that in Table 8 calculated for 25°C. In addition, increased solubility of n-alkanes at the lower temperature would slightly increase the calculated rain concentrations.

b. Direct Gas Exchange with the Ocean

In addition to precipitation scavenging, direct gas exchange with seawater removes trace gases from the atmosphere. Using the Henry's Law constants and assumed vapor phase n-alkane concentrations, the concentrations of n-alkanes in seawater in equilibrium with the atmosphere may be determined. If this calculated concentration is higher than the actual concentration in surface seawater, then the n-alkane flux is into the sea. If the calculated concentration is lower than the actual seawater concentration, then the n-alkane flux is into the atmosphere. The Henry's Law constants from Table 7 are for distilled water and must be adjusted for seawater. Using Sutton and Calder's (1974) n-alkane seawater solubility data and the saturated vapor pressures for vapor phase n-alkanes from Table 7, Henry's Law constants can be calculated for n-alkanes in seawater. These values increase for n-C_{12} to n-C_{26} from a factor of 1.2 to 20 times the H values calculated from the n-alkane solubilities in distilled water. This increase is due to an increased salting out effect with increasing molar volume of the n-alkanes in accordance with the McDevit-Lang theory.

Using these seawater H values and the assumed vapor phase concentrations from Table 4, equilibrium seawater concentrations for n-alkanes are calculated to be ~ $10^{-9\pm3}$ μg/l for Case A and even lower for Case B. Boehm et al.

(1980) have found dissolved n-alkane values averaging 0.01 μg/l per n-alkane from n-C_{20} to n-C_{29} in surface seawater from several stations in the western North Atlantic. These values are several orders of magnitude higher than the equilibrium n-alkane concentrations in seawater as calculated above. Hence the sea is a source for these compounds in the atmosphere rather than a sink, and the n-alkane flux is into the atmosphere. Although there is very little information on < n-C_{18} alkanes, studies by other investigators concur with the conclusion that n-alkanes < n-C_{18} partition almost completely into air. Schwarzenbach et al. (1978) calculated pentadecane and heptadecane to have partition coefficients into air of 10^4 - 10^5. These authors conclude that if n-alkanes are present in solution in shallow coastal waters, they will exchange rapidly into the atmosphere in < 4 days. Using vapor pressures and solubilities for both aromatic and aliphatic hydrocarbons, Harrison et al. (1975) predicted that losses of aromatic hydrocarbons due to evaporation from the sea surface would be 10^2 times faster than losses from dissolution. Aliphatic hydrocarbons are 10^5 times faster

As mentioned earlier, the Henry's Law constants can also be calculated using the non-extrapolated n-alkane solubilities of Figure 3, after adjustments due to the lower n-alkane solubilities in seawater (Sutton and Calder, 1974). For Case A conditions, the calculated equilibrium seawater concentrations for n-C_{27} to n-C_{29} alkanes using these H values are 0.001 - 0.003 μg/l. For n-C_{30} the calculated concentration is 0.009 μg/l. Calculated concentrations for n-alkanes less than n-C_{27} are lower than 0.001 μg/l and decrease with decreasing carbon number. As in the case when we used H values from Table 7, the calculated n-alkane seawater concentrations are lower than the concentrations actually observed. Thus the sea is a source for these atmospheric n-alkanes. However, for this latter case the n-C_{27} to n-C_{30} calculated seawater concentrations for Case A are within an order of magnitude of the observed n-C_{22} to n-C_{30} concentrations in seawater, i.e. ~ 0.01 μg/l. Considering the uncertainties in both the calculated and observed seawater concentrations, we have calculated the maximum n-alkane gas exchange into the sea by assuming that there is zero concentration of n-C_{27} to n-C_{30} alkanes in the sea, i.e., the sea is a perfect sink for direct vapor exchange of these substances. Using Liss and Slater's (1974) two layer film model, we calculate the maximum input of n-C_{27} to n-C_{30} alkanes via direct gas exchange to be ~ 0.02 Tg/yr for Case A. Using the same assumptions, the maximum input of n-C_{27} to n-C_{30} alkanes via direct gas exchange is calculated to be ~ 0.004 Tg/yr for Case B.

