TRANSPORT MECHANISMS FOR PESTICIDES IN THE ATMOSPHERE

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ABSTRACT

It is fairly certain that large-scale transport of pesticides such as DDT occurs primarily via the atmosphere. Atmospheric transport is therefore of basic importance for the regional and global distribution of these trace substances. Global variability of constituents within the troposphere is strongly correlated to tropospheric residence time. If this is longer than about half a year the constituent shows a fairly uniform distribution, so that the details of the atmospheric transport are unimportant. The parameters which determine the residence time of pesticides and PCBs are discussed, and it is shown that at the present time we can not be certain about its magnitude even for DDT. If the residence time is similar to that of aerosols, i.e. about a week, atmospheric transport and removal processes become very important. Some of them are briefly discussed.
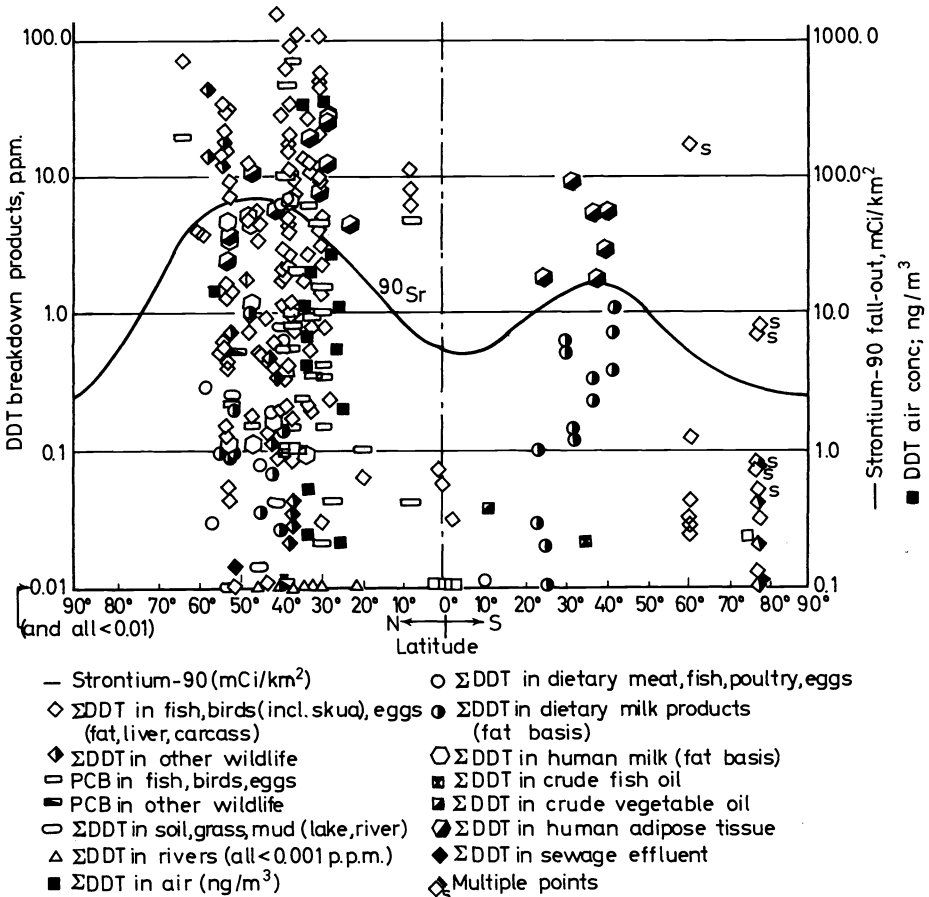
INTRODUCTION

At this Congress, which is devoted to the role of pesticides in our environment, we are concerned, among other things, with the possibilities for nature to cope with the variety of substances introduced by man into his 'Lebensraum' and with the resulting large-scale-scale and long-term distribution and its variation of these substances in soil, water and atmosphere. Because of the toxicity of some of these substances as well as their chemical stability, it has become apparent that some of the pesticides have in certain areas reached dangerous levels for the biosphere. This serious threat to life has led to intense interdisciplinary research to look into the details of chemical and biological degradation of these substances in nature and their fate on a local, regional and global basis.

