

**FINAL REPORT**

**SURVEY OF  
MATHEMATICAL MODELS**

**AD HOC COMMITTEE ON MATHEMATICAL MODELING  
RESEARCH PANEL  
FEDERAL WORKING GROUP ON PEST MANAGEMENT  
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FINAL REPORT

SURVEY OF PREDICTIVE MATHEMATICAL MODELS

Ad Hoc Committee on Mathematical Modeling

Research Panel

Federal Working Group on Pest Management

Dr. P. R. Datta, Chairman	EPA
Dr. J. Mossiman	NIH
Mr. L. S. Joel	NBS
Dr. J. E. Fletcher	NIH
Dr. R. G. Nash	USDA
Captain T. A. Miller	DOD
Mr. Duncan MacDonald	DOI
Dr. William Schaff	NOAA
Dr. R. J. Peterle	Ohio State (ERDA)
Dr. S. D. Haseltine	Ohio State (ERDA)
Dr. Arthur Emery	ONR (DOD)

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OVERVIEW

The work of the ad hoc Committee on the survey of mathematical model(s) capable of predicting the fate and movement of pesticides or other toxic pollutants in the environment has been terminated. In its surveillance of the existing global models, the Committee finds that the Randers and Meadows (R&M) model is the most detailed global model available, and that other available models can be integrated into it. The R&M model has been found to be suitable for refinement and adaptation as new data and knowledge become available.

The interagency committee members from NBS have implemented the DYNAMO simulation language with the R&M model. Thousands of parametric "test runs" using the primitive compiler, DYNAMO O, with various scenarios and the available data -- or imaginary data in various compartments with or without modification of the structure of the model by the addition or deletion of parameters or compartments -- were conducted at NBS for purposes of: (1) gaining familiarity with the interfacing of the R&M model computer technology and the DYNAMO simulation language; (2) assessing the structure and extension of the parameter compartments of the R&M model for purposes of defining the refinements required; (3) determining the priority of "data needs" in each compartment of the model via sensitivity analysis; and, (4) analyzing the usefulness of the model concept in the decision-making process of pesticide regulatory matters.

After an examination of these results, it became apparent to the ad hoc Committee members that the perplexities and complexities of simulation DYNAMO language computer model(s) for application to DDT as a model pesticide were overwhelming, primarily due to the paucity of data on DDT in each compartment of the R&M model; although, in truth, there is more voluminous data on DDT than any other pesticide.

Furthermore, the "test run" results revealed "data needs" in various compartments, for example:

1. DDT in the abyssal layer of the ocean;
2. Sedimentation below the mixed layer of the ocean;
3. Benthic fish rate of uptake and elimination of DDT;
4. Photodegradation rate of DDT in the atmosphere;
5. Evaporation from the ocean surface and the oil layer of the ocean;
6. DDT in fresh water lakes and sediment;
7. Uptake and elimination of DDT by fresh water fish or other aquatic organisms; and,
8. Rate and flow of DDT from an aquatic environment to terrestrial environmental organisms, such as birds.

An in-depth literature survey of DDT data for each compartment of the model was subsequently completed by Drs. Peterle and Haseltine of Ohio State University (under a \$14K contract from ERDA, See Appendix 2). The accuracy and reliability of these data, however, were never verified due to a lack of funds, nor was there ever an opportunity to incorporate these data into the appropriate compartments of the model.

After the "test runs" had been completed and analyzed, the ad hoc Committee recommended, and was authorized to purchase (EPA Project #2050407), a second generation DYNAMO compiler system vastly superior to the DYNAMO 0, called DYNAMO II<sub>F</sub>, which is adaptable to operation on a UNIVAC 1108 computer.

This system was finally installed at NBS after a lengthy delay due to legal complications in the procurement and contract procedures. The compiler has recently (July, 1976) undergone acceptance testing at NBS. While it appears that the DYNAMO simulation language, using the DYNAMO II<sub>F</sub> compiler, is adequate for the resolution of the fate and movement of a pesticide pollutant in the environment, the complete integration and expected "test runs" have not been conducted due to a lack of funds or transfer of funds from EPA to NBS. A request for funds was denied by EPA.

A systematic investigation regarding "sensitivity analysis" was also not conducted due to a lack of funds. It is of the utmost importance that sensitivity analysis be conducted before the use of any mathematical model to predict the fate and movement of a pesticide (such as DDT) or other pollutant in the environment.

Other related activities of the Committee included: (1) the obtaining of several ocean core samples from the U.S. Geological Survey, and the arranging for their preliminary analysis by the Buefort Laboratory of NOAA. However, a further systematic investigation was not initiated due to the Committee's funding constraints; and, (2) the securing from the United Nations Focal Point Information Center located in EPA information identifying the

sources of data on the behavior of DDT in the environment in various countries of the world. However, none of these data was ever obtained due to a lack of funds and administrative authorization.

The consensus of the interagency committee members is that the predictive modeling of pesticide flow in the environment is extremely important:

- (a) To gain knowledge about the effect of a pesticide in the ecosystem;
- (b) To resolve controversy over the use of a pesticide;
- (c) To avoid use of an ascientific method;
- (d) To obtain scientifically informed judgments on the behavior of a chemical or pesticide in the environment; and, finally,
- (e) To provide a framework for integrating scientific information with social value judgments in a manner which is scientifically, socially, and ethically defensible.

For these reasons, a predictive mathematical model would be an invaluable tool in the policy and decision-making process and of inestimable worth as an aid in evaluations for the registration and regulation of pesticides.

At present, the ad hoc Committee is disbanded until EPA or other agencies express an intent to support the Committee's recommendations.

## INTRODUCTION

Pesticides are used as chemical agents for the management of pests in agriculture and health. The uses of pesticides have considerable economic benefits in the production of food and fibers and in control of insect-borne diseases in public health. The presence of residual pesticides and/or their degradation products in plants and animals, including man, and in soil, air, water, fish, etc. of the biosphere constitutes environmental pollution. The persistence and toxicity of these pesticidal pollutants could result in the contribution of adverse effect(s) on human health and welfare.

Reliable methodologies for the quantitative measurement (ppm level or less) and for the identification of residual pesticides and/or their degradation products are currently available for direct monitoring and for the establishment of tolerances. However, the rates of movement of residual pesticides and/or their degradation products and their degree of bioaccumulation, if any, are difficult to measure directly.

Since it is desirable to understand the fate and movement of pesticides and/or their degradation products in the ecosystem now and in the projected future, the development of predictive mathematical models is of importance. Such predictive mathematical models could be used as an analytical tool in the formulation of "balance decisions" and scientifically informed judgments on the use patterns of a specific pesticide.

Based on the published literature, there have been relatively few serious attempts to develop true quantitative analytical methodologies as models useful

for determining and/or predicting the residual fate of pesticides and/or their degradation products or other pollutants in the environment or to survey those which are available. Thus the *raison d'être* of this ad hoc Committee.

#### BACKGROUND

On March 21, 1973, the Chairman of the Research Panel, FWGPM, asked Dr. P. Datta of that Panel to organize and chair an interagency and interdisciplinary ad hoc Committee to assess the "state of the art" of mathematical models capable of predicting the behavior of pesticides in the environment, and to focus attention on the residual fate of DDT via models.

On July 18, 1973, Dr. Datta chaired the first meeting of this ad hoc Committee which was made up of four Research Panel members as well as various resource personnel from NIH, NBS, USDA, NOAA, DOD, and EPA. At this meeting the Committee discussed, clarified, and resolved its mandate. The ad hoc Committee's charges were perceived to be basically two-fold and it was decided to pursue them simultaneously. These were:

- 1(a) To provide the Research Panel with a compendium of mathematical models which depict -- or attempt to -- the behavior (i.e., degradation, transport, modification, biomagnification, etc.) of pesticides in soil, air, and other environmental components;
- (b) To indicate to the Panel those models most suitable and useful for assessing and predicting pesticide residues in the environment and the health impact(s) thereof;

- (c) To classify, organize, and evaluate all models related to the behavior of DDT in the environment. DDT was chosen as the model compound because substantial data on DDT is in the published literature; and,
- 2. To suggest the critical need(s) for research relating to this problem area.

The ad hoc Committee met for four monthly meetings and reviewed all available mathematical models on DDT and other pesticides. These models are of two types:

- (1) Those which are primarily descriptive of a specific physical, chemical, and/or biological process or a concatenation of such processes; and,
- (2) Those models which are primarily predictive -- i.e., intended only to forecast changes in state over time of an aggregate system, using parameters which are generally composed of various processes in ecosystem compartments.

Published models were analyzed for mathematical assumptions, functions, and underlying theories of mathematics, and for fundamental assumptions which determine the behavior of specific pollutants in the environment.

The Committee specifically looked into the explicit and implicit explanations contained in each model on DDT as to: how the decisions were arrived at; what assumptions were included; what information was included; how the information or data was processed; whether the model under examination made a "balance decision" on DDT behavior in the environment; and, relevancy of hazards to wildlife, fish, flora, fauna, and humans.

As a result of several meetings, the ad hoc Committee reached a consensus about the following items:

- (1) That the literature searches being conducted by individual Committee members for, and of, available information sources needed to complete the compendium of mathematical model(s) were proceeding satisfactorily and, in due time, the cumulative reference materials would be transmitted to the ad hoc Committee chairman for compilation, etc.; and,
- (2) That the survey of the theoretical mathematical models must be supplemented by actual computer runs of existing models, using DDT as a model compound, in order to gain information on the computational behavior of the models and to learn computational responses to assumptions of the models and resolution of various assumptions embodied in the various values of DDT parameters and, therefore, an Action Program for this specific purpose must be recommended to the FWGPM.

Such an Action Program was deemed urgently needed in order to:

- (a) Indicate to this Committee and to the Research Panel of the FWGPM which model(s) is/are the most suitable and useful for evaluating and predicting DDT or other pesticide residues in environmental media (i.e. soil, water, and air) and the health hazards thereof; and,
- (b) Identify the critical needs and priorities of research data relating to the problem areas of environmental safety and health safety.

COMMITTEE'S ACCOMPLISHMENTS IN THE "ACTION PROGRAM"

In late 1974, pursuant to these circumstances and findings, the above projects were sponsored as follows: NBS, FY 75, Project #2050156, Dr. Goldman and Mr. Joel; EPA, FY 75, Project #2050407, Mr. Dan Cerelli of TSD/OPP; and an information retrieval FY 75, support project of ERDA (under contract to Dr. Peterle of Ohio State University).

The objectives of these interagency projects were: (1) to test existing predictive mathematical models; (2) to secure a literature survey of the published data on DDT by information retrieval; and, (3) to identify critical research needs in this field of modeling to facilitate future predicting of the fate and movement of DDT or other pesticides in the ecosystem of the biosphere.

The ad hoc Committee members, being volunteers, could not dedicate their full time to the appropriate research needed for the "Action Program." Drs. J. Mossiman and J. E. Fletcher of the Computer Division of NIH completed the survey of the concepts and underlying assumptions of published predictive models; however, they were not available, due to time constraints, to "test run" the existing predictive mathematical models.

During their preliminary survey, four existing global models for DDT were identified. It was decided to confine the "test runs" to the Randers and Meadows global model (Chapter 3 of Toward Global Equilibrium: Collected Papers, Wright-Allen Press, 1973) because it was apparently the most nearly complete and the report included the listing of the computer program for the model in DYNAMO language.

Bearing this in mind, the Committee agreed to undertake the above FY 75 projects in the following terms:

- (a) Mr. L. S. Joel, under the guidance of Dr. A. J. Goldman and the direction of Dr. W. H. Kirchhoff (Deputy Director of the Office of Air and Water Measurements, NBS), would "test run" the R&M model using a "DYNAMO" compiler obtained (gratis) from UNIVAC until EPA transferred \$20K - \$25K to allow purchase of a second-generation  $II_F$  compiler and to cover the costs of computer time sharing and electronic data processing;
- (b) Dr. R. J. Peterle of Ohio State University with \$14K of ERDA funds, in close cooperation with Mr. Dan Cerelli of TSD/OPP/EPA, would gather all the relevant data base information on DDT required for each compartment or component of the R&M model from the published literature through their respective information-retrieval systems; and,
- (c) The results of the "test runs" and the literature survey would be submitted to the ad hoc Committee intermittently for evaluation purposes and for identifying critical research and data needs required for the modeling activity.

The Committee directed NBS to pursue the following activities regarding the evaluation of the R&M mathematical predictive model:

1. Evaluate the mathematical assumptions in depth underlying the model parameters;
2. Evaluate the structure of the model;
3. Operate the model and make predictive runs employing various scenarios -- future rate application, non-application, etc.;
4. Perform parameter sensitivity analysis of the model;
5. Investigate the possibility of refinement of the model (disaggregation, seasonal cycles, fish type, river type, soil type, sediment type, etc.) and model extension; and,

6. Estimate the scope of applicability of the model and identify critical data needs and directions for its refinement.

Accordingly, in January 1975, Mr. L. S. Joel of the Applied Mathematics Division of NBS began to "test run" the model documented in J. Randers' "DDT Movement in the Global Environment (which is Chapter 3 of Toward Global Equilibrium: Collected Papers, edited by D. L. Meadows and D. H. Meadows, Wright-Allen Press, 1973) with the following goals:

- (a) To verify the portability of the model by operating it through a DYNAMO compiler compatible with the NBS computer and its operating system;\*
- (b) To check that the system dynamics model accurately represented the differential equation(s) system which follows directly from the defining transfer relationship;
- (c) To identify the most critical model assumptions and parameters in terms of sensitivity of outputs; and,
- (d) To identify the model assumptions most questionable because of the absence of corroborating data (or the presence of alternative plausible hypotheses also compatible with data); and,
- (e) To identify critical directions and data needs for refining the model.

Also, in 1975, Drs. R. J. Peterle and S. D. Haseltine at Ohio State University, and Mr. Dan Cerelli of TSD/OPP/EPA, began to search all the literature on DDT for each compartment of the model or components of the ecosystem. Drs. Haseltine and Datta also searched all the EPA information files of the DDT hearings to obtain data, and Dr. Haseltine indexed the literature references on DDT which

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\* The "test runs" were conducted using a rather primitive DYNAMO O compiler obtained (gratis) from UNIVAC.

belonged within the various parameters of the R&M model. The listing of these references is included in Appendix #2. After a cursory inspection of this listing, it was readily apparent that several of the published data and ongoing research were not reflected in the list. A further search of the literature for data on DDT was deemed warranted, but the necessary funds were lacking. A follow-up search is still needed.

The data from the above annotated literature list were not submitted, due to lack of funding by EPA, to academic institutions or other expert scientists in the various disciplines to evaluate and certify their reliability, accuracy etc. The Committee believes that the examination of these data would be a worthwhile task, since the evaluation of the model at NBS was substantially constrained to mathematical and system theoretical criteria only.

#### RESULTS OF "TEST RUNS"

Briefly, relative to the above-stated goals for the "test runs," the results showed:

- (a) The model per se is operable on a variety of computers (i.e., is "portable"), but difficulties with the DYNAMO compiler system may be encountered in transferring from one computer installation to another;
- (b) Computationally, the DYNAMO model is equivalent to the appropriate system of differential equations;
- (c) & (d) As might be expected, the outputs (DDT residues) are highly sensitive to some model parameters (transfer rates, etc.) and insensitive to others; and,
- (e) The model appears to be suitable for analysis of long-term global behavior of DDT (and other pollutants), but would require considerable revision to afford information about concentrations in a more finely grained ecosystem.