C. Total Input to the Ocean

Table 9 presents a summary of our calculations of the input of n-alkanes to the ocean. The total estimated input of atmospheric n-alkanes is 0.03 to 0.3 Tg/yr. It is clear, within the caveats described previously, that the primary input mechanism is via rain scavenging of n-alkanes on particles. However, we must have better solubility data for n-C_{20} to n-C_{30} n-alkanes before we can more fully assess the importance of rain scavenging of gases and direct gas exchange in the deposition of n-alkanes to the sea surface.

The estimates of the input of n-alkanes to the ocean via rain could be evaluated relatively easily by making measurements of the n-alkane concentrations in rain from samples collected, for example, in open ocean North Atlantic and North Pacific regions - the regions where we suggest most of the atmospheric petroleum hydrocarbons are entering the oceans. We recommend strongly that such rain measurements be made.

As stated in the introduction, n-alkanes constitute approximately 30 percent of the organic components of petroleum. Cycloalkanes, PAH, and heteroatomic (nitrogen, sulfur, and oxygen) organic constituents make up the remainder. No data are available for the cycloalkane and heteroatomic compounds. Only a few numbers are available for PAH. We strongly recommend that these other organic constituents of petroleum be measured in vapor, aerosol and rain samples.

It should be pointed out that the approach we have taken in using n-alkanes to estimate the input of petroleum to the ocean via the atmosphere is problematic. On one hand, using n-alkanes may give a maximum value of petroleum hydrocarbon atmospheric input because many natural marine and terrestrially derived n-alkanes are included in the overall n-alkane deposition value. On the other hand, many organic components of petroleum such as alkenes and alkylated aromatics, which react very fast with OH radical to produce oxygenated species that fall to the ocean surface, are not included in our approach. This suggests that using n-alkanes as an atmospheric input "marker" for petroleum would underestimate the input. More precise estimates of the atmospheric input of petroleum to the ocean will have to await more information on the inputs of the various components of petroleum to the sea surface and further understanding of the reaction products, pathways and rates of transformation of these compounds in the atmosphere.

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Table 1.

PARTICULATE n-ALKANE CONCENTRATIONS IN THE MARINE ATMOSPHERE (ng/m^3 STP)

n-alkane	Loophead, Ireland[1]	JASIN Site[2]	Cape Grim[3]	Tropical N. Atlantic[4]	Enewetak*[5]
n-C_{15}	0.06	0.10	0.12	4.1	
n-C_{16}	0.13	0.12	0.27	3.2	
n-C_{17}	0.08	0.26	0.32	4.2	
n-C_{18}	0.19	0.17	0.13	2.5	
n-C_{19}	0.16	0.20	0.13	8.2	
n-C_{20}	0.33	0.24	0.17	1.3	
n-C_{21}	0.22	0.26	0.35	1.1	0.0017
n-C_{22}	0.26	0.28	0.11	3.0	0.0020
n-C_{23}	0.31	0.29	0.15	2.0	0.0023
n-C_{24}	0.45	0.21	0.18	0.4	0.0021
n-C_{25}	0.37	0.33	0.18	0.6	0.0030
n-C_{26}	0.27	0.28	0.20	0.5	0.0022
n-C_{27}	0.23	0.37	0.52	0.6	0.0067
n-C_{28}	0.22	0.19	0.40	0.3	0.0037
n-C_{29}					0.0170
n-C_{30}					0.0033

References:

[1] Eichmann et al. (1979) and Hahn, personal communication (1981)

[2] Hahn, personal communication (1981)

[3] Hahn, personal communication (1981) and Eichmann et al. (1980)

[4] Ketseridis and Eichmann (1978)

[5] Zafiriou and Gagosian (1981) and Gagosian et al. (1981a)

* Average of 6 samples

Table 2.