With respect to the topic of my paper, two important facts have so far emerged from these studies with a high degree of certainty. First, some of these substances have reached the biosphere ranging from pole to pole and indicating the degree of global dissemination, as for instance demonstrated by *Figure 1*. Interpreting this figure we have to keep two things in mind: the occurrence of DDT and other substances in certain tissues of animals (and particularly man) is no direct and accurate measure of the general occurrence in the environment because of strong local influences in areas of application on both hemispheres and because of a large variety of biological amplification factors due to the peculiarities of the food chain, etc. The best

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indicators for large-scale distribution are likely to be the birds, and considering only these data in *Figure 1* we see that even in Antarctica DDT and PCB are abundant (see also ref. 2). The same is true for the Arctic regions of the North Atlantic[3], where considerable amounts of PCB and DDT were found in birds more than 250 miles north of the mainland and in species which never migrate far south in areas where the sea water is affected by Europe. I would have preferred for our discussion instead of *Figure 1* a similar one for concentrations of these substances in air or rainwater, but unfortunately such data are still very scanty or unreliable at the present time.

The second important fact for our discussion is that at least for DDT most of the material is transported through the atmosphere (and not via rivers) into the oceans, which most probably act as the huge and final sink area. Apart

Key:
- — Strontium-90 (mCi/km^2)
- ◇ ΣDDT in fish, birds (incl. skua), eggs (fat, liver, carcass)
- ◆ ΣDDT in other wildlife
- ▭ PCB in fish, birds, eggs
- ◖ PCB in other wildlife
- ◯ ΣDDT in soil, grass, mud (lake, river)
- △ ΣDDT in rivers (all < 0.001 p.p.m.)
- ■ ΣDDT in air (ng/m^3)
- ○ ΣDDT in dietary meat, fish, poultry, eggs
- ◐ ΣDDT in dietary milk products (fat basis)
- ◒ ΣDDT in human milk (fat basis)
- ⊠ ΣDDT in crude fish oil
- ◨ ΣDDT in crude vegetable oil
- ◑ ΣDDT in human adipose tissue
- ◆ ΣDDT in sewage effluent
- ◈s Multiple points

Residue values of 0.001 p.p.m. plotted at 0.001 p.p.m., as are non-detected values

Figure 1. Global distribution of chlorinated hydrocarbons and other trace substances in the biosphere, according to Appleby[1]

from the fact that direct injection into the air by spray application is very common, any DDT in soil or deposited on plants is shown to disappear primarily by vaporization[4, 5]. Typical half-life times in soil seem to be 5 years, varying somewhat with soil type and other conditions, such as total content and degree of depletion. These two facts indicate that transport processes by and through the atmosphere are of basic importance for our understanding of regional and global distribution problems.

If we consider the large-scale conditions for transport and distribution of trace substances in and by the atmosphere, it soon becomes clear that they are determined in an important way by two things, namely by the chemical characteristics of the substance itself as well as by the meteorological transport, mixing and other processes in the atmosphere. The chemical properties of trace substances introduced by man (not only pesticides) range from those of almost noble gases to those of reactive water-soluble substances with or without any vapour pressure which can only be present in the form of aerosols. In the subsequent sections we shall point out the importance of both these factors.

THE ROLE OF RESIDENCE TIME FOR THE GLOBAL TRANSPORT AND DISTRIBUTION OF A TRACE CONSTITUENT

For the cycle and behaviour of pollutants injected by man we can restrict our discussion to that part of the atmosphere which is bounded by the tropopause in 8–16 km altitude and by the earth surface. It is known as the region of active weather and is called the troposphere. All trace substances present in the troposphere have certain average global residence or lifetime (we prefer the expression residence time) which is determined by the efficiency of their removal by rainout, washout, chemical destruction and such processes at the earth surface as absorption, impaction, sedimentation, etc. If this efficiency is low, the residence is long, and vice versa.