Accurate data is needed for critical parameters in the global model and a fortiori in any more detailed modifications.

These findings are discussed in detail later.

KNOWLEDGE GAINED IN THE USE OF THE DYNAMO COMPILER  
IN A SIMULATION SYSTEM

In evaluation of a model as a prototype for global tracing of pollutants, the total programming system which produces the outputs is as important as the actual model formulation, because such models might be constructed and run at a variety of sites with differing physical and operational computer systems. Thus, a narrative description of the implementation experience at NBS (on the UNIVAC 1108 computer) is pertinent to decisions about the utility of the Randers and Meadows model.

DYNAMO was originally developed in about 1959-60 for the IBM computer at MIT as a tool for implementing models according to J. W. Forrester's "system dynamics." A succession of refinements ensued as the modeling technique gained acceptance, primarily among industrial managers and some scientists. It seems to be particularly popular with ecological scientists with orientation toward "systems analysis." The DDT flow model of Randers and Meadows was apparently realized through a "second generation" DYNAMO compiler on an IBM computer, judging by the program listing in the published version of their report.

The DYNAMO compiler furnished to NBS by the UNIVAC Corporation was a translation by a Japanese contractor to UNIVAC, of the original DYNAMO system, into a form suitable for operation on the 1108 computer. This system is designated here as DYNAMO O.

The R&M model was transcribed for operation at NBS by making the modifications of the published version necessitated for conformity with the somewhat restrictive conventions of DYNAMO O.

After some time lost in the incorporation of the DYNAMO O compiler into the NBS computer executive system (exacerbated by occasional orientalism in the text of the compilers' documentation), the NBS computer replicated the model outputs in the Randers and Meadows paper and both the model and the compiler were provisionally considered operational. [The difficulty with the computer executive system is not unusual. In spite of much research and prodigious efforts at standardization over a period of almost 20 years, portability of complicated computer programs is a well-known pervasive source of problems in the use of computers. This is stated to mitigate, partly, the implied dissatisfaction with the DYNAMO O compiler.]

Subsequently, however, errors occurred in runs of the transcribed model with no changes other than variation of the basic time increment of the model (the magnitude of the smallest computational interval -- distinct from the model time "unit" which is 1 year), in the course of the numerical experiments comparing DYNAMO model outputs with those of Runge-Kutta integration of the difference equations. As the model was modified to include representations of additional flux processes (which were judged to be significant because of new baseline data, possible relevance to pesticides with physical characteristics different from those of DDT, or both), an increasing difficulty in running the modified versions and finally in compiling them was encountered. As a result, after the preliminary "test runs," the ad hoc

Committee recommended purchase of a second generation DYNAMO compiler system called DYNAMO II<sub>F</sub>, which is roughly equivalent to the version of DYNAMO used by Randers and Meadows, but amenable to operation on a UNIVAC 1108 computer. Purchase of this compiler was funded by EPA Project #2050407. This system has just recently (July 1976) completed acceptance tests.

Implementation of DYNAMO II<sub>F</sub> could not be initiated for six months after acquisition of the system was authorized as a result of contract negotiations with the proprietary owner of the system (such delays in acquisition of software systems are so commonplace as to escape comment, usually). The technical process of dovetailing DYNAMO II<sub>F</sub> with the computer executive system required two additional months.\*

#### STRUCTURE AND EXTENSION OF PARAMETERS OR COMPARTMENTS IN THE MODIFIED MODEL

The R&M model uses a set of "material budget" difference equations to trace over time the flow and accumulation of DDT among/in 5 major ecological "compartments" (soil, air, rivers, oceans, and fish), each considered as a single homogeneous worldwide aggregate. The flow, which is triggered by application of DDT and its mathematical analysis, stops short of considering the uptake of DDT by life forms higher than fish.

Randers and Meadows described the environmental flow of DDT as follows: "When DDT is sprayed onto a crop or in a home, only part of it reaches the target. The rest remains suspended in the atmosphere. Much of the DDT reaching the target also eventually finds its way into the atmosphere by evaporation from

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\* This DYNAMO II<sub>F</sub> compiler enabled proceeding with the most elaborate version of the model, in a form which is undoubtedly overburdened with little bits and pieces of phenomenological representations. The availability of the up-to-date DYNAMO compiler will facilitate any process of sensitivity testing and paring the system down to a form in which it will be more nearly realistic while maintaining the concision of Randers and Meadows original version of the model.

the soil. Once in the air, the pesticide can be carried long distances before it finally falls back on soil or into the ocean. Some DDT is also washed downstream in watersheds.

"Some of the DDT in the ocean will be taken up by plankton and other organisms; as the plankton are eaten by fish, the DDT enters higher animals. Ultimately, fish-eating birds and man can absorb DDT by eating the DDT-containing fish — this is the food chain effect. The concentrations of DDT usually become higher as it progresses up the food chain, an effect commonly called biological concentration. Some DDT also returns to the ocean through excretion from fish, or simply when the fish dies. DDT residues survive this long journey because of their great stability. DDT is removed from the environment at each stage through degradation in soil, in water, and in living organisms.

"Notice that we chose not to include in the model an explicit representation of higher levels of the food chain -- for example, fish-eating birds and human beings. This exclusion does not invalidate the accounting of DDT flows because the amounts of DDT that actually enter terrestrial organisms are very small relative to the flows included in the model. (The excluded small flows are important to ecosystem stability, however, because they are relatively concentrated.)

"There is reasonable consensus that Figure 1 does in fact represent the flow of DDT in the environment. Some disagreement may exist about the relative importance of DDT transportation in rivers, of the sedimentation of DDT in oceans, of the uptake of DDT in plants, and of local or regional differences in DDT concentration, but by and large the heated discussions on DDT do not

question the structure outlined here. This disagreement occurs over the precise numerical values involved in the processes illustrated in Figure 1. For instance, how fast does DDT break down? How much of it sediments? At what rates does it evaporate? By what factor does it concentrate in fish?"

Randers and Meadows also stated, "Experience with radioactive debris injected into the troposphere by nuclear explosions has established that mean half-life of residence in the atmosphere for small particles ranges from a few days to about a month. Following Woodwell, we assumed that these data also apply to pesticide crystallites and pesticide absorbed to dust particles. We thus concluded that once injected, DDT particles remain in the lower atmosphere for a period -- the precipitation half-life, PHL -- varying between a few days or a month. In that time they can easily move around the globe.

"The amount of pesticide degraded in the air by sunlight and reactive compounds is unknown (HEW publication "Pesticides and their Relationship"). However, given the short residence time (2 weeks) compared with the degradation half-life in soil (10 years), it seems safe to assume that the amount of DDT degraded in the atmosphere is small; hence it was neglected."

One could reasonably say that the R&M model at its given level of detail can possibly be strengthened, that is made more flexible and better approximative of our perception of the real world, by incorporating representations of additional sinks or reservoirs of DDT, sources of feedback between compartments and processes that mediate (primarily delay) flows between the compartments of the system. At a somewhat more demanding level of detail, but without

appreciably extending the objective of the model, that of estimating the global fate of DDT, the model can be expected to furnish more reliable time predictions if it is disaggregated to represent the effects of spatial and temporal concentrations resulting from variations in the physical milieu, e.g., meteorological conditions, and by extending the boundaries to include higher levels in the trophic chain, hence uptake and release at higher levels of bioaccumulation.

Randers and Meadows' assumption of relatively small flows in higher trophic levels was verified by the NBS model test runs in which a very crude replication of their "fish" equations was used as a representation of "higher carnivores", with their "DDT in consumed fish" as the exclusive source of input to this compartment and back-of-the-hand estimates of excretion and mortality rates furnishing a release rate to the soil.

Phenomena relating to the oceans are of critical importance to the determination of global persistence of DDT (and indeed of any readily dispersed microbiotic substance without sufficient volatility for the atmosphere to become its primary reservoir). For this reason further efforts and resources should be committed to attempts to improve the state of knowledge of, e.g., sedimentation in continental shelves and on the pelagic bottom, surface evaporation, degradation (metabolic and other), and all possible mechanisms of transfer from benthic regions to the mixed layer. This should be done irrespective of any decision to modify or refine the structure of the current model.

If degradation processes in lakes differ drastically from those in the oceans, and if lakes are non-negligible catchbasins for "wash off" in

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If degradation processes in lakes differ drastically from those in the oceans, and if lakes are nonnegligible catchbasins for "wash off" in

land masses, global longevity will be affected. Lake and pond phenomena should be studied more intensively, and in this case the model must be appropriately extended.

The principal mechanisms absent from the original R&M model are:

(1) photodegradation of DDT in the atmosphere, (2) evaporation of DDT from ocean surfaces, and, (3) sinking of DDT below the ocean's "mixed layer" into the benthic deep. For example, with the parameter values chosen, insertion of (1) and (2) led after 100 simulated years to a total of 30% less DDT in the 5 stipulated compartments (of the original model), but more than before in all but the ocean compartment. The sixth compartment postulated by (3), with the chosen parameters, proved a potent and quickly reached sink.

The needed modifications will entail substantive restructuring of the original R&M model and even more stringent data. The possible payoff would include the possibility of getting much closer to an assessment of perils, if any, associated with the persistence of DDT, because clearly exposure is more closely related to local concentration over time than to mean global presence.\*

In addition, the disaggregated modified model for the study of spatial concentration will permit one to apply the R&M type modified model to the investigation of the flow of water-soluble pesticides, such as kepone, or highly persistent toxic compounds such as PCB.

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\* During the study, a crude initial attempt in this direction was made, splitting the R&M soil compartment into two "continents." DDT was applied on one of them and the other received its burden through flows from the first. The experiment proved unrewarding because, totally lacking data, we had to assume all transport rates.

PAUCITY OR LACK OF DATA IN VARIOUS COMPARTMENTS

OF THE R&M MODEL

DDT in the Atmosphere

Randers and Meadows assumptions were consistent with information available at the time they formulated their model. Current literature continues to reflect great uncertainty concerning these matters. Woodwell and Craig (1971) estimate atmosphere residence time of DDT as high as 3.3 years. Bidleman and Olney (1973) determined atmosphere residence time over the Sargasso Sea at 40-50 days or "20 times shorter than previously estimated for DDT from rainfall. . .data." But note that their estimate is itself about 3-4 times greater than the 2 weeks cited by Randers and Meadows in 1968. Similarly, doubt has been cast on earlier estimates that the rate of photolysis of DDT is negligible in the atmosphere by Ivie and Casida (1971) who determined that pesticide decay in the atmosphere can be substantially accelerated in the presence of other compounds which potentiate photolysis. Because of these considerations and the possibility of evaporation of DDT from the ocean's surface which results in additional cycling of DDT into the atmosphere (discussed further below under "DDT in Oceans"), photolytic decay of DDT was incorporated into the revised model. Model runs using an "extreme" photodegradation rate (half-life of 0.1 year) reduced the time of total disappearance of DDT from the model ecosphere by 30%. The Committee believes that acquisition of data (unavailable during the study because of funding constraints) from researchers currently engaged in measurements of photodegradation and effective buoyancy of pesticides in the atmosphere is important.

### DDT in Soil

The R&M "best estimate" of the fraction of DDT applied by crop dusting that reaches the soil directly is probably low, in that they assume that the DDT which is not "on target" is all carried by convection into the atmosphere. It seems more likely that a substantial fraction falls to earth near the sprayed target (Woodwell, 1971; Cramer, 1972). As R&M point out, in the absence of definitive physical experiments, one can "experiment" with the model by varying values of the model parameter ABF (See Appendix 1), which defines the function of applied DDT which is deposited on soil directly. In any event (confirming intuition), the short term effect of changing this fraction in model runs is great only for "soil" levels of DDT, and the long-term effects are negligible in all compartments.

Woodwell, in 1971, stated that the chemical decomposition of DDT in soil was probably greater than had been assumed previously (R&M information about degradation reflects research prior to 1968). Members of the ad hoc Committee have been told informally at several symposia that researchers believe that the chemical degradation of DDT (in air and water as well as soil) is related to pH and temperature and is probably not negligible, as assumed by R&M, in comparison to biological degradation.

As with the soil/air partition of applied DDT, independent variation of the degradation rate in soil and the solution rate over the (fairly substantial) ranges defined between the R&M "optimistic" and "pessimistic" values, produced very small long-term effects in runs of the model. Increasing the solution rate produced a fairly large rise in the level of DDT in "rivers" over the short term, a fact which will be discussed under DDT in Rivers and Lakes.

The Committee feels that the DDT soil data needs further scrutiny and that the analytical methods used before 1968 for measurement of DDT residues also need to be reviewed.

#### DDT in Oceans

The oceans in the R&M model are a vast storehouse toward which virtually all paths point and in which all DDT, except for some minor sinks ashore (degradation in soil) and some inconsequential losses through "fish consumed" quietly degrades over a period of about 100 years.

On balance this scheme is plausible, but its integument displays some lesions into which the virus of skepticism may enter. Firstly, R&M assume that DDT brought to the ocean surface will eventually dissolve if not ingested. But Woodwell suggests that some of the pesticide strongly sorbed to larger particles of other matter may sink to the bottom over a period of 4 to 7 years. Assuming sedimentation, the disappearance of DDT into the abyss could be fairly abrupt, and indeed, model runs with this effect included showed DDT reduced to zero levels in the mixed (upper) layer of the ocean in about 2/3 the time for this to happen in the standard model. But this, too, is open to question. DDT at great depths can be considered banished to the figurative abyss only if no route of return to upper levels exists. There is very little knowledge in this area. Recent research at the Woods Hole Oceanographic Institute resulted in findings of negligible amounts of DDT in two or three core samples (suspected, at that, of being contaminated in the trip to the surface), and examples of benthic fish with low concentrations of DDT, but high concentrations of DDE.

(Many ocean core samples were obtained from the U.S. Geological Survey for analysis by the Buefort Laboratory of NOAA. Some samples were analyzed along

with a few benthic fish, turtles, etc. The Committee was unable to invite the researcher to present his data at a Committee meeting due to a restriction of funds.)

At the ocean surface, R&M exclude representation of evaporation on the grounds that the concentration of DDT in the ocean is very small and, that if significant evaporation occurs, "the DDT will simply cycle back again through the atmosphere and settle back on land or water." This statement provokes some criticism of the conceptual elaboration of the R&M thesis because it casually dismisses the application of a basic notion of the system underlying Meadows' cosmogony - that of feedback analysis.

Moreover, in adducing low concentrations as a justification for the omission, R&M disregard the fact that the level of DDT in the ocean in their model is several orders of magnitude larger over time than the level in any other compartment, so that with the model's "standard" formulation of exponential rates of release depending on the absolute magnitude of the source, even small rates would result in the transfer of large quantities to the atmosphere. Evaporation from the ocean, if it occurs to any substantial extent, can certainly affect the duration of the DDT life cycle appreciably, a fact which was borne out by model runs in which evaporation of DDT from the ocean surface was introduced (constrained by the fraction of DDT in the ocean considered to be contained in the surface microlayer and hence subject to evaporation).