VAPOR PHASE n-ALKANES IN THE MARINE ATMOSPHERE (ng/m^3 STP)

n-alkane	Loophead, Ireland[1]	JASIN Site[2]	Cape Grim[3]	Enewetak[4] (Florosil)	Enewetak[4] (PUF plugs)	Enewetak[5] (PUF plugs)
n-C_{10}	12	15	21			
n-C_{11}	14	9	20			
n-C_{12}	11	5	8			
n-C_{13}	9	4	8	0.23		
n-C_{14}	9	3	6	0.19		
n-C_{15}	14	6	11	0.66		
n-C_{16}	8	4	8	0.13		
n-C_{17}	10	5	9	0.55		
n-C_{18}	12	5	8	0.07		
n-C_{19}	10	5	10	0.07		
n-C_{20}	18	6	9	0.07		
n-C_{21}	14	6	11	0.07		
n-C_{22}	20	5	4	0.07		
n-C_{23}	32	5	6	0.08	0.11	
n-C_{24}	22	3	6	0.09	0.14	0.032
n-C_{25}	16	3	6	0.10	0.14	0.095
n-C_{26}	9	2	5	0.08	0.10	0.088
n-C_{27}	7	2	3	0.06	0.08	0.055
n-C_{28}	6	1	2		0.06	0.024
n-C_{29}					0.006	0.019
n-C_{30}						0.013

References:

[1] Eichmann et al. (1979) and Hahn, personal communication (1981)

[2] Hahn, personal communication (1981)

[3] Eichmann et al. (1980) and Hahn, personal communication (1981)

[4] Atlas, personal communication (1981)

[5] Zafiriou and Gagosian (1981)

Table 3.

ATMOSPHERIC PARTICULATE n-ALKANE CONCENTRATIONS USED IN MODEL CALCULATIONS (ng/m^3 STP)

n-alkane	Case A	Case B
n-C_{15}	0.11	0.0006*
n-C_{16}	0.20	0.0011*
n-C_{17}	0.29	0.0016*
n-C_{18}	0.15	0.0008*
n-C_{19}	0.17	0.0009*
n-C_{20}	0.21	0.0011*
n-C_{21}	0.31	0.0017
n-C_{22}	0.20	0.0020
n-C_{23}	0.22	0.0023
n-C_{24}	0.20	0.0021
n-C_{25}	0.26	0.0030
n-C_{26}	0.24	0.0022
n-C_{27}	0.45	0.0067
n-C_{28}	0.30	0.0037
n-C_{29}	0.20*	0.0170
n-C_{30}	0.18*	0.0034

* Extrapolated Concentrations

Table 4.

ATMOSPHERIC VAPOR PHASE n-ALKANE CONCENTRATIONS USED IN MODEL CALCULATIONS

n-alkane	Case A		Case B	
	(ng/m^3)	(10^{-13}atm)	(ng/m^3)	(10^{-13}atm)
n-C_{10}	18	28	0.60*	1
n-C_{11}	15	22	0.50*	0.7
n-C_{12}	7	9	0.25*	0.3
n-C_{13}	6	7	0.23	0.3
n-C_{14}	5	6	0.19	0.2
n-C_{15}	9	10	0.66	0.7
n-C_{16}	6	6	0.13	0.1
n-C_{17}	7	7	0.55	0.5
n-C_{18}	7	6	0.07	0.06
n-C_{19}	8	7	0.07	0.06
n-C_{20}	8	6	0.07	0.06
n-C_{21}	9	7	0.07	0.05
n-C_{22}	5	4	0.07	0.05
n-C_{23}	6	4	0.11	0.08
n-C_{24}	5	3	0.09	0.06
n-C_{25}	5	3	0.12	0.08
n-C_{26}	4	2	0.09	0.06
n-C_{27}	3	2	0.07	0.04
n-C_{28}	2	1	0.04	0.02
n-C_{29}	0.5*	0.3	0.01	0.007
n-C_{30}	0.5*	0.3	0.01	0.007

* Extrapolated Concentrations

Table 5.