The magnitude of the residence time of a constituent is very important with respect to its global atmospheric transport and distribution. If we assume the injection rate of a trace constituent into the atmosphere to be balanced by its removal rate on a global basis, i.e. if we assume steady state conditions, the average variability throughout the troposphere given, for instance, by the standard deviation σ is approximately inversely related to the residence time T, as demonstrated in *Figure 2* (in which all relevant data on atmospheric trace constituents so far available are compiled). Based on these results it can be estimated that σ is smaller than about 0.3 if T is longer than about half a year, which is approximately the case for carbon monoxide. This is an important realization. It means that a constituent does not on the average vary much more than by a factor of about 2 if its residence time is longer than about half a year. This does, of course, not exclude the fact that concentrations are much higher near sources, but we are here primarily concerned with the large-scale distributions. If, therefore, we know that a constituent has a T of more than about half a year, we need not be concerned about the atmospheric transport processes at all if we want to know whether it affects remote areas. It passes even the equatorial region sufficiently fast to be present in both hemispheres at about the same level if the sources are preferentially located in one hemi-
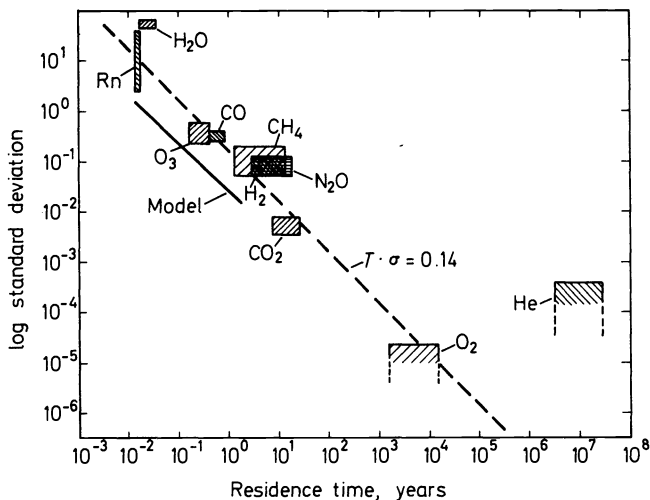
Figure 2. Log standard deviation from the average tropospheric mixing ratio of a trace gas as function of residence time, according to a compilation of all available data[6]. The size of the boxes gives the uncertainty of the data. For helium the measuring method is not accurate enough to obtain the real variations; for oxygen the technique applied is on the limit. The dashed line indicates a representative line through the data. The solid line represents calculations for a simple atmospheric model.

sphere. If, on the other hand, a constituent has a T shorter than half a year, the tropospheric transport mechanisms become more and more important for our understanding of its distribution within the troposphere. In this case the average concentration will vary considerably with the geographical location and climatological condition and will decrease considerably with increasing distance from the source area.

THE FACTORS THAT DETERMINE THE RESIDENCE TIME OF A TRACE CONSTITUENT

The question which arises at this point is what determines T and what do we know about T for pesticides and related pollutants? We can generally say that T is to a large extent determined by the chemical properties of the constituent because they control the efficiency with which the various cleansing mechanisms of the atmosphere work. This efficiency is, for instance, very low in the case of a stable and inert gas which does not absorb at the land surface and at the aerosol particles in the air and is not or only slightly soluble in the ocean water. In this case it has no choice other than to stay or accumulate in the atmosphere. Noble gases of the atmosphere are the best examples. They have accumulated during the earth's history in the atmosphere and are very stable constituents of the atmosphere which show no variations. More interesting for our considerations is trichlorofluoromethane (CCl_3F), which is exclusively produced by man and widely used as a propellant solvent for aerosol dispensers, etc. It behaves almost like a noble gas, is very stable,