#### DDT in Rivers and Lakes

R&M treat rivers as conduits which transfer small amounts of DDT directly from the soil compartment to oceans (delayed by the low solution rate). Thus, the identification of all fresh water bodies with rivers is explicated in the text of their paper, but merely tacit in the model. In point of fact, it can be

conjectured that large lakes (and possibly small ones, also) could be a critical distinguishable component of the system of flows of DDT in the biosphere, their small fractions of the earth's water volume and surface area notwithstanding.

Lakes acting as drains in the vicinity of application sites (and to a lesser extent elsewhere with respect to precipitated DDT) capture some portion of the pesticide. Typically, concentrations found in lakes vary (Woodwell, 1970; Peterle, 1971; and Portmann, 1971) in an interval far higher than concentrations in rivers or in the ocean. In lakes, sedimentation might produce sinks for appreciable amounts and, concomitantly, lakes are feeding troughs for lacustrine biota, thus allowing for metabolic degradation of some DDT (along with chemical degradation, if any, occurring in benthic aquatic environments) and transmittal of some upward through the food chain. Uptake of DDT by fresh water fish, of course, affords justification for reopening the question of extension of the boundary of the basic model to include some higher level food chain flows, in spite of the lack of strong effect exhibited by previously mentioned model runs representing ocean fish as DDT donors to extra-aquatic predators, because total flows into and from a "carnivore" compartment may not, after all, be negligible in their effect on global fate.

A summer intern at NBS conducted a search for data on freshwater lakes and found that very little is known about the rates and routes of DDT transport in and out of lakes. Furthermore, she showed justifications for including a lake compartment in the modified R&M model. For details see Appendix 3.

#### SENSITIVITY ANALYSIS

The identification of critical parameters in the model by comparison of outputs from model runs resulting from changes in the parameter values is an

example of a process known as sensitivity analysis. In the current study, for instance, the rate of sedimentation of DDT in the oceans could be judged critical because changes in this (rate) parameter substantially affected the total duration of DDT in the model biosphere. In general, with a complicated system, the response of the system to changes in particular individual parameters (inputs and/or specifications), or combinations of parameters while all others remain fixed, is not easily predictable in advance. For a mathematical model of a system, sensitivity analysis becomes an orderly plan for operating the model with changes in the values of parameters in order to learn something about the underlying subject system and to measure, by comparison with real world data, the validity of the model. Because, in principle, all possible combinations of changes may have to be examined, this may become an impossibly expensive and time-consuming task, particularly if "differential" (very small) as well as "discrete" (moderately large) changes are of interest.\* In consequence, increasing study has been devoted in the literature of modeling and systems analysis to the development of sophisticated strategies for obtaining relevant information from tractably sized sets of parameter combinations. One of the motivations for seeking more precise estimates of the rate constants in the DDT study is that the range of tests involving parameters (representing phenomena that are not subject to actual physical change) can obviously be greatly reduced if these parameters are known precisely.

The Committee believes that an adequate program of sensitivity analysis must be an integral step in the development of a refined working model for any predictive purpose.

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\* Very crude sensitivity tests of the DDT model have required over 100 model runs.

CRITICAL ANALYSIS AND USEFULNESS OF THE R&M MODEL  
OR ITS MODIFIED VERSION

Simple, highly aggregated models such as the Randers/Meadows model cannot be expected to produce really accurate predictions of the global persistence or distribution of DDT residues. This is so because the rate constants that control the behavior of the model are not truly average values, but composites from analyses of many phenomena that are still imperfectly understood or "ex post facto" measurements of concentrations whose actual mean values depend on the very distributions such models are intended to discover.

But it is also unlikely that any model whatsoever, within the present reach of the world community of science, can give substantially better predictions of these global quantities, regardless of wealth of detail or sophistication of mathematical structure. By "substantially better," one means that the great inherent risk in using model outputs as a primary basis for drastic and binding policy decisions would not be perceptibly reduced by replacing the model by one with greater detail in the next year or two.

Moreover, for establishing a perspective or framework for the consideration of policy alternatives, for clarifying the relationships that define the long-term disposition of DDT or any other of a large number of the potentially undesirable substances that are released into the biosphere, and for identifying critical directions for continued research, models of the type addressed in this report achieve a balance between convenience and reliability which make them very useful.

In other words, this model (R&M) is cast in a form which is easy to comprehend, easy and inexpensive to modify, and exhibits graphic outputs that facilitate qualitative analysis, yet mirrors known data well enough to be plausible. This does not mean that the model should not be improved, i.e., that a moderately substantial outlay of resources would be either redundant or foolish. Indeed, it could be stated that additional investigation in several areas is important for tying up loose ends and for the possibility of obtaining outputs at a level of confidence to soften the caveat against precipitate use in policy matters. The recommendations set forth herewith for additional disaggregated models for the study of spatial concentrations, etc., will clarify the above statement.

Broad brush system representation, such as the DDT flow model by Randers and Meadows which partitions the world into a small number of distinct structurally differentiated homogeneous entities, and in which dynamic processes are described by mean rates of change, are adequate and, one is tempted to say, uniquely suitable for the study of pesticide flow and fate in the biosphere, given the present state of knowledge of the physical properties of these substances.

The output of the model affords an examination of the dynamic course of the flows which will be of heightened importance if the cumulative effect of identified feedbacks results in cyclic behavior. Moreover, systematic variation of parameter values or structural alteration of the system can be accomplished with far less effort than is needed to make a scratch pad calculation, once the basic outputs are conveniently specified and readily grasped in graphic depictions of system behavior over time.

Objections to "the" model center around the extravagantly vague estimates of the values of key parameters, and can be dismissed more or less out of hand because they are tantamount to the denial of validity to any model, or more broadly, any descriptive or predictive analysis of any system whatsoever, unless it is supported by detailed accurate data. The real problem is a philosophical one relating to our subjective preceptions of context and it arises from the uses to which models are put rather than from their methods of formulation.

Numerical values embedded in informal conjectures retain their aura of uncertainty. Unfortunately, for many people including those who should know better, conjectures formalized into computer models accompanied by printed outputs develop an existence on their own right independent of the real world from which the models were "correctly" or "incorrectly" abstracted, and the values of the ancillary parameters come to be accorded Mosaic status, despite disclaimers. This is the reason why some thoughtful men will not counterance any model not supported by parameter values below a predetermined standard of reliability.

Is a model as broadly aggregated as R&M useful for investigating the global persistence of a pesticide? Superficially, the prospects are discouraging:

- (1) Inasmuch as all the flow and decay rates are global mean values, a set of estimates of these rates could be employed in an even simpler formulation to yield projections of total "lurking" duration and the fraction of the substance entering the food chain, in a few hours calculation with a desk calculator, at a level of confidence not substantially below that of the current model with all its paraphernalia of integration of difference equations.

- (2) The outputs are useless because the rates themselves remain only vaguely specified, after much painstaking and expensive research, to such an extent that, for example, our conjectures about the phenomena of sedimentation in lakes and the ocean, and volatilization from the ocean surface, and transport and loss to the upper atmosphere, which in an orderly universe would be mutually exclusive sets of behavior whose selection would depend solely on mass and perhaps vapor pressure, are so complicated by questions of sorption, turbulences, differential solution rates, and whatnot, that any, or none of these processes may, in fact, be significant and, to date, we are not sure which. In general, the determination of reasonable characteristic values or even acceptable estimates of parameter ranges from scanty data is a very chancy undertaking.

However, these arguments are straw men, and can be countered as follows:

- (1) The supercrude single number of scratch calculations may be adequate as a benchmark for discussion purposes, but the R&M model, or some modification of it, or another equivalently detailed, is necessary for obtaining any insight into the dynamic behavior of the DDT flows with any one set of system parameters and a fortiori for any investigation of the sensitivity of the accumulations and decays to variations in these parameters. Although the construction of the model required orders of magnitude of effort greater than scratch pad analysis, once it is available for use, variations in parameter values can be effected (with voluminous graphic as well as tabular outputs produced) virtually by a "stroke of the pen," while the back-of-the-hand calculations would have to be repeated on the back of the hand, i.e., manually, many times, each replication furnishing just one numerical output.

- (2) As for the difficulty resulting from imprecision in rate estimates, the validity of any model must suffer great damage if baseline data are inaccurate. The more elaborate or detailed the model, the greater the risks. There is a certain virtue in opting for mean-value formulations, as long as the analyst or user doesn't hypnotize himself into overconfidence in the outputs. The point here is that if any formal analysis at all is worth undertaking (and surely it is better than raw guesswork, once again given requisite caution in interpreting outputs), realistic bounds should be imposed on the degree of fine focus in the early stages of the investigation, i.e., the initial model, but the extent of abstract simplification should also be constrained to insure some specificity in the meaning of the outputs.

One judges models of the R&M type to be substantially at the proper level of detail for the investigation of the flow and fate of pesticides in geographical or geomorphological systems ranging in size from a U.S. state, e.g., Michigan or Pennsylvania, to global. Global models can illuminate the mean persistence of pesticides in the various compartments, but there then remain serious questions concerning local concentrations, even if one temporarily tables questions about toxicity or ecological effects.

Firstly, if one is interested in the differential intensity of use in different parts of the world, i.e., the extent to which a nation that calls the tune can cause another to help pay the piper, the inchoate "two-continent" modification must be amplified full-scale with detailed mechanisms of transport, meteorological movements, ocean currents, etc., unless it can be established that the assumption of homogeneous diffusion over time on which

the R&M model rests is true. Also, as in our previous suggestion of the possible importance of lakes, if various routes of transport are accompanied by different degradation rates, then again, the paths must be explicitly modeled in spite of ultimate homogeneous distribution.

Another facet of the relationship between concentration and persistence that must be studied further before it can be neglected in estimating persistence, is the possibility that some release rates are as much dependent on degree of concentration, as on total levels, as in the model. An example of this (not necessarily significant except for illustrative purposes) is that, in general, evaporation is controlled by surface area, i.e., a given mass of almost anything will evaporate more rapidly strewn or dispersed than it will in a coherent lump.

Lastly, one has a major phenomenological question which is likely to require study of local concentrations, where by "local" one means local in time as well as in space. This is the estimation of probability of episodic or chronic exposure of individual organisms or of a "species of interest" to various levels of pesticide concentrations as a determinant of health or ecological effects. It would obviously be desirable here to mount research leading to parsimonious model formulation. Otherwise, one would be faced with the necessity of a completely unwieldy, highly detailed, large-scale model, or a host of small ones, involving stratification according to depth, altitude, climatology, season, land use, human and zoological population densities, etc.

The consensus of the Committee is that all of these considerations are germane to a wide spectrum of substances beyond DDT, or even pesticides in general, and that the relevant modeling methodologies are sufficiently fungible that continued investigation would be rewarding.

RELATED MISCELLANEOUS WORK INITIATED AND/OR ACCOMPLISHED

- (A) Since this model was based on global movement and fate of pesticides (DDT as model compound), an attempt was made to obtain information on DDT behavior in environmental media (soil, water, air), ecological systems (flora, fauna), and sediments in various countries through the United Nations Food Point Information Center located at EPA.

The responses to the inquiry were overwhelming. Scientists from each country contacted replied and indicated they would extend full cooperation in obtaining the data needed for the development of predictive mathematical model(s) by the interagency Committee and an interest in this novel undertaking. However, none of these data was ever obtained by the Committee due to a lack of funds and administrative authorization.

- (B) A visiting team of Russian scientists under a USA/USSR cooperative program were very much interested in this U.S. Federal Government-wide program to develop models to describe the fate of pesticides around the globe. The details of the correspondence are in Appendix 4.

- (C) The Committee approached the U.S. Geological Survey to obtain ocean core samples for analysis of chlorinated hydrocarbons, particularly DDT and its major metabolites. Several samples from the Atlantic and Pacific Oceans were obtained for curiosity analyses. The samples were sent to the Buefort Laboratory of NOAA (Department of the Interior) for analysis. A few samples (ca 6 to 10) were analyzed; however, a further systematic investigation could not be initiated due to funding constraints.

- (D) The Woods Hole Laboratory in Massachusetts, the Oceanographic Institution of Lajolla, California, and the Ocean Environmental Science Department of Rhode Island University are a few examples of interested

academicians and research scientists in the USA who wished to participate in the modeling activity by providing data from their "ongoing" research and to evaluate input data to each compartment of the model. However, this was not possible due to lack of funds for contract research to boost the "ongoing" projects and travel funds for participation in Committee deliberation activities.

#### AID TO POLICY AND DECISION-MAKING PROCESS

The decision on mankind's use of DDT or other pesticides should rest on the answers to the following basic questions:

- (1) What are the actual benefits in health, comfort, and agricultural productivity gained by a given level of DDT or other pesticide usage?
- (2) What are the total costs in human health and in adverse effects on natural ecological balances incurred as a result of a given level of DDT or other pesticide usage?
- (3) How are the benefits and costs (i.e., risks) of a given pattern of DDT or other pesticide usage distributed over space and time?
- (4) How do possible alternative measures of insect control compare with DDT or other suspect pesticide(s) in terms of costs and benefits distributed over space and time?

Although all these questions are important to policy makers, the third question is of global interest and the fourth question is of particular interest to EPA's Substitute Chemical Program of the OPP. The questions concerning the distribution of DDT's -- or any other pesticide's -- costs through time as a function of different application rate is of interest because analysis may reveal that policies which seem to be beneficial in view of

their short-term effects may no longer seem so when the long-term consequences of the policy actions are realized and taken into account. The application of system dynamics analysis to the time aspect of the third question is relevant in our effort to devise a "working" mathematical model of predictive quality.

It is hoped that further analysis of the results of test running the R&M model and its preliminary modifications will identify the research priorities and data requirements for the development of a model sufficiently detailed, i.e., disaggregated, to produce significant answers to question (3).

#### AID IN EVALUATION FOR THE REGISTRATION AND REGULATION OF PESTICIDES

Policy makers and scientists disagree on how scientific facts are to be integrated with social value judgments. There is an endless debate about the role of science and scientists in the body politic. Current methodologies to integrate scientific facts and social value judgments in the formation of responsible public policy are either of the adversary procedure or the person-oriented approach. In the adversary method, scientists with differing judgments are pitted against one another in front of a judge or jury or both. This method is limited because of an ascientific commitment to victory rather than truth. In the person-oriented approach, one searches for and uses scientists with mysterious talents and reputations for wisdom in the exercise of judgments. This approach is also limited by an ascientific focus on persons and their motives rather than on the adequacy of methods. The major shortcoming of these approaches is that they are primarily self-serving.

Recently, scientists have recognized the need for explicit methods or system analysis methods for decision making in areas where science and public

interest interface, for example, the regulation of pesticides in the environment. Predictive mathematical model(s) is an explicit method and is based on system analysis. The predictive model(s) is readily subject to scientific criticism because it meets the required standard of replication, quantification, logic, and availability to public inspection as to the locus and degree of perfection in method used and subsequent improvement by modification. Therefore, this mathematical modeling method is scientifically defensible. This method also separates scientific judgments from social value judgments.