PREDICTED RAIN CONCENTRATIONS AND DEPOSITION FROM PARTICULATE n-ALKANE SCAVENGING

	n-alkane	Case A Concentration (ng/Kg rain)	Case B Concentration (ng/Kg rain)
	n-C_{15}	9 - 90	0.05 - 0.5
	n-C_{16}	17 - 170	0.09 - 0.9
	n-C_{17}	24 - 240	0.13 - 1.3
	n-C_{18}	13 - 130	0.07 - 0.7
	n-C_{19}	14 - 140	0.08 - 0.8
	n-C_{20}	18 - 180	0.09 - 0.9
	n-C_{21}	25 - 250	0.14 - 1.4
	n-C_{22}	17 - 170	0.17 - 1.7
	n-C_{23}	18 - 180	0.19 - 1.9
	n-C_{24}	17 - 170	0.18 - 1.8
	n-C_{25}	22 - 220	0.25 - 2.5
	n-C_{26}	20 - 200	0.18 - 1.8
	n-C_{27}	38 - 380	0.56 - 5.6
	n-C_{28}	25 - 250	0.31 - 3.1
	n-C_{29}	17 - 170	1.4 - 14
	n-C_{30}	15 - 150	0.28 - 2.8
	Total	310 - 3100	4.2 - 42
Total Rainfall:		7.5×10^{16} Kg/yr	31×10^{16} Kg/yr
Total Deposition		0.023 - 0.23 Tg/yr	0.0013 - 0.013 Tg/yr

Table 6.

ESTIMATED DRY DEPOSITION OF PARTICULATE n-ALKANES TO THE OCEAN SURFACE

	Dry Deposition	
n-alkane	Case A Concentration (10^{-18}g/cm^{2}sec)	Case B Concentration (10^{-18}g/cm^{2}sec)
n-C_{15}	5.5 - 55	0.030 - 0.30
n-C_{16}	10 - 100	0.055 - 0.55
n-C_{17}	15 - 150	0.080 - 0.80
n-C_{18}	7.5 - 75	0.040 - 0.40
n-C_{19}	8.5 - 85	0.045 - 0.45
n-C_{20}	11 - 110	0.055 - 0.55
n-C_{21}	15 - 150	0.085 - 0.85
n-C_{22}	10 - 100	0.10 - 1.0
n-C_{23}	11 - 110	0.12 - 1.2
n-C_{24}	10 - 100	0.11 - 1.1
n-C_{25}	13 - 130	0.15 - 1.5
n-C_{26}	12 - 120	0.11 - 1.1
n-C_{27}	23 - 230	0.34 - 3.4
n-C_{28}	15 - 150	0.19 - 1.9
n-C_{29}	10 - 100	0.85 - 8.5
n-C_{30}	9 - 90	0.17 - 1.7
Total	190 - 1900	2.5 - 25
Total Area:	8×10^{17} cm^2	28×10^{17} cm^2
Total Deposition	0.0048 - 0.048 Tg/yr	0.00022 - 0.0022 Tg/yr

Table 7.

p_o, s_o, AND H FOR n-ALKANES AT 25°C

n-Alkane	p_o (atm)	s_o (g/m^3)	H (atm m^3/g)
n-C_{10}	9.7×10^{-4}	3×10^{-2}	0.03
n-C_{11}	5.7×10^{-4}	1×10^{-2}	0.06
n-C_{12}	1.9×10^{-4}	4×10^{-3}	0.05
n-C_{13}	6.5×10^{-5}	8×10^{-4}	0.08
n-C_{14}	1.9×10^{-5}	4×10^{-4}	0.05
n-C_{15}	6.2×10^{-6}	8×10^{-5}	0.08
n-C_{16}	8.9×10^{-7}	3×10^{-5}	0.03
n-C_{17}	7.0×10^{-7}	7×10^{-6}	0.1
n-C_{18}	2.5×10^{-7}	2×10^{-6}	0.1
n-C_{19}	5.7×10^{-8}	6×10^{-7}	0.1
n-C_{20}	1.9×10^{-8}	1×10^{-7}	0.2
n-C_{21}	8.6×10^{-9}	2×10^{-8}	0.4
n-C_{22}	2.6×10^{-9}	7×10^{-9}	0.4
n-C_{23}	8.6×10^{-10}	2×10^{-9}	0.4
n-C_{24}	2.6×10^{-10}	5×10^{-10}	0.5
n-C_{25}	8.6×10^{-11}	1×10^{-10}	0.9
n-C_{26}	2.6×10^{-11}	4×10^{-11}	0.7
n-C_{27}	8.6×10^{-12}	1×10^{-11}	0.9
n-C_{28}	2.6×10^{-12}	3×10^{-12}	0.9
n-C_{29}	8.6×10^{-13}	7×10^{-13}	1.
n-C_{30}	2.6×10^{-13}	1×10^{-13}	3.

Table 8.