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inert and only slightly water-soluble and has apparently accumulated in the atmosphere over about the last 5 years, as Lovelock, Maggs and Wade[7] have shown. They have measured the north–south profile over the Atlantic ocean in Winter 1971/72 as shown in *Figure 3*. This profile can be explained by the accumulation of the total production of 1.2×10^6 ton up to the end of 1971, assuming a doubling time in production every 3.5 years and a release primarily in the northern hemisphere. The sea-water concentrations seem to decrease rapidly below the mixing layer in about 100 m and indicate that the total amount of CCl_3F dissolved in the ocean is small compared with that present in the atmosphere. CCl_3F must, therefore, have a very long residence time of many years. Even if in this case the condition of steady state is obviously not fulfilled, so that *Figure 2* does not apply correctly, *Figure 3* shows that for all practical purposes the differences between the north and south poles are not very large. Sulphur hexafluoride (SF_6), another inert pollutant, which was found in the atmosphere at a level of about 10^{-13} parts by volume[8] can be expected to behave in a similar way.
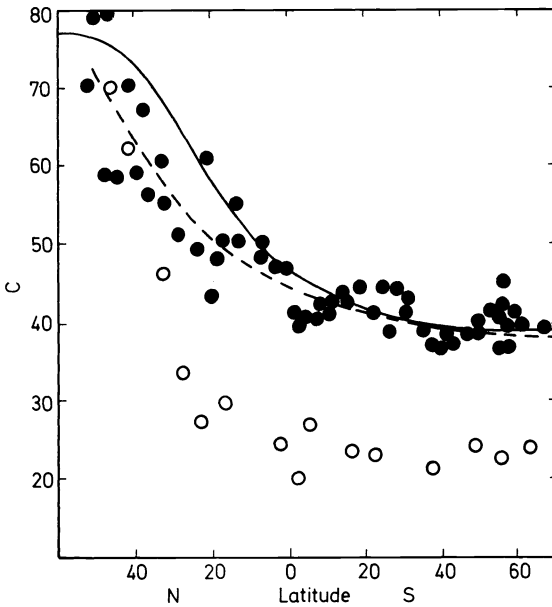

Figure 3. Measurements of CCl_3F in air and sea-water by Lovelock *et al.*[7]. The solid line assumes release in the northern hemisphere with a doubling time of about 2 years and accumulation. The slope of the dashed line, which is the best fit of the data, is less steep, which agrees with a longer doubling time of CCl_3F of about 3.5 years

The efficiency of removal is, on the other hand, high, if the substance is present either as a reactive gas which readily adsorbs or chemically reacts with aerosols and with the land surface and which is easily soluble in ocean water, or which has such a low vapour pressure that it can only exist as an aerosol. Aerosols have a residence time T of about a week, and if the fraction ε of a

trace gas is attached to the aerosols, its residence time T_g must be equal to or smaller than T_a/ε since there are still other removal processes at work than rainout and washout of aerosols. If, for instance, $\varepsilon = 0.1$, T_g must be shorter than 10 weeks. Absorption on aerosols is, therefore, important for T_g. The fraction ε depends on the chemical properties of the trace gas but also on the relative concentrations of gas to aerosol and on the saturation vapour pressure. If the concentration of the gas is high—for instance in the p.p.m. range—the amount adsorbed on aerosols is very small, because in clean air the aerosol concentrations are only about 50 µg/m³ or less. If, on the other hand, the gas concentration is small compared with that of aerosols, ε may be large. SO_2 is a good example which in most parts of the troposphere is to a large extent oxidized to sulphate so that its residence time can not be much longer than that of aerosols. If a trace constituent has no vapour pressure and can only exist as an aerosol, its residence time is close to that of the natural aerosols, i.e. about a week, and widely independent of its chemical nature.

THE CHEMICAL CHARACTERISTICS OF DDT AND OTHER CHLORINATED HYDROCARBONS AND THEIR ATMOSPHERIC RESIDENCE TIME

Let us now apply these considerations to two important examples of chlorinated hydrocarbons, DDT and PCB. These are among the most abundant substances of this type on a global scale. Although they have received much attention in recent years, very little effort was devoted to the question of their presence, behaviour, transport and distribution in the atmosphere and the exchange with the adjacent reservoirs of ocean and soil. Let us critically review our present state of knowledge.

Table 1. Chemical data on some chlorinated hydrocarbons for 25°C[10]

	DDT	Lindane	Dieldrin	Aldrin	Aroclor 1260 $C_{12}H_4Cl_6$
Vapour pressure (mmHg)	1×10^{-7}	1×10^{-5}	1×10^{-7}	6×10^{-6}	4×10^{-5}
Solubility in water (µg/l)	1	7×10^3	3×10^2	2×10^2	3

Table 1 gives some useful chemical data for our discussion. We see that, in general, the vapour pressures and solubilities of pesticides and PCBs are very low. Aroclor 1260 is a mixture of different PCBs but with a chlorine content almost as high as those found in the environment. Since both the vapour pressure and the solubility of PCBs decrease with increasing number of chlorine atoms, the values of the environmental PCBs should be equal or even lower.