The predictive mathematical model(s) can be utilized as a scientific aid for the registration and regulation of pesticides, for example:

- (1) When the issue with respect to a given pesticide reduces to whether there is a significant exposure through environmental transport, or whether the steady-state build-up of a toxic compound in a certain compartment of the environment is at an unacceptable level over background, this type of predictive model could permit a much earlier decision than would otherwise be possible;
- (2) When one intends to substitute one pesticide for an alternative one and the decision-maker wants to know what are the choices of pesticides from which he can choose, a comparison of the steady-state build-up values for each pesticide under consideration or its toxic degradation products in the various compartments of the model representing the various compartments of the ecosystem will quantify the degree of build-up above background level of each compound. This information would be helpful in the Substitute Chemicals Program of OPP/EPA;

- (3) If the development of forecasting mathematical model(s) for social value judgments is carried out simultaneously, analytical method(s) for integration of the results of the social value judgment model with the results of the predictive mathematical model(s) for the distribution of pesticides in the environment could be developed. This would permit quantitative estimation of the risk/benefit relationship utilized for the formation of public policy. The integrative phase would provide an overt, rather than covert, process for combining facts and values, and would integrate the scientific facts with social value judgments analytically, instead of judgmentally, and thus would provide a socially responsible public policy which would be scientifically, socially, and ethically defensible.

#### RECOMMENDATIONS

The Committee members keenly appreciate the need for mathematical, statistical, ecological, and biochemical expertise in the development of workable predictive mathematical model(s) for pesticide flow in the ecosystem. The Committee is also acutely concerned that such endeavor be promoted in interagency collaboration, with field studies and the leadership needed for a national effort in this area.

The Committee therefore recommends that the EPA or some other agency with authority establish a permanent group to:

- (a) Conduct research of its own in this endeavor of mathematical modeling of pesticide flow;
- (b) Establish and administer a research grants program and interagency collaborative studies to develop working model(s) and collect needed data;

- (c) Make an effort to integrate analytically, not judgmentally, the scientific information and knowledge gained on the behavior of pesticide(s) in the environment via modeling with social value judgments; and,
- (d) Advise on the possible import of policy decisions regarding regulation and registration of pesticides and their effects on the environment by a scientifically, socially, and ethically defensible means, rather than by the current widespread use of ascientific methodology (i.e., the adversary system and the person-oriented approach).

FIGURE AND APPENDICES

Figure 1: The Flow of DDT in the Environment (R&M model).

Appendix 1:

(A) Survey of Concepts of Predictive Mathematical Model(s)

by Dr. J. E. Fletcher and Dr. J. Mossiman, NIH

(B) Brief Description of Mathematical Equations

by Mr. L. S. Joel, NBS

Appendix 2:

Literature Survey of DDT for the R&M Model Compartments

by Dr. S. D. Haseltine and Dr. R. J. Peterle, Ohio State University

Appendix 3:

Search for Data on DDT Movement in and out of the Freshwater Lakes

Compartment of the Model

by a summer student at NBS

Appendix 4:

Write-Up on USA/USSR Cooperative Program of EPA

by Dr. P. R. Datta, EPA, and Mr. L. S. Joel, NBS

APPENDICES

1A and 1B

FIGURE 1

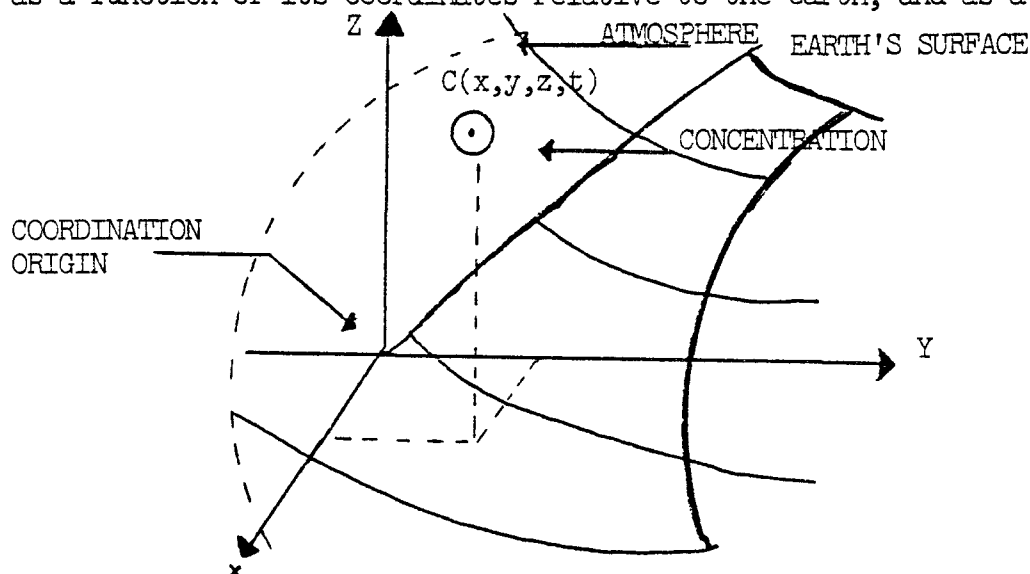
APPENDIX 1 (A)

"SURVEY OF CONCEPTS OF PREDICTIVE MATHEMATICAL MODEL(S)".

by Dr. J. E. Fletcher & Dr. F. Mossiman.

## MODELING CONCEPTS

There are basically two approaches to modeling using deterministic mathematics. The first, called a distribution parameter model, attempts to describe a given quantity relative to its location in space and time. That is, for example, the concentration of DDT might be given or computed as a function of its coordinates relative to the earth, and as a function



Typically such an approach involves a vector-partial differential equation in time and space of the form.

$$\frac{\partial c}{\partial t} = -\vec{v} \cdot \vec{\nabla} c + \vec{\nabla} \cdot (D \cdot \vec{\nabla} c) + f(x, y, z, t).$$

where  $f$  represents sources and sinks,  $\vec{v}$  is the flow velocity vector,  $D$  is the diffusivity of the substance, and  $\vec{\nabla}$  is the vector differential operator:

$$\vec{\nabla} = \vec{i} \frac{\partial}{\partial x} + \vec{j} \frac{\partial}{\partial y} + \vec{k} \frac{\partial}{\partial z}.$$

The solution of such an equation with the proper initial and boundary conditions would provide a global map of the DDT concentrations.

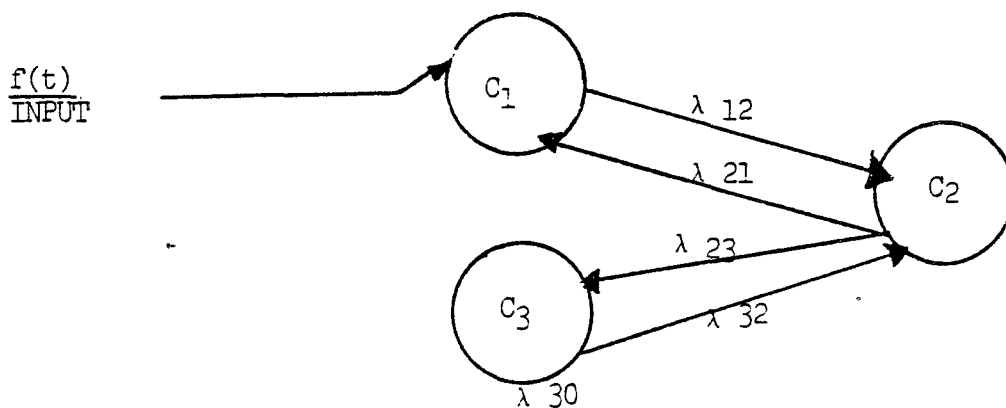
However, such a model has not yet been constructed and if it were available, its solution is not likely to be amenable to computation for the following reasons:

1. The geometry of the model is highly irregular. That is, the interfaces of land, air, sea, and rivers have no describable pattern.

2. The flow properties in lakes, rivers, and oceans, as well as the atmosphere, are not well defined.
3. The Scale of the model rules out a numerical solution via computer due to the large number of variables necessary for problem descriptions.

Possibly such a model could be used on a local level where the scale can be controlled.

An alternative to this model is a lumped parameter model where all quantities lose their spatial identity. In this formulation, all similar quantities are "lumped" into a single entity or compartment. For example, air, water, soil, etc., are not distinguished according to location. The interactions or exchanges among these compartments are called transfer or exchange rates. An example of such a model is the following:



The system of differential equations can be written down as balance equations.

$$\frac{dc_1}{dt} = \lambda_{12} C_2 + \lambda_{21} C_1 + f(t) \quad (\text{inflow minus outflow})$$

$$\frac{dc_2}{dt} = \lambda_{12} C_1 - \lambda_{21} C_2 - \lambda_{23} C_2 + \lambda_{32} C_3$$

$$\frac{dc_3}{dt} = \lambda_{13} C_1 - \lambda_{31} C_1 - \lambda_{32} C_3 - \lambda_{30} C_3$$

The compartments will have initial conditions

$$C_1(0) = A_1,$$

$$C_3(0) = A_3,$$

$$C_2(0) = A_2,$$

and these initial conditions represent known conditions at the starting time  $t = 0$ . If the exchange rates are specified, then the time course of the compartments can be calculated from these equations. Note that one obtains a "lumped average" as a function of time and there is no

identification with geographical location in this model. We list the following as features of this type of model:

- 1) Specific entities lose their identity.
- 2) Transfer rates are necessarily lumped averages.
- 3) Compartmental values represent lumped averages.
- 4) Local variations and predictions are lost in the lumping process.

Advantages:

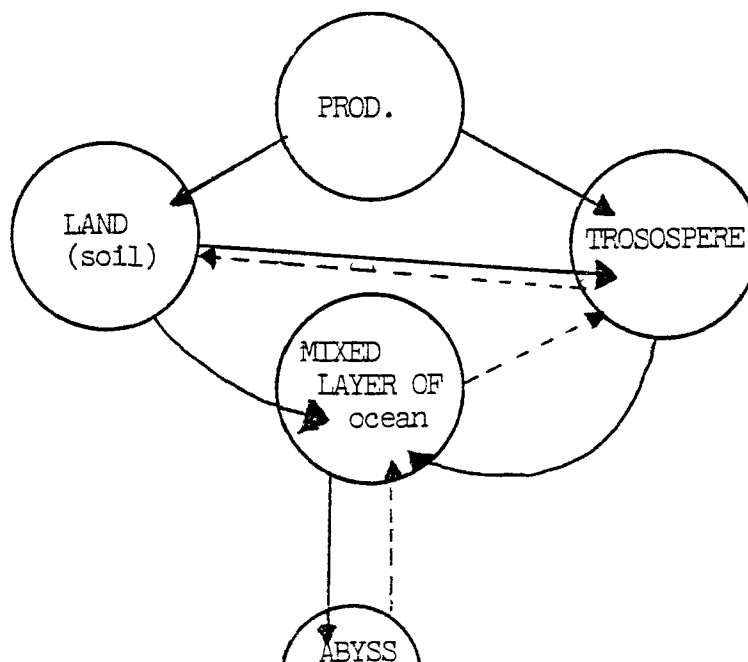
- 1) Model generates ordinary differential equations.
- 2) Solution possible by existing techniques.
- 3) Fewer parameters and relationships needed for simulation.
- 4) Easily modified, components added, deleted, etc.

Validating Model:

- 1) Parameters come from independent measurements or experimental tests.
- 2) Results should predict past history or known results.
- 3) Parameter sensitivity tests to examine relative importance of factors and assumptions.
- 4) Predict future trends after model is validated.

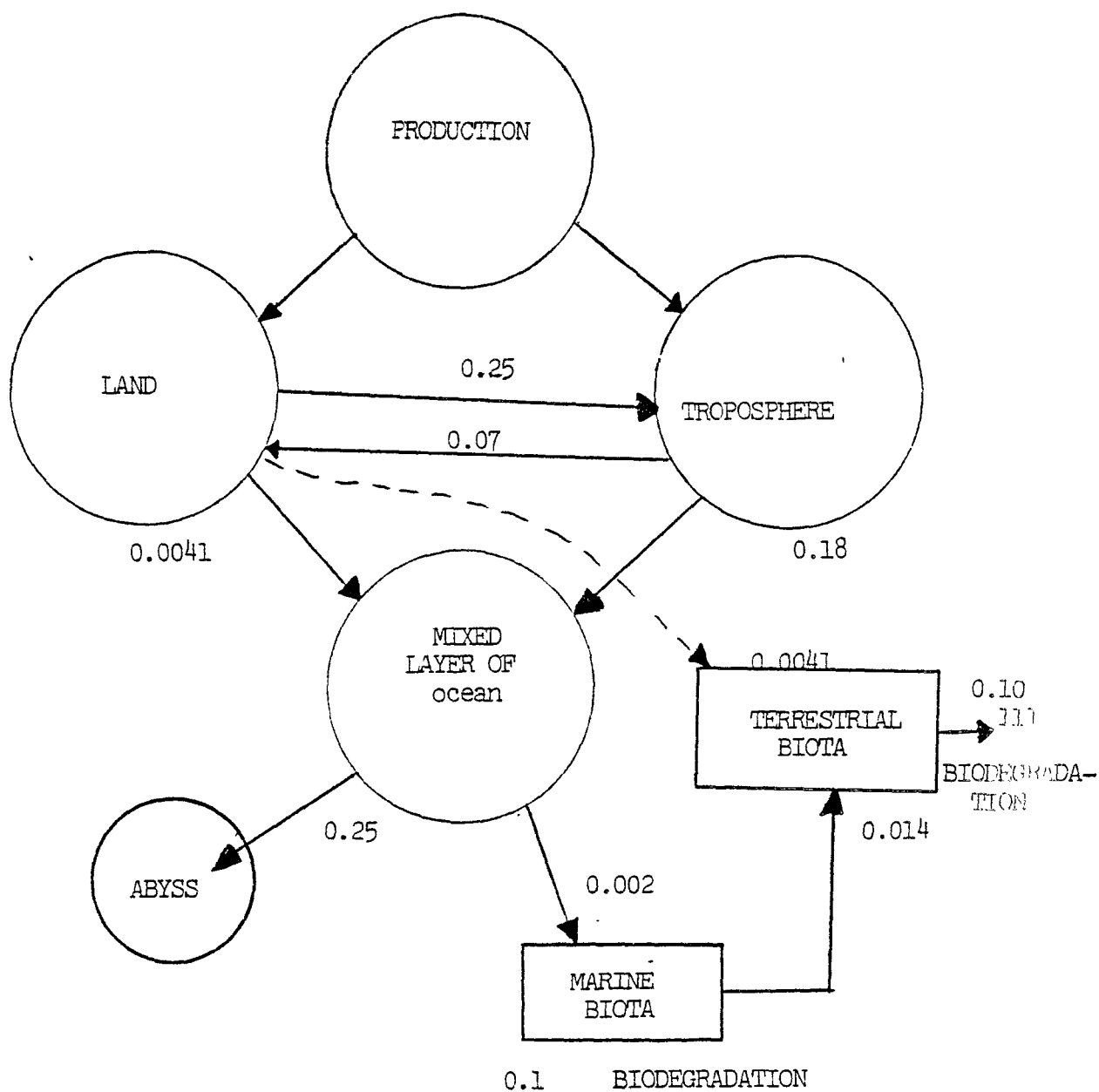
Survey of Existing Models:

- 1) Woodwell et al., conceptual model of DDT

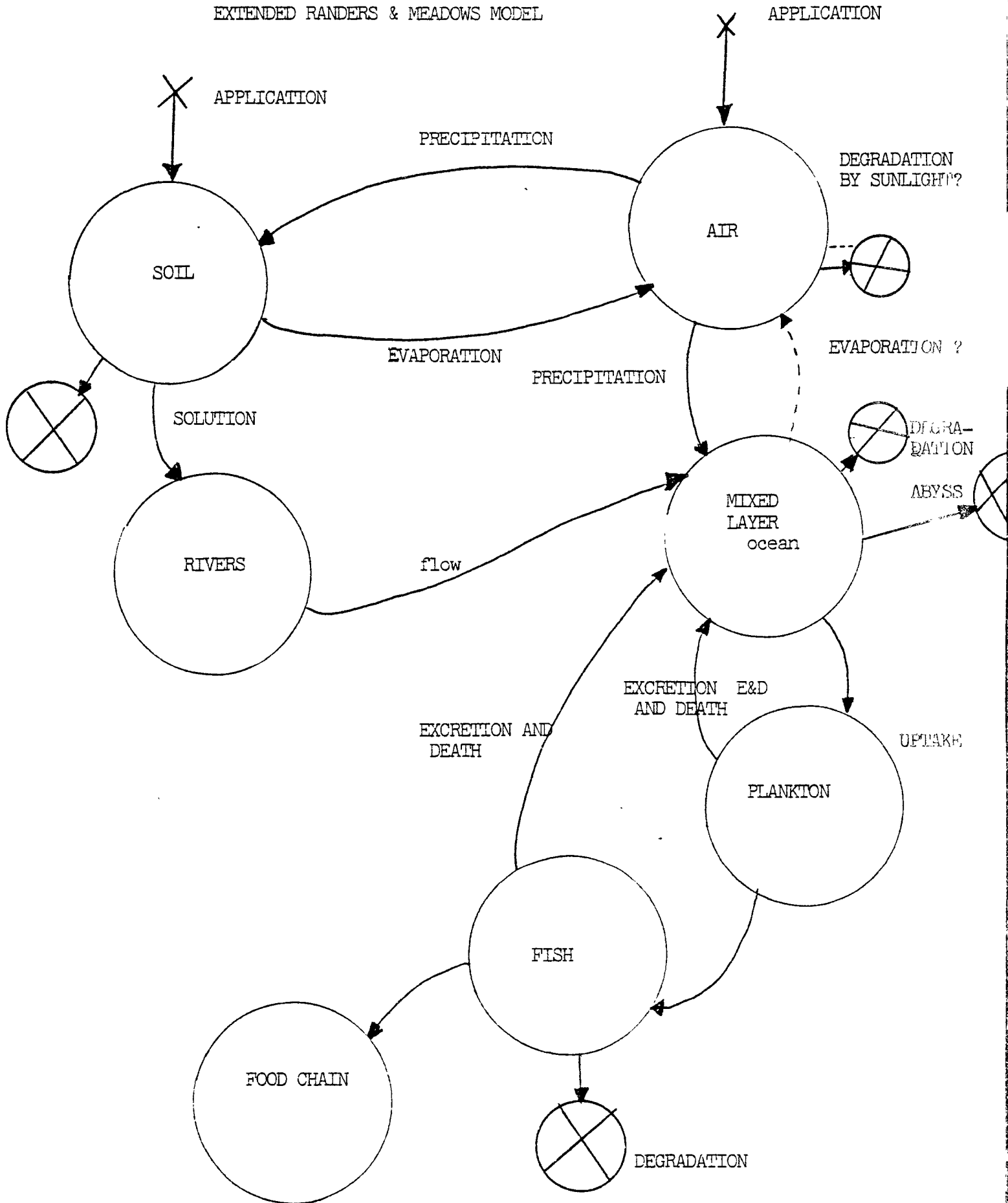


# EXTENTION OF WOODWELL MODEL

CREWS, W.B.



EXTENDED RANDERS & MEADOWS MODEL



APPENDIX 1 (B)

THE "BASIC MODEL" IS THE UNMODIFIED RANDERS AND MEADOWS MODEL

By Mr. L. S. Joel

## SOME REMARKS ON THE MATHEMATICAL DDT MODEL

The vehicle which carried our investigation of the utility of mathematical models for the study of pesticide fate in the environment, was a version of a computer model proposed in 1970-71 by Randers and Meadows, based loosely on the techniques of J. W. Forrester's "System Dynamics" and cast in the associated DYNAMO simulation language. That model is documented in J. Randers' "DDT Movement in the Global Environment", chapter 3 of Toward Global Equilibrium: Collected Papers (ed: D. L. Meadows and D. H. Meadows, Wright Allen Press, 1973).

The model uses a set of linear material-budget equations involving "levels" and transformation rates, to trace over time the flow and accumulation of DDT in a system consisting of five major ecological compartments ("soil," "air," "river," "ocean," and "fish") each considered as a homogeneous worldwide aggregate. Very large fresh water bodies are considered integral with the "ocean," while all other fresh water is subsumed under "rivers."

Life-forms higher than fish are excluded from the model, except to furnish a "sink" for some portion of the systems DDT, as noted below.

The driving force for the system is the rate of application of DDT. Because in reality, most application is assumed to occur as crop dusting of cultivated land areas, the model splits application into "air" and "soil" components to represent convective dispersion during the dusting process.

The Randers paper explicitly indentifies the following flows;

- (1) from soil-to air by evaporation, to rivers by solutions, percolation or wash off and out of the system by bacterial and chemical degradation.
- (2) from air-to soil and oceans by precipitation and out of the system by photochemical degradation\*.
- (3) from rivers-to the ocean by runoff.
- (4) from the ocean-to air by evaporation\*, to fish by ingestion through plankton, and out of the system through sedimentation, i.e., settling into the abyssal depths\*.
- (5) from fish-into the ocean by excretion and mortality and out of the system through destructive metabolism (labeled "harmless excretion") and trophic predation by higher life forms.

The model equations contain terms representing these phenomena except that: (1) in the flow from soil to rivers, percolation and wash off are not distinguished, nor are chemical and biological degradation from soil. (2) Photodegradation in the atmosphere and evaporation and sedimentation from the ocean (marked by asterisks above), were excluded from the originial model based on data available in 1969; the model was modified at NBS to include them.

Sample model equations in the DYNAMO notation give the level of DDT in rivers:

$$R.K. = R.J + (DT)(SR.JK - ROR.JK)$$

$$SR.KL = S.K/(1.5*SHL)$$

$$ROR.KL = R.K/(1.5*ROHL)$$

R = DDT in Rivers (Tons)

S = DDT in Soil (Tons)

ROR = Run off Rate (Tons/Year)

SR = Solution Rate in Soil (Tons/Year)

ROHL = Run off Half-life (Years)

SR = Solution Half-life (Years)

DT = Time step \*(Years)

R = 0

RI = RI Initial value

RI = 0

K, J are time signatures for forward and current time periods

JK, KL are time signatures denoting intervals

Written using standard algebraic notation, this set of equations becomes

$$(1) \quad Y_{1,k+1} = Y_{1,k} + h(a_1 Y_{1,k} + a_2 Y_{2,k})$$

which can be recognized as a iterate in the solution by Euler's method, of differential equations of the form

$$(2) \quad Y_1(t) = a_1 Y_1(t) + a_2 Y_2(t); Y_1(0) = Y_0$$

In the difference equation (1) we have replaced DT by h, R.K by  $Y_{1,k+1}$ , R.J by  $Y_{1,k}$ ,  $ROR.JK = R.K/(1.5 ROHL)$  by  $a_2 Y_{2,k}$ , etc., whereas in (2) the Y's are functions of t (time) and Y is dY/dt.

Use of the term "Half-life" in the parameter designations for the transformations throughout the model indicates that they are exponential functions of time of the form  $Y = aY$ , i.e.,  $Y = Y_0 e^{-at}$ . (The recurrent constant  $1/1.5$  is an approximation of the value  $1/\log 2$  which occurs in the determination of the constant  $a$  by solving  $Y_0/2 = Y_0 e^{-at_h}$  where  $t_h$  is the given half-life for the exponential process.)

Thus the underlying set of differential equations is the linear system (using matrix notation)

$$(3) \quad \vec{Y} = A\vec{Y} + f(t) \quad \vec{Y}(0) = \vec{Y}_0$$

where  $Y$  is the 5 component vector of DDT levels,  $A$  is a constant matrix and  $f(t)$  is the forcing function, (the application rate of DDT).

The solution of this system for  $Y(0) = 0$  is

$$(4) \quad Y = \int_0^t e^{A(t-s)} f(s) ds$$

The system has desirable properties, ecologically speaking, if  $A$  is a "stability matrix", that is, one for which the real parts of all characteristic roots ("eigenvalues") are negative, as turns out to be true in our case for any plausible range of the parameter-values. For an application function which becomes zero the value of  $Y$  approaches zero. Thus the underlying mathematical system and the model computational outputs confirm our intuition by yielding ultimate decay to zero DDT levels after all application has ceased. Again, the mathematical theory for the differential equations and for the solutions of the difference equation system by Euler's method tells that for  $f(t)$  constant, that is a constant

Page 5

application rate of DDT, the levels in all compartments rise to values at which they remain constant, rather than increasing indefinitely. This was borne out of runs of the model. Finally, although a simple linear system can be solved explicitly in closed form, Dynamo using Euler's method (1) gives convenient stepwise values of the output functions and (2) as we learned by comparing computations Dynamo solutions to the difference equations were not appreciably less accurate nor more time consuming than solution by stepwise Runge-Kutta integration, the most popular standard method for numerical solution of differential equations.

## PLOT SYMBOLS & SCALES

* = APPLICATION RATE (TONS/YEAR)	SCALE: (0 - 500,000)
A = DDT IN ATMOSPHERE (TONS)	SCALE: (0 - 50,000)
F = DDT IN FISH (TONS)	SCALE: (0 - 500)
Ø = DDT IN OCEANS (TONS)	SCALE: (0 - 2,500,000)
R = DDT IN RIVERS (TONS)	SCALE: (0 - 500)
S = DDT IN SOIL (TONS)	SCALE: (0 - 500,000)

TIME SIGNATURE:      YEAR "O" REPRESENTS 1940

# RANGE OF VALUES USED TO TEST THE SENSITIVITY OF THE MODEL

The first group is from the basic model. The second group represents added terms. "Optimistic" values are those for which disappearance of DDT residues should be rapid. "Pessimistic" values are those which should increase persistence of residues.

		Optimistic	Best estimate	pessimistic
ABF	AIRBORNE FRACTION (DIMENSIONLESS)	.1	.5	.9
BWEPY	BODY WEIGHTS EATEN PER YEAR (1/YEAR)	5	10	50
COF	CONSUMED FRACTION (DIMENSIONLESS)	.5	.5	.5
DFRA	DEGRADED FRACTION (DIMENSIONLESS)	1	.1	0
DHLO	DEGRADATION HALFLIFE IN OCEAN (YEARS)	8	15	30
DHLS	DEGRADATION HALFLIFE IN SOIL (YEARS)	3	10	30
EHLS	EVAPORATION HALFLIFE FROM SOIL (YEARS)	.5	2	10
EXHL	EXCRETION HALFLIFE FROM FISH (YEARS)	.05	.3	.7
HLF	HALFLIFE OF FISH (YEARS)	1	3	10
MF	MASS OF FISH (TONS)	$6.10^8$	$6.10^8$	$6.10^8$
MML	MASS OF MIXED LAYER (TONS)	$3.10^{16}$	$3.10^{16}$	$3.10^{16}$
OPCF	OCEAN-PLANKTON CONCENTR. FACTOR (DIMENSIONLESS)	1,000	2,000	10,000
PHL	PRECIPITATION HALFLIFE (YEARS)	.01	.05	.2
ROHL	RUN-OFF HALFLIFE (YEARS)	.05	.1	1
SF	SOIL FRACTION (DIMENSIONLESS)	.3	.3	.3
SHL	SOLUTION HALFLIFE (YEARS)	200	500	2,000
DHLA	DEGRADATION HALFLIFE IN AIR (YEARS)	.05	1	2
EHLO	EVAPORATION HALFLIFE FROM OCEAN (YEARS)	.5	2	10
FOS	FRACTION SUBJECT TO EVAP. OCEAN (DIMENSIONLESS)	.05	.05	.05 PURE GUESS
SHLA	SEDIMENTATION HALFLIFE TO ABYSS (YEARS)	1	4	10
SPF	FRACTION SUBJECT TO SEDIMENTATION (DIMENSIONLESS)	.3	.3	.3 PURE GUESS

Iteration	Iteration	Iteration	Iteration	Iteration
00000	100000+03	200000+03	300000+03	400000+03
00000	100000+05	200000+05	300000+05	400000+05
00000	100000+06	200000+06	300000+06	400000+06
00000	100000+07	200000+07	300000+07	400000+07
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00000	100000+54	200000+54	300000+54	400000+54
00000	100000+55	200000+55	300000+55	



[illegible]

.50000+03 PF  
 .50000+05 A  
 .50000+06 \*S  
 .25000+07 0

RUN FOUR BASIC WITH  
 "BEST ESTIMATE"  
 SEDIMENTATION  
 PHOTOCHEMICAL  
 OCEAN EVAPORATION ADDED

Run Five  
Basic With  
Fast PHOTODEGRADATION  
(HALF LIFE .1 YEAR)