CALCULATED RAIN CONCENTRATIONS AND DEPOSITION OF n-ALKANES IN EQUILIBRIUM WITH ASSUMED VAPOR PHASE CONCENTRATIONS AT 25°C

n-Alkane	Case A Rain Concentration (10^{-14} g/Kg)	Case B Rain Concentration (10^{-14} g/Kg)
n-C_{10}	9.	0.3
n-C_{11}	4.	0.1
n-C_{12}	2.	0.06
n-C_{13}	0.9	0.04
n-C_{14}	1.	0.04
n-C_{15}	1.	0.09
n-C_{16}	2.	0.03
n-C_{17}	0.7	0.05
n-C_{18}	0.6	0.006
n-C_{19}	0.7	0.006
n-C_{20}	0.3	0.003
n-C_{21}	0.2	0.001
n-C_{22}	0.1	0.001
n-C_{23}	0.1	0.002
n-C_{24}	0.06	0.001
n-C_{25}	0.03	0.0009
n-C_{26}	0.03	0.0009
n-C_{27}	0.02	0.0004
n-C_{28}	0.01	0.0002
n-C_{29}	0.003	0.00007
n-C_{30}	0.001	0.00002
Total:	23	0.73
Total Rainfall:	7.5×10^{16} Kg/yr	31×10^{16} Kg/yr
Total Deposition:	2×10^{-8} Tg/yr	2×10^{-9} Tg/yr

Table 9.

SUMMARY OF ATMOSPHERIC INPUTS OF n-ALKANES TO THE OCEAN

Mechanism	Case A (Tg/yr)	Case B (Tg/yr)
Rain scavenging of particles	0.023 - 0.23	0.0013 - 0.013
Rain scavenging of gases	$< 1 \times 10^{-7}$ - 0.03	$< 1 \times 10^{-7}$ - 0.002
Dry deposition of particles	0.0048 - 0.048	0.00022 - 0.0022
Direct gas exchange	0-0.02	0-0.0004
Total	0.028 - 0.32	0.0015 - 0.018
Grand Total	0.03 - 0.3 Tg/yr	