DDT and the PCBs are both similar to CCl_3F and other fluorochlorine

carbon compounds known under the trade name of Freons in inertness and stability, but their vapour pressures are much lower. (CCl_3F has a vapour pressure of about 760 mmHg at 25°C.) One would expect from this that all these substances should occur in the atmosphere in the vapour phase but with ε values much larger than with CCl_3F, for which ε must be expected to be very small (no data available). The only data we found in the literature on ε were for DDT for two urban and two rural sites in the US[9] ranging from $\varepsilon = 0.31$ to 0.93 for total DDT concentrations of 3.8 to 6.6 $\mu g/m^3$, and $\varepsilon = 0.5$ for 600 $\mu g/m^3$. It is uncertain whether the increase in ε is typical for the 100 times higher concentration. If it is representative, we may expect even lower ε for areas with lower aerosol concentrations. These data on ε indicate residence times of DDT not much longer than that of natural aerosols, i.e. about a week or even less. This means that we should find considerable differences in DDT concentrations if we proceed from source areas to unaffected clean air areas. How does this agree with observations? According to Stanley et al.[9], concentrations were lowest at times when no spraying was reported in the area and in urban areas. These concentrations, which may be considered roughly representative for surface air over the US continent, ranged between 1 and 5 ng/m^3 for DDT, in agreement with some earlier data. Recently data from four measuring stations in West Germany became available[11] which gave the following average values of DDT concentrations (in g/m^3) for the year 1970:

Westerland (coast of North Sea)	0.35×10^{-9}
Waldorf (northern part of W.G.)	0.24×10^{-9}
Deuselbach (western part of W.G.)	0.54×10^{-9}
Schavinsland (mountain in the Black Forest, southern part of W.G.)	0.37×10^{-9}

All these stations are located in non-polluted rural areas, and they can be considered fairly representative of average conditions in Central Europe. Risebrough et al.[12] measured over the Atlantic ocean near Barbados in the trade winds and found 8×10^{-5} ng/m^3 on aerosols (no attempt was made to determine the gas phase). If very tentatively we estimate the total DDT content to be 10 times higher, it would still be 10^3 times lower than over the USA. This factor of 10 is based on the estimate that the total aerosol content in Barbados is about 10 times lower than in the US and on the assumption that the ratio of the specific DDT concentration of the aerosol to the gas phase concentration remains the same. If these differences in total DDT content are representative, they may point to even shorter residence times according to Figure 2, implying that the fraction present in the gas phase would be much lower than we assumed. Clearly the question of ε and T for pesticides and PCBs must be considered wide-open owing to lack of data, but the evidence so far available points to residence times similar to those of aerosols.

Since no ε data seem to be available for other chlorinated hydrocarbons and no data on their concentrations in the atmosphere, we can only infer from Table 1 that the situation with respect to ε and T may be comparable for DDT. But it is possible that for some other types of pesticides not considered here owing to a complete lack of data the combination of chemical properties is such that small ε values and long residence times result, and it was the purpose to point to the implications of such possibilities.

THE DDT BUDGET OF THE ATMOSPHERE

We can also obtain information on the mean tropospheric residence time of DDT by global budget considerations as attempted by Woodwell, Craig and Johnson[4]. The DDT burden of soils suggests that DDT does not accumulate there but leaves the soil primarily by evaporation into the atmosphere[5]. Half of the DDT in soil seems to disappear after a few years but the loss rate may slow down with decreasing soil content. Considering the fact that large proportions of DDT enter the atmosphere more or less directly after application, it is reasonable to assume that the main route of most DDT produce is via the atmosphere, starting as vapour. If we accept an annual production of 10^{11} g and take the volume of the troposphere $V = 5 \times 10^{18}$ m^3, the *average* tropospheric DDT concentration would be

$$c = \frac{10^{11}}{5 \times 10^{18}} \times T = 2 \times 10^{-8} \times T \frac{g}{m^3} = 20 \times T \frac{ng}{m^3}$$