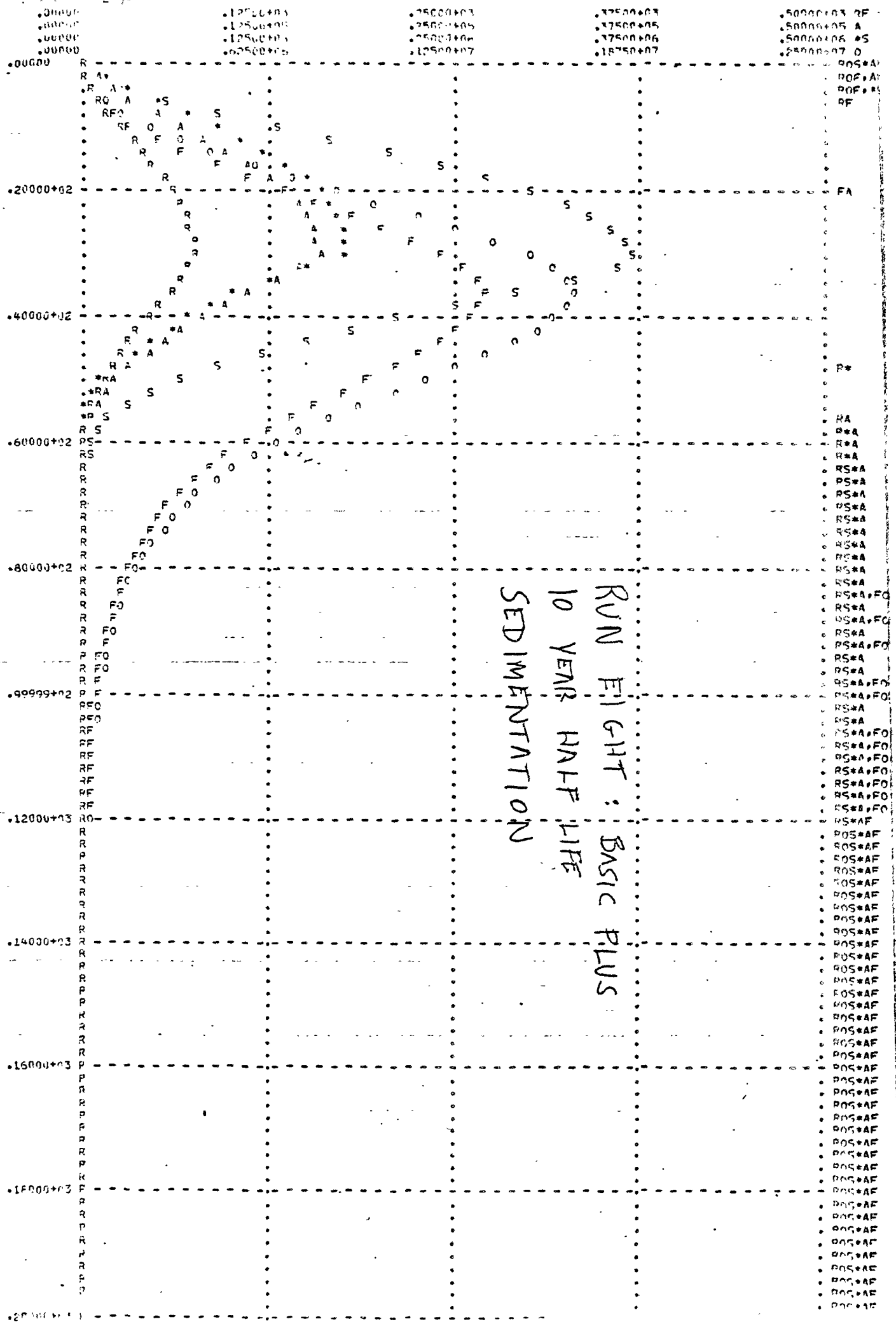


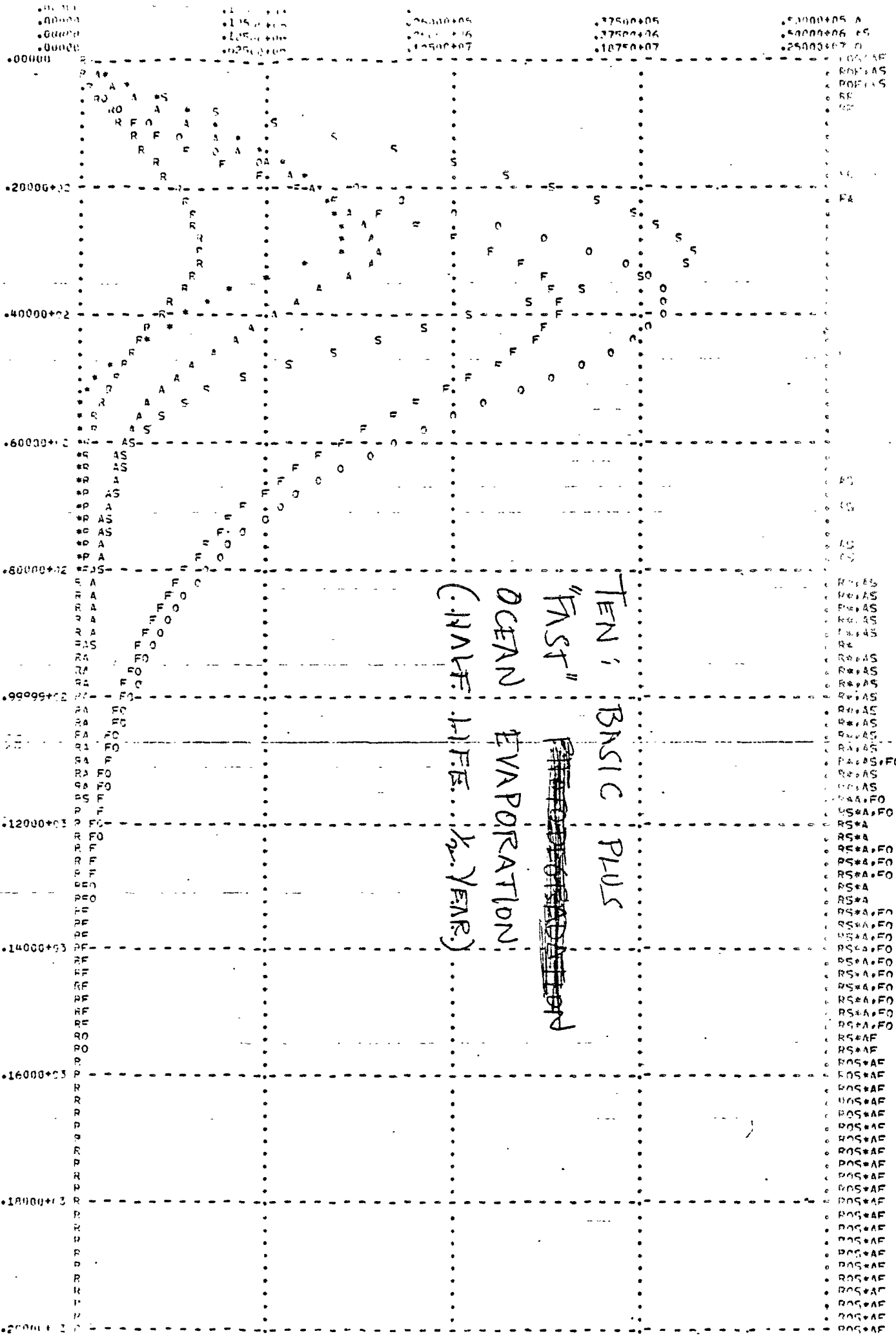
- 50000+03 RF
- 50000+05 A
- 50000+06 05
- 25000+07 0

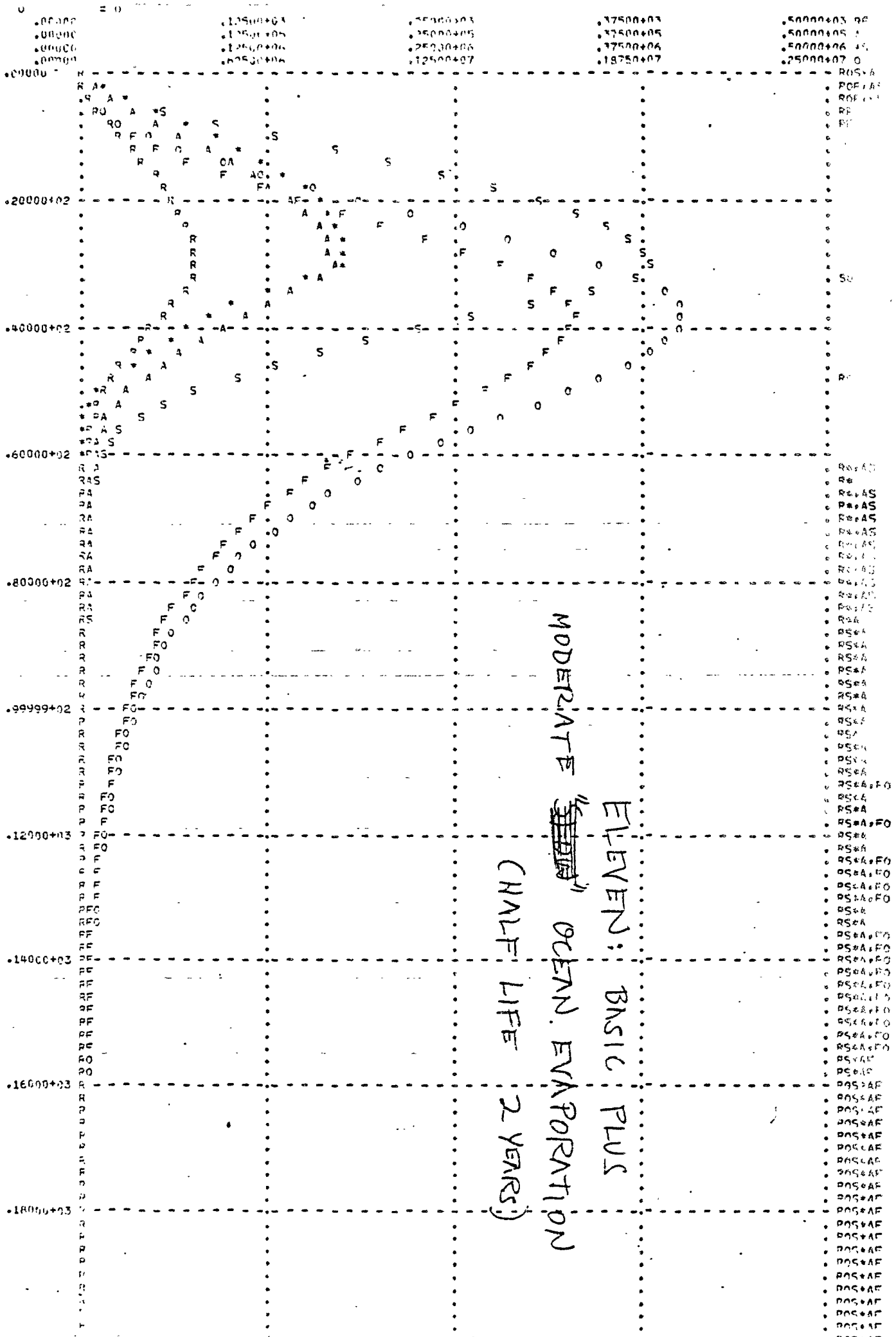
• • • • •

RUN 7  
 BASIC PLUS  
 "BEST ESTIMATE"  
 SEDIMENTATION  
 (HALF LIFE 4 YR)

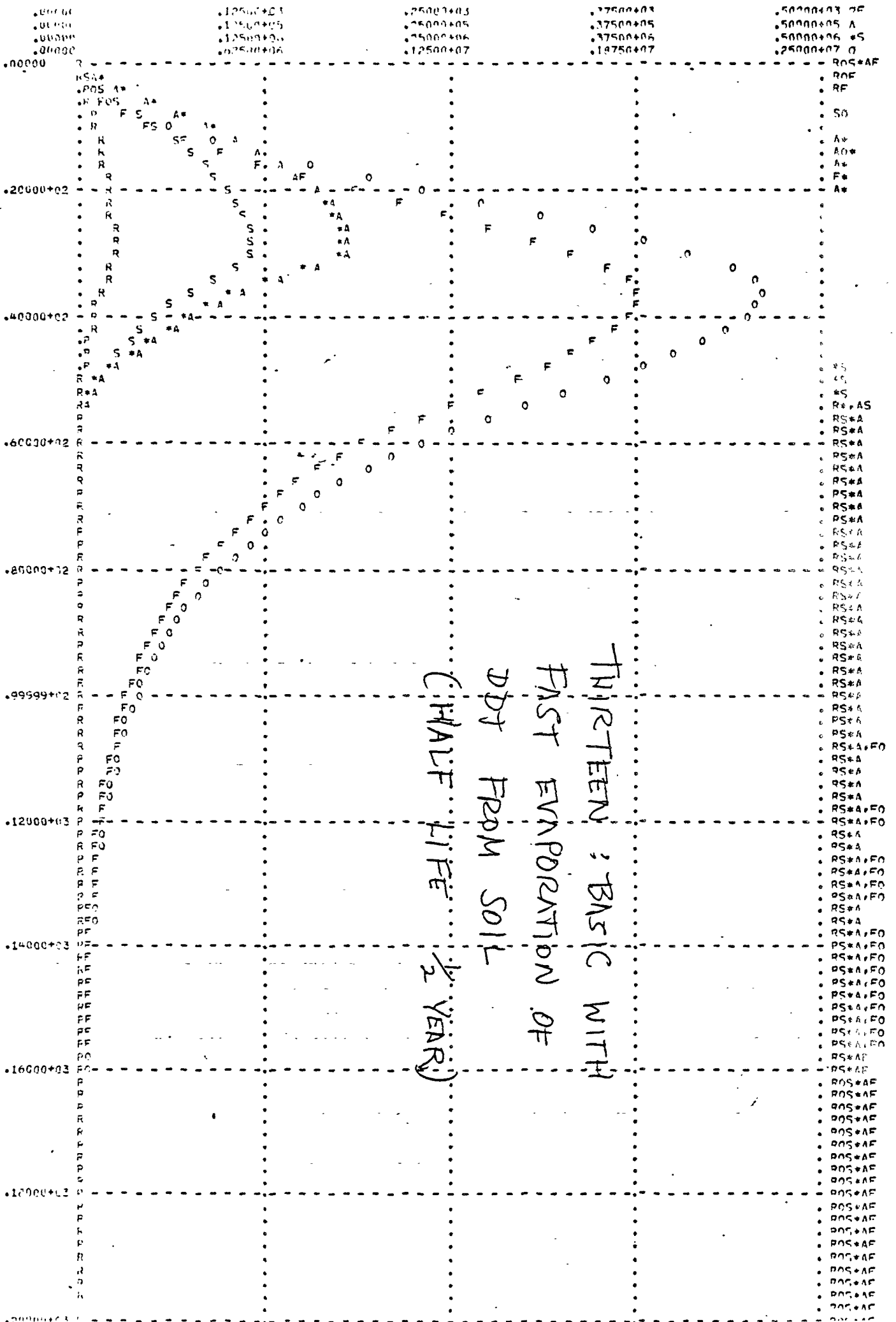
RUN 7  
BASIC PLUS  
"BEST ESTIMATE"  
SEDIMENTATION  
(HALF LIFE 4 YR)