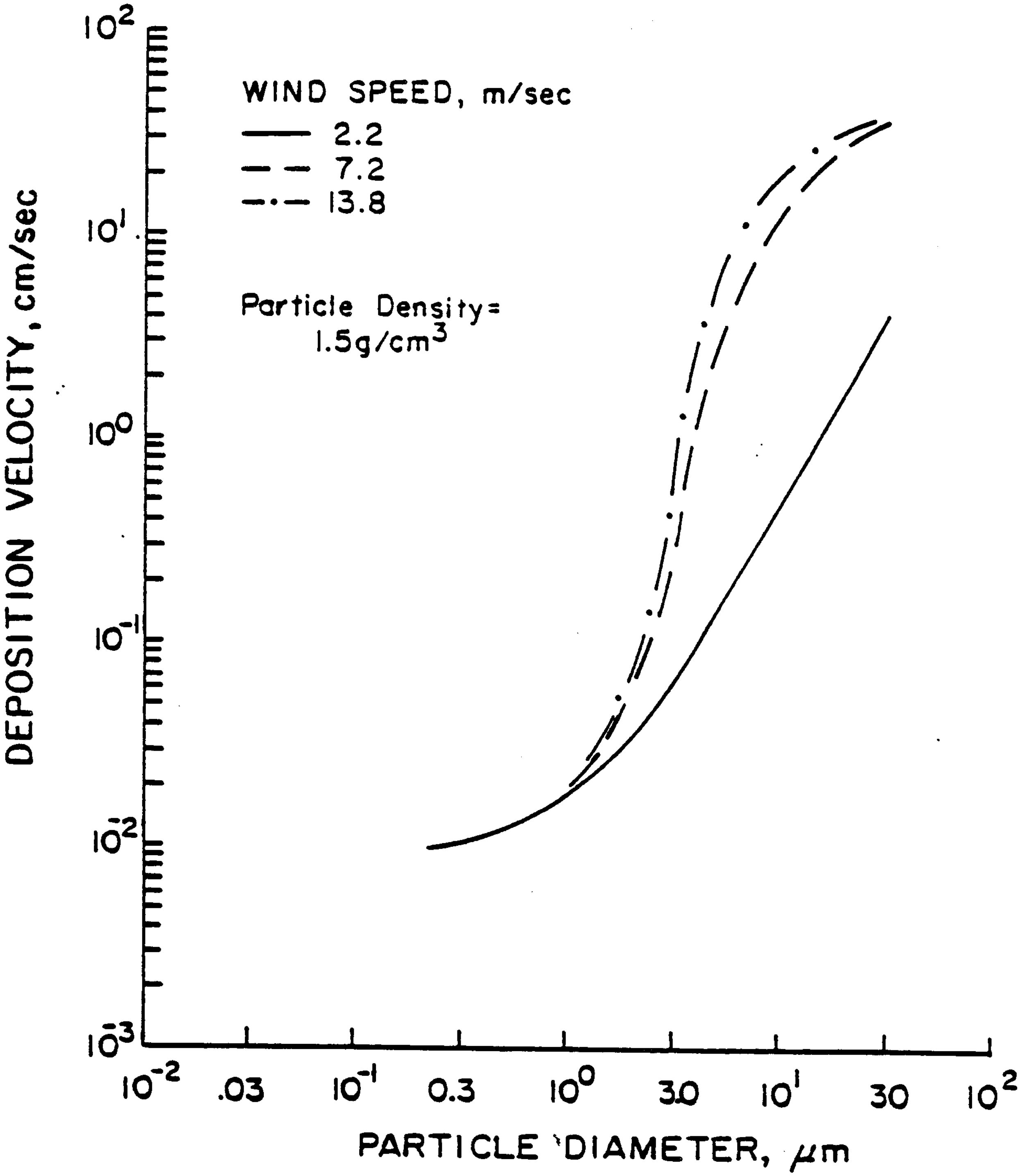

Figure 1. Atmospheric particle dry deposition velocity, v_d, to a water surface as a function of particle size and wind speed from wind tunnel studies (After Sehmel and Sutter, 1974).