where T is the residence time in years. Woodwell *et al.*[4] suggest an atmospheric residence time of 4 years, which would correspond to $c = 80$ ng/m^3. This is higher by one order of magnitude than the US surface air data given above, and much higher than the Barbados data. This points to much lower residence times. If we take T to be 1 week, i.e. $T = 2 \times 10^{-2}$, we obtain $c = 4 \times 10^{-1}$ ng/m^3. This falls between the US and the Barbados data but seems still to be somewhat high. Since the figure for the global production rate can not be grossly wrong and since it is difficult to reduce T much further, the only way to eliminate this discrepancy is by assuming higher gas phase concentrations, i.e. smaller ε values, implying that the few data available are not representative and that T is longer. We feel that with the data presently at hand it is not possible to resolve this question. With the magnitude of T for DDT and all the other pesticides, chlorinated hydrocarbons, etc., uncertain, it is on the basis of *Figure 2*, rather difficult to assess the importance of the meteorological transport processes in the global distribution and to give a reasonable estimate of the large-scale variability of these substances. In a final section we shall therefore briefly review the main transport mechanisms within the troposphere in the case where T is short, as implied by the observed ε values. But before we do this we wish to point out that it is very worthwhile to study this question of T further in a more systematic way, not only for DDT but for a variety of substances, including the PCBs.

Woodwell *et al.*[4] conclude that DDT must finally enter the mixed layer of the oceans, from where it is removed to the deep sea by transport through the marine biosphere, in which it becomes enriched via the food chain and where it comes to rest (see, e.g., ref. 13). This would end the environmental cycle.

THE MAIN TRANSPORT PROCESSES IN THE TROPOSPHERE

If, as might be the case, the residence time of DDT and other pesticides is similar to that of aerosols, the transport processes of advection and large-scale mixing, together with the various removal mechanisms for aerosols,

such as rainout, washout, sedimentation, etc., will become important. This will result in considerable regional differences in concentrations. In any case the important first step is the injection into the surface over land and spread throughout the planetary mixing layer of about 1–2 km thickness. The intensity of mixing in this layer shows a strong diurnal variation with a maximum around noon, resulting in a fairly uniform distribution of all trace substances up to these altitudes. Once spread in the vertical, transport in the horizontal direction can start to become effective. We can distinguish three main large-scale transport processes, which we will briefly explain.

(1) West–east transport in the west wind circulation belt primarily between lat. 30° and lat. 70°. This circulation shows strong variations with time, longitude and season. If it is well developed, air masses from the North American continent are transported within a few days to Europe, carrying with them fractions of the original aerosol burden. This could be shown, for instance, by observations of the mineral dust and fly ash content across the North Atlantic[14]. DDT and other pesticides can therefore be transported (easily) from continent to continent across oceans. During this process the circulation spreads to both southern and northern latitudes, so that even polar and subtropical latitudes are affected.

(2) Another large-scale transport mechanism is in the trade wind belt between about 20°N and 20°S. In this belt the air moves east–west up to the middle troposphere and higher at the equator in a more or less steady stream. A well-known example of aerosol transport across the equatorial Atlantic Ocean is the dust from the Sahara which reaches Central America. This process occurs fairly regularly with pulses throughout the year, and is so important that it provides most of the material for the deep sea sediments in the Atlantic[15]. The DDT found in the Barbados area must have originated from Africa or Europe[12].

(3) It is now well established that it takes on the average about 1 year for a tropospheric air molecule to cross the equator and enter the other hemisphere. It can easily be shown that for a constituent with a residence time of T (in years) only the fraction $\varphi = e^{-1/T}$ can on the average penetrate into the other hemisphere. For aerosols $T \approx 2 \times 10^{-2}$, so that φ is practically zero. It can be concluded that there is very little exchange of short-lived constituents between the hemispheres, so that, for instance, the DDT found in the southern hemisphere must have originated there. If the residence time of DDT were 1 year, about 30% could be exchanged between the hemispheres. This illustrates fairly well the role of T in the global distribution. These conclusions were excellently confirmed by the spread of debris from Russian nuclear tests during 1958–1959[16], which was stopped at the equator and did not penetrate farther south.

In conclusion, we may say that one of the major difficulties in understanding the global transport and distribution of pesticides and similar inert, chemically stable substances with a small but measurable vapour pressure is the lack of knowledge of their chemical behaviour in the atmosphere which determines their average residence time. Until this is better understood little progress can be expected in this field.

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