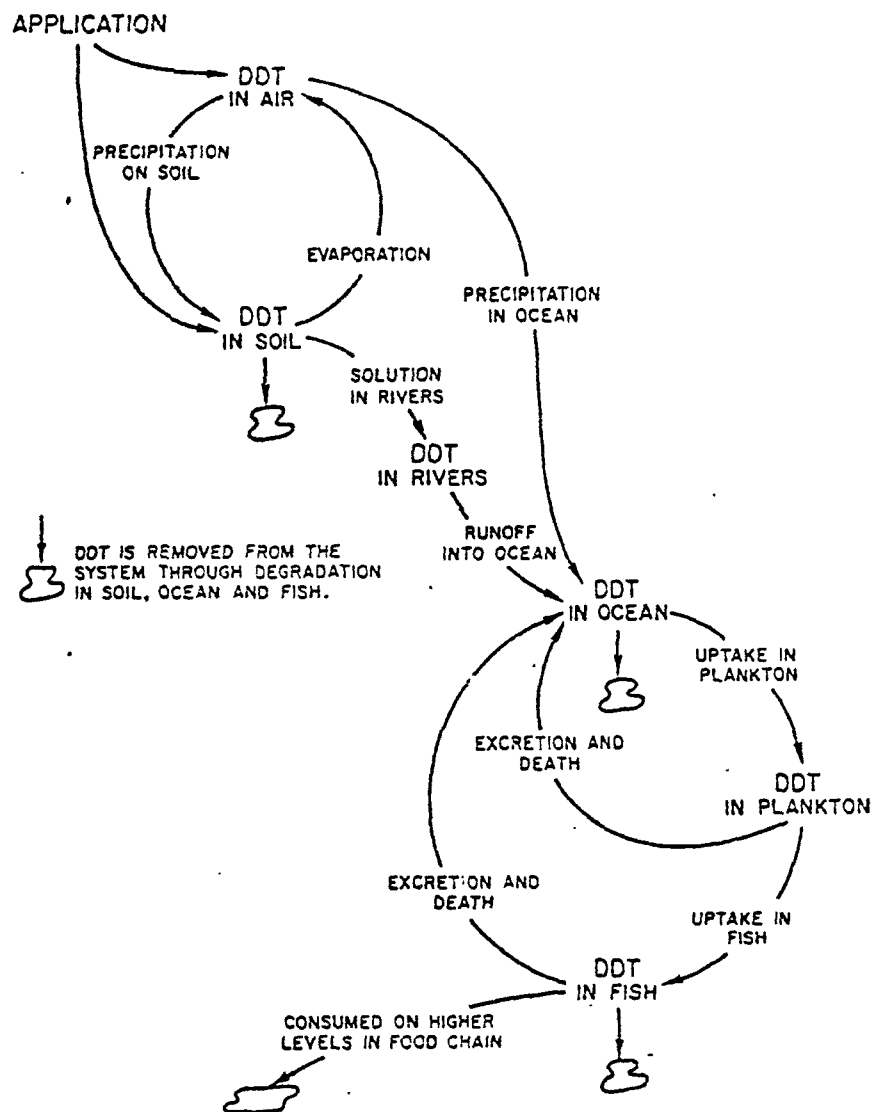


FIGURE 1 THE FLOW OF DDT IN THE ENVIRONMENT  
(Randers & Meadows)

APPENDIX -2

## REFERENCES

Abbott, D. C., R. Harrison, J. Tatton, and J. Thompson. 1965. Organo-chlorine pesticides in the atmospheric environment. Nature 208: 1317-1318.

pp' DDT  $\alpha$  and  $\lambda$  BHC in London atmosphere rainwater; insufficient to determine  $\beta$ -BHC, pp' TDE or pp' - DDE. Other samples of rain and snow around London showed similar results, along with dieldrin. Two samples from remote Scotland  $\rightarrow$  negligible contamination. 'Scrubbing out' therefore occurs. -air 10-20 ppb.

Abbot, D. C., R. B. Harrison, J. Tatton, and J. Thompson. 1966. Organochlorine pesticides in the atmosphere. Nature 211:259-261.

Rain may "scrub" pesticides from the air as it passes through.  
How get into atmosphere

- (1) Direct drift from spraying - inversely to distance from spray site - local.
- (2) Vaporize from soil - slow, long term process
- (3) Industrial processes - pesticide manufacture or mothoring air 10-100X less pesticide than rainwater, but greater volume may make important. Soil acts as gas chromatograph. Treated soils will lose, while untreated soils gain.

BHC, DDT, DDE, TDE found and dieldrin - London; Dieldrin - Norfolk; Aberystwytle - none.

Also breakdown products of organochlorine pesticides are indicated by GLC.

Acree, F., M. Bowman, and M. Beroza. 1963. Codistillation of DDT with water. J. Agr. Fd. Chem. 11:278-280.

- (1) 25, 30, 35°C, 0.36-81 ppb, for 24 hr.
- (2) Related to DDT concentration in solution up to 100 ppb.

Ahr, W. 1973. Long-lived pollutants in sediments from the Laguna Atacosa National Wildlife Refuge, Texas. Geol. Soc. Am. Bull. 84: 2511-2515.

- (1) Cores 5 cm diameter and 153 cm long
  - a) Animals may mix DDT in cores in burrowing - so don't trust dating
- (2) Water sediment, plants, fish, birds showed increased DDT levels

Albone, E. S., G. Eglinton, N. Evans, J. Hunter, and M. Rhead. 1972. Fate of DDT in Severn estuary sediments. Environ. Sci. Tech. 6: 914-919.

Field - 14°C - DDT

Estuarine sediments - 46 days, small amount of pp'DDD 48:1, 13:1 pp'DDT/pp'DDD, but all DDT in one spot.

Lab - (under H<sub>2</sub>) 30 ppm DDT  $\rightarrow$  21 days 1/1.1, 1/3.3 DDT/DDD, when DDT is dispersed. Some polar products.

Anaerobic sewage sludge (H<sub>2</sub>)  $\rightarrow$  1/7.2, 1/17, 1/2, 1/5.4 with more polar metabolites.

DDT reduced bacterial counts in both anaerobic and aerobic mud cultures, but most bacteria could decompose DDT to at least DDD.

Aloone, E. S., G. Eglinton, N. Evans and M. Rhead. 1972. Formation of bis (p-chlorophenyl)-acetonitrile (pp'DDCN) from pp'DDT in anaerobic sewage sludge. Nature 240:420-421.

400 ml sludge, 5% w/w solids, pH 8.2 at 37°C for 88 days with  
7.45 ng  $^{14}\text{C}$  - pp<sup>2</sup>DDT and 20 g minced beef (4.7  $\mu\text{Ci}$ )  
Liquid  $\rightarrow$  0.4  $\mu\text{Ci}$ ; solid extract  $\rightarrow$  1.5  $\mu\text{Ci}$ , solid  $\rightarrow$  1.5  $\mu\text{Ci}$ .  
Solid extract  $\rightarrow$  Zones AEC - 62:29:9% radioactivity

A = pp'DDT and pp'TDE

B = pp'DDCN 11.7%

C = ?

Alexander, M. 1965. Persistence and biological reactions of pesticides in soils. Soil Sci. Soc. Amer. Proc. 29:1-7.

DDT life in soil = 10 yr (at least)

A general statement on the difficulties of considering soil micro-organisms omnipotent in biodegrading ability and in applying lab results to natural conditions.

Concentrates on herbicides (phenols).

Alexander, M. 1973. Nonbiodegradable and other recalcitrant molecules. Biotechnol. Bioeng. 15:611-647.  
General Review

Anderson, J. P., E. Lichtenstein and W. Whittingham. 1970. Effect of Mucor alternans on the persistence of DDT and dieldrin in culture and soil. J. Econ. Entomol. 63:1595-99.

- (1) 1 ppm DDT for 8 days with live mycelium  $\rightarrow$  42% recovery by GLC (fungal enzymes).
- (2)  $^{14}\text{C}$  DDT at 50  $\mu\text{g/ml}$  for 4 days  $\rightarrow$  49.5% in fungus and medium, 47.5% in aqueous phases, metabolized to soluble molecule
- (3) This did not work in soil just in pure cultures.

Anderson, J. P. E. and E. T. Lichtenstein. 1972. Effects of various soil fungi and insecticides on the capacity of Mucor alternans to degrade DDT. Can. J. Microbiol. 18:553-560.

- (1) Always to water soluble derivatives.
- (2) Other fungi depressed or obliterated the response.
- (3) Lindane, parathion and Dyfonate also decreased the response.
- (4) Fungus does not use DDT as a carbon source (1970).

Antonmaria, P., M. Corn, L. DeMaio. 1965. Airborne particulates in Pittsburgh. Associated with pp'-DDT. Science 150:1476-1477.

June - Dec., 1964, 1.22 m<sup>3</sup>/min air flow for 14 consecutive days and nights.

- a) Only pp'DDT was quantified although DDD, DDE or pp'DDT was also present.
- b) Highest = 1.36  $\mu/1000 \text{ mm}^3$ ; range 0  $\rightarrow$  0.23 next highest value

Bailey, G. W., R. R. Swank and H. P. Nicholson. 1974. Predicting pesticide run-off from agricultural land: A conceptual model. J. Environ. Qual. 3:95-102.

Single rainfall, single application, single watershed model.

Barker, P. S., F. O. Morrison, R. S. Whitaker. 1965. Conversion of DDT to DDD by Proteus vulgaris, a bacterium isolated from the intestinal flora of a mouse. Nature 205:621-2.

Pure pp'DDT in evaporated ethanol in tubes, media introduced and inoculated with mice gut isolates. 5 days at 30°C.

Methanol and chloroform → paper chromatography.

(1) P. vulgaris only → DDT. (P. vulgaris invades tissues after death) 5.45 mg DDT

Time of Incubation (day)	DDD in mg	
	30°C	37°C
6	0.355	—
10	—	0.395
15	0.270	0.355
20	0.243	0.300

(3) This does not work with DDE cultures.

(4) DDD being further metabolized from quantity results (paper chrom. (?)).

Bevenue, A., J. Ogata, and J. Hylin. 1972. Organochlorine pesticides in rainwater, Oahu, Hawaii, 1971. BECT 8:238-241.

Rainwater - 1-14 pp trillion, mean 4 ppt.

Snow - 15 ppt.

Lakewater - 5 ppt.

Birrell, K. S. 1963. Thermal decomposition of DDT by some soil constituents. New Zealand J. Sci. 6(2):169-

(1) Couldn't obtain reference.

Bishara, R. H., G. Born and J. E. Christian. 1971. An observation on the multiple development of DDT and some metabolites on aluminum oxide thin-layer chromatograms. J. Chromatog. 57:444.

DDT, DDE, DDD, DDA, DDMU were allowed through solvent systems then hit for 2 min with UV light.

All metabolites showed additional spots of different R<sub>f</sub>. This did not happen when normal light was used.

It did not happen with Uv light when silica gel plates were used.

Bowman, M. C., F. Acree, Jr. and M. Corbett. 1960. Solubility of Carbon-14 DDT in water. J. Agr. Food Chem. 8:406-8.

(1) 1.2 ppb or less at 25°C.

(2) Does not take into account undissolved DDT particles on carrier.

Bowman, M. C., F. Acree, C. Lofgren, and M. Beroza. 1964. Chlorinated insecticides: Fate in aqueous suspensions containing mosquito larvae. Science 146:1480-1481.

20 hours at 26.5°C with chlorinated hydrocarbon, then assayed for residues.

- (1) More than 1/2 of DDT in system lost by codistillation with H<sub>2</sub>O. This was expected but other insecticides had low recovery too.

Use electron-affinity gas chromatography on low conc. aqueous solution.

Bradshaw, J. S., E. L. Loveridge, K. P. Rippee, J. L. Peterson, D. A. White, J. R. Barton and D. K. Fuhrman. 1972. Seasonal variations in residues of chlornated hydrocarbon pesticides in the water of the Utah Lake drainage system - 1970 and 1971. Pest. Monit. J. 6: 166-170.

DDE in water samples preceded by rain storms. DDT recorded once. Up to 4 ppb.

Smaller younger fish contained less DDT, use Declining? 0.05-0.96 ppm DDE in fish.

Bridges, W. R., B. Kallman, and A. Andrews. 1963. Persistence of DDT and its metabolites in a farm pond. Trans. Am. Fish Soc. 92:421-7.

0.02 ppm DDT in water

- (1) After 3 wk, nothing water.
- (2) 8 wk, mud had declined to control levels, but vegetation still high.
- (3) 1 yr after treatment, vegetation levels were control values (new crop).
- (4) Fish - 3-4 ppm after 1 month.
- (5) 17 months later, 2-3 ppm DDD and DDE
- (6) Crayfish levels generally 1/2 of fish.

Burdick, G. E., H. Dean, E. Harris, J. Skea, R. Karcher and C. Frisa. 1969. DDT: The effect of time and rate of feeding on the reproduction of Salmonid fishes, reared and held under control conditions. (Rough draft, in press).

#### Gas Chromatography

Loss of fry-brown and brook trout - from females fed DDT and not - time and dosage controlled

- (a) Only one stage showed diff. mortality hatch → feeding therefore fry must intake DDT itself though yolk sac. - Brown trout adults 3.39 mg/kg body wt (44 wk)

Brook trout - below environmental levels.

Burdick, G. E., E. Harris, H. Dean, T. J. Walker, J. Skea, and D. Colhy. 1964. The accumulation of DDT in lake trout and the effect on reproduction. Trans. Am. Fisheries Soc. 93: 127-136.

Lake George, New York

Fry dying at period of fat glyceride absorption. 1951-55, 7,3000 lb DDT on Lake for gypsy moth. 1955-57, 25,950 lb and private use extensive - some figures pp'DDE or pp'DDT.

All fish and egg samples were dry weight - spectrophotometry, paper chromatography but calculated as wet.

- (1) Conc. of DDE was not correlated to mortality in fry.
- (2) High range of DDT in fish oil, but prep. to water content.
- (3) No relation of female content and egg content.
- (4) 4.75 ppm is starting point for mortality, 2.95 by spectrophotometry.

Burge, W. D. 1971. Anaerobic decomposition of DDT in soil: Acceleration by volatile components of alfalfa (J. Agr. Ed. Chem.) 19:375-8.

DDT was stable in aerobic soil, even with alfalfa; main product in anaerobic is DDD, but radioactivity disappears.

pp'DDT, DDD, DDE and DDA 1.0-2.0 mg. DDT was added to a 100 g sample and that mixed with other soil; glucose and alfalfa were added the same way.

DDT converted to DDD in 46 days (anaerobic was enhanced by alfalfa distillate), but not in aerobic, this disappeared in 166 days.

DDD and DDE are stable in both anaerobic and aerobic setups. Above 2% oxygen the cultures did not transform DDT; at 2% probably all oxygen was used before transformation began.

Butler, P. A. 1966. Fixation of DDT in estuaries. Trans. NA Wildl. Conf. 31:184-189.

7-10 ppb will inhibit shell deposition in oysters.

Add anhydrous sodium sulfate to sample to preserve pesticide - 3-10X weight of sample homogenized. Oyster concentrate and flush DDT at constant rate, fish concentrate and only lose when starve. increased trophic level → increased DDT.

Castro, T. F. and T. Yoshida. 1971. Degradation of organochlorine insecticides in flooded soils in the Philippines. J. Agr. Ed. Chem. 19:1168-1170.

15 ppm - Laboratory reconstruction

DDT and DDD degraded faster in flooded than upland and in soils with higher organic components. DDD accumulated in DDT treated soil.

Upland = 80% water holding capacity.

Chacko, C. I., J. L. Lockwood, and M. Zabik. 1966. Chlorinated hydrocarbon pesticides: Degradation by microbes. Science 154: 893-5.

Aerobic

Cultured for 6 days with 5 to 10 µg of pesticide/ml (gas chromatography).

Nine actinomycetes and 8 fungi.

- (1) 6 of 9 actinomycetes, but no fungi degraded DDT to DDD. Most effective Nocardia erythropolis, S. aureofaciens, S. viridochromogenes, and S. cinnamomeus.
- (2) Maximum degradation of 25% was achieved in 6 days.
- (3) Degradation occurred only in the phase of active growth.

Check, R. M. and M. T. Canario. 1972. Residues of chlorinated hydrocarbon pesticides in the northern quahog (hard-shell clam), Mercenaria mercenaria - 1968 and 1969. Pest. Monit. J. 6:229-23.