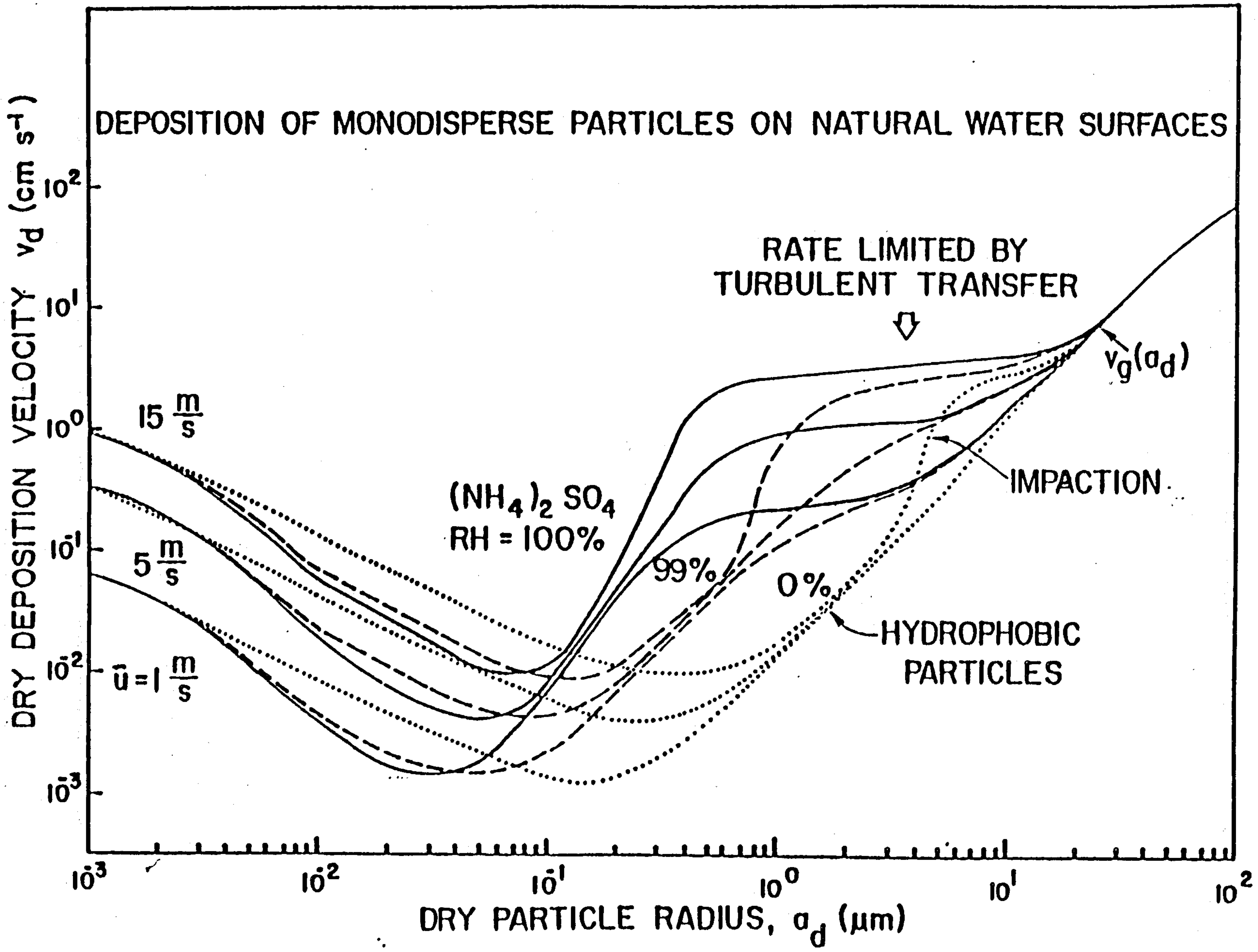

Figure 2. Theoretically derived particle dry deposition velocity, v_d, to a water surface as a function of particle size and wind speed (After Slinn and Slinn, 1980).

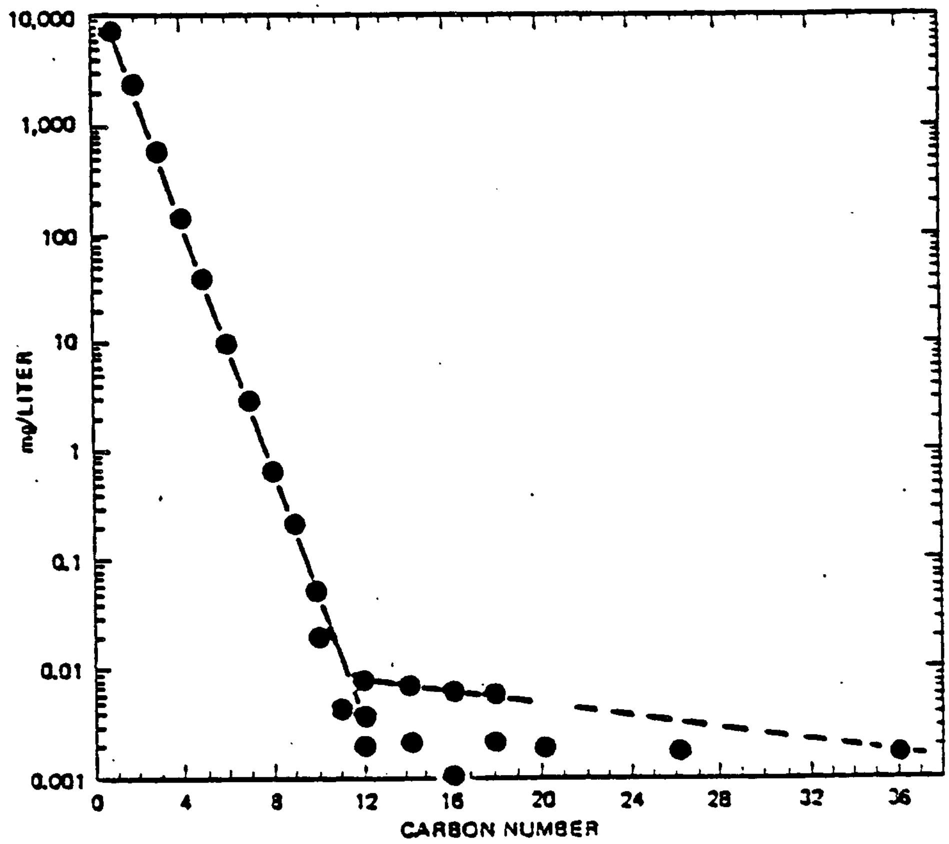

Figure 3. Solubilities of n-alkanes as summarized by McAuliffe (1980).