Narragansett Bay, R.I. 56 composite samples pp'DDD in 3 samples  
0.026 ppm. No detectable DDE or DDT was found.  
Northern bay increased more than southern in residues.

Cliath, M. M. and W. F. Spencer. 1972. Dissipation of pesticides from  
soil by Volatilization of degradation products I. Lindane and DDT.  
Environmental Science and Technology 6:910-914.

30°C vapor pressure pp'DDE (109 ng/l) 8X vapor pressure pp'DDT  
(13.6 ng/l).

- a) pp'DDT or pp'DDE (10 µg/g) to Gila silt loam, 30°C.
- b) Saturation vapor density - 15-39 µg/g soil.
- c) Vapor density of pp'DDE reach 1.4 ng/l in 65 days.
- d) 66% of atmospheric DDT after an agricultural area was pp'DDE  
(no rates) (7 yr, not for 14 months).

Soil - 23.1 ppm DDT's

Air - 4.96 ppm DDT's

Cole, H., D. Barry and D. H. Frer. 1967. DDT levels in fish, streams,  
stream sediments and soil before and after DDT aerial spray appli-  
cation for fall cankerworm in northern Pennsylvania. BECT 2:127-  
146.

0.5 lb DDT/acre

Small levels before treatment

Pretreat

- (1) Trout 20-100X watershed soils and stream sediments.
- (2) White suckers 6-15X the trout (lake)
- (3) TDE were found in fish, but not soil.

Post-treat

- (4) TDE and pp'DDT increased for four months after treatment, then  
decreased. Soils stayed same.

Cory, L., P. Fyeld, and W. Serat. 1970. Distribution patterns of DDT  
residues in the Sierra Nevada mountains. Pest. Monit. J. 3:204-211.

Frogs - pp'DDE was the most common residue.

Contamination throughout even above 12,000 ft.

Highest in central and south, lowest in north.

Highest on west slope, wind blown from aerial spraying in  
California.

Yosemite was high, but sprayed in 1953-1956.

Courtney, C. H. and J. K. Reed. 1972. Accumulation of DDT from food  
and from water by golden shiner minnows, Notemigonus crysoleucas.  
Proc. 25th Annual Southeastern Assn. Game and Fish Commis. pp. 426-  
431.

Not able to locate.

Cox, J. L. 1970. Accumulation of DDT residues in Triphoturus mixicanus.  
Nature 227(5254):192-193.

- (1) Not near hot spots of DDT. Gulf of California, mid water fish.
- (2) 13-79 ppb wet wt.
- (3) ↑ in DDE with ↑ body wt.

of pesticide residues in wild animals. Ann. N. Y. Acad. Sci.

- (1) Pesticides low solubility in water makes them cling to plants and bottom sediments to be taken up by invertebrates or fish or both (from water too at least in fish)
- (2) If fish or invertebrates become resistant to pesticides by changing to non-toxic substance, good predators; If merely store large quantities unchanged → bad for non-resistant predators. Also on land, although earthworms and slugs cannot concentrate as some oysters and fish. Plants accumulate also.
- (3) Build-up does not go on indefinitely (storage, metab., absorption and excretion). If equilibrium at low levels, no problem; if high → toxicity and death. The equilibrium value may change with [conc.] of pesticides in environment.
- (4) Food habits and metabolism → residue levels (+ history of exposures).
- (5) Correlation - DDT and + repro. from
  - (a) the higher residues in declining than non-declining
  - (b) timing of declines and large-scale treatment
  - (c) decline in areas of pesticide use
- (6) Physiological effects: (a) ↑ liver enzymes; (b) ↑ drug metabolism → ↑ fent; (c) nervous system → aberrant behavior; (d) egg shell thinning; (e) storage in fact - good or bad depending on circumstance; (f) molt (g) disturbance.

Earnest, R. D. and F. E. Benville. 1971. Correlation of DDT and lipid levels for certain San Francisco Bay fish. Pest Monit. J. 5: 235-241.

Copy not at CSU libraries.

Eichelberger, J. W. and J. J. Lichtenberg. 1971. Persistence of pesticides in river water. Environ. Sci. Technol. 5:541-544.

- (1) Eight wk, 10 µg/l
- (2) Little Miami River water, GLC for 0 and 8 wk determinations.
- (3) DDT, DDE and DDD did not degrade; DDE and DDT did not degrade in distilled water either.

Ernst, W. 1972. Degradation of [<sup>14</sup>C]DDT on silica gel G chromatograms under laboratory conditions. J. Chromatogr. 67:179-181.

- (1) In dark
- (2) Laboratory daylight
- (3) Under a fluorescent lamp - shortwave UV → polar substances even after only a 15 min period → 4 compounds
  - (a) all others caused some polar formation

No quantitative data.

Framer, W. J., K. Igue, W. F. Spencer and J. P. Martin. 1972. Volatility of Organochlorine Insecticides from soil. I. Effect of Concentration, Temperature, Airflow Rate and Vapor Pressure. Proc. Soil Sci. Soc. Am. 36(3):443-47.

No water movement (net) during volatilization

- (a) controlled by vapor pressure and conc.
- (b) Maximum DDT loss was 5 kg/ha/yr, (2-2.2%/day) as soil conc. ↓.

8 ml/s air flow, 10% soil water, 100% humidity, 30°C.

(c) Gila silt loam to ethylene glycol traps

(d) 10, 50, 100 or 500 µg of  $C^{14}$  pesticide.

Vapor pressure Lindane > dieldrin > DDT

Fateyeva, O. F. 1972. DDT residues in the soil and in roots of apple trees following repeated spraying. Khim. Sel. Khoz. 10(3):195-198. (Russian)

DDT - 15,000 lb/ha, 7 g DDT/lb - 2-3 applications

(1) 0-5 cm had highest DDT

(2) 1 yr after = 52.4-63.2% decrease in DDT

(3) 2-3 yr = 20-36% decrease in DDT

(4) Apple seeds contained large quantities of DDT (4.6-60 mg/kg), but not the fruit.

Frank, R. 1971. Unpub. Rep., Provincial Pesticide Residue testing Laboratory, Ontario Dept. of Agr. and Food, Guelph, Ont., in Hurtig H. (1972).

Fish, Ontario recreational areas

<u>Location</u>	<u>No.</u>	<u>ppm Muscle</u>	<u>% Fat</u>	<u>ppm Fat</u>
Trent River	329	.507	1.75	29.0
Holland Marsh	312	.682	2.77	24.6
Muskoka Lakes	519	7.91	3.60	221.4
Great Lakes	404	.750	4.25	17.6
Ottawa River	57	.118	3.22	3.66

Freed, V. H., R. Hague and D. Schmedding. 1971. Vaporization and environmental contamination by DDT. Chemosphere (in press) Tech Paper No. , Oregon Agr. Expt. Sta.

(a) Aerosol spray or dust suspension.

(b) Wind erosion of contaminated dust.

(c) Vaporization

Soil diff. from glass use  $\frac{W_1}{W_2} = \frac{P_1}{P_2} \times \frac{M_1^{1/2}}{M_2^{1/2}}$ ; 1 and 2 are water and DDT

68°F (20°C) = 0.082 ppm of water in field 10% efficient

86°F (30°C) = 0.133 ppm of water  
0.1 lb/acre/yr is real value

Soil Exp. - 25°C, 10 ppm DDT in sandy loam soil 1/2 moistened  
1/2 dry

No loss in either sample after 10 days

Even when soil in thin layer and constant wind, no loss in 7 days

Thus losses in soil are different from vaporization from the chemical or from inert surfaces.

French, A. L. and R. A. Hoopingarner. 1970. Dechlorination of DDT by membranes isolated from Escherichia coli. J. Econ. Entomol. 63: 756-759.

(1) Washed membranes after lysosomal treatment and osmotic shock (incubated 4 hr with  $^{14}C$ -DDT)

- (2) Gas and TLC for DDT analysis
- (3) DDT → DDD occurred and was enhanced by the additions of Kreb's cycle cofactors (FAD but not NAD)
- (4) FAD, inorganic phosphate and unboiled membranes → 72.6% DDT, 22.5% TDE.

Fricke, G. 1972. Comparison of the soil contamination with organochlorine insecticides in 1969 and 1972. (Part I: Large scale vegetable gardening. Gesunde Pflanz. 24:177-179.

- (1) 48% of gardening area free from DDT in 1969.
- (2) DDT residue 0.01-0.1 ppm - 1969, Avg = 0.102 ppm.
- (3) By 1972, that was down to 1/10 of 1969 levels, Avg = 0.015 ppm.

Gakstatter, J. H. and C. M. Weiss. 1967. The elimination of DDT-C<sup>14</sup>, dieldrin-C<sup>14</sup>, and Lindane-C<sup>14</sup> from fish following a single sublethal exposure in aquaria. Trans. Am. Fish. Soc. 96:301-307.

60-70 (bluegill, Lepomis macrochirus; goldfish, Carassius auratus) in tank with 0.03 ppm DDT C<sup>14</sup> for 5 to 19 hr. Recovery tanks for 32 days. Only 50% of DDT was eliminated. Transfer to control fish occurred even though water in control tank was changed by circulation 2.5 times/day. Initial conc. of DDT averaged 5.1 ppm (whole body) after exposure.

George, J. L. and D. E. H. Frear. 1966. Pesticides in the Antarctic. J. Appl. Ecol. 3(suppl.):155-167.

Levels in individual organisms.

Georgii, H. W. 1973. DDT in the biosphere. Hippokrates 44(1):98-100. German.

20 yr to degrade DDT  
Some 20,000 tons/annum by precipitation - nothing

Gram, C. S., A. R. Hauks, R. L. Richardson, W. M. Sachett and M. K. Wong. 1972. DDT, DDE and polychlorinated biphenyls in biota from the Gulf of Mexico. Pest. Monit. J. 6:139-143.

Coastal areas were higher than open water samples. Fish, shrimp, crabs, - all samples were contaminated.

Grib, N. V., V. Kovban and A. Burtsev. 1972. Zapadnogo Poles' ya insektitsidami (pri bor'be s gnusom) na ikk gidrobiologicheskiiy rezhim. Gidrobiol. Zh. (kiev) 8(1):98-101 (Russian) - Abstracts.

0.2 g/m<sup>3</sup> DDT was given for 30 min → 0.1 mg/l DDT in 20 hr.  
8 km from point of introduction - 0.18 mg/l - 3 hr benthic  
0.125-0.175 mg/kg  
Death of infusoria and arthropods and proliferation of diatoms  
+ Ca, + Mg

Grice, G. D., G. Howey, V. T. Bowen and R. H. Backus. 1970. The collection and presentation of open ocean marine organisms for pollutant analysis. BECT 7:125-132.

mg/kg lipid (means)

Sorgassum - 0.35 ppb; zooplankton 0.4 ppb; flying fish - 2.3 ppb; trigger fish - 0.1 ppb; dolphin - 49 ppb; mesopelagic fish (5; whole) - 12, Chauliodes danae; mesopelagic crustacean (17, whole) 5.7, Systellaspis debilis.

Grzenda, A. R., H. P. Nicholson, J. I. Teasley and J. H. Patric. 1964. DDT residues in mountain stream water as influenced by treatment practices. J. Econ. Entomol. 57:615-618.

0.59 lb/acre technical DDT

0.346 ppb in streams when sprayed; after 2 months, none in stream. 49% of basin sprayed. No DDT in sediments or waters. Paper chromatograph, Infrared spectroscopy

Grzenda, A., D. Paris and W. J. Taylor. 1970. The uptake, metabolism and elimination of chlorinated residues by goldfish (Carassius auratus) fed a  $^{14}\text{C}$ -DDT contaminated diet. Trans. Am. Fish. Soc. 99(2):385-396.

Couldn't locate reprint.

Guenzi, W. D. and W. E. Beard. 1968. Anaerobic conversion of DDT to DDD and aerobic stability of DDT in soil. Soil Sci. Soc. Amer. Proc. 32:522-4.

$^{14}\text{C}$ -DDT and DDT were added to Paunee silt loam with or without 1% alfalfa extract.

- (1) One set aerobic and other anaerobic.
- (2) DDT  $\rightarrow$  DDD and 6 other products in anaerobic conditions.
- (3) Less than 1% DDT present after 12 wk with alfalfa.
- (4) 6 months, 75% of DDT present in aerobic samples, 4% DDE and trace DDD.
- (5) Less than 1%  $^{14}\text{C}$  in  $\text{CO}_2$  after 6 months.

Guenzi, W. D. and W. E. Beard. 1970. Volatilization of lindane and DDT from soil. Proc. Soil Sci. Soc. A. 34:443-447.

- (1) Loamy sand to clay, 10 ppm  $^{14}\text{C}$ -DDT, 30°C and 55°C.
- (2) Above 15 bars tension water, volatilization was related to temperature, adsorptive characteristics of soil and conc. of pesticide
- (3) DDT  $\rightarrow$  DDE ranged from 6.7% to 21.2%.
- (4) No volatilization when water not a monolayer.
- (5) Volatilization was related to soil surface area.

Hamelink, J. L., R. C. Waybrant and R. C. Ball. 1971. A proposal: Exchange equilibria control the degree chlorinated hydrocarbons are biologically magnified in lentic environments. Trans. Am. Fish. Soc. 100:207-214.

The avg DDT-R conc. in H<sub>2</sub>O was directly related to DDT conc. placed in the bottom. Hydrosol (14 ppm DDT and DDD) in the first 5 days decreasing over the year. Percentage breakdown of DDT to DDD was inversely related to DDT conc. Algae absorb DDT-R so what is there in ppm of tissue is a function of water conc. and algae biomass. Invertebrates followed H<sub>2</sub>O conc., rapidly up than down. There was a stepwise increase in pesticide content of different trophic levels whether the intervening trophic levels were there or not. So in lentic environments the rule must be resorption and absorption vs. release; solubility differences most - lipid and water but fish → water → blood → fat -  $1 \times 10^5$  concentration, pesticides are less hazardous in a eutrophic lake since the sediments act as a reservoir and are more soluble to DDT-R in a eutrophic lake.

Hartley, G. S. 1969. Evaporation of pesticides. Adv. in Chem Series 86:115-134.

1.2 lb/acre vaporization in England (glass plate)

- (a) pesticide vaporization is ↑ for bulk flow of water to surface as it evaporates pulls pesticide with it to ↑ conc. and volatilization at surface

Helrich, K., S. Race and J. Reed. 1970. DDT residue disappearance from field sprayed lettuce. BECT 5(1):30-33.

- (1) Lettuce was not at low levels for 50 days.
- (2) Rainfall did not affect disappearance rate.

Herzel, F. 1972. Organochlorine insecticides in surface waters in Germany - 1970 and 1971. Pest Monit. J. 6:179-187.

All in pptr. (ng/l range  
DDD and DDE found infrequently except for the Berlin Teltowkareal (suspended solids)

Hicks, G. G. and T. R. Corner. 1973. Location and consequences of 1,1,1,-trichloro-2,2-bis(p-chlorophenyl) ethane uptake by Bacillus megaterium. Appl. Microbiol. 25:381-387.

No detriment when cultures started with up to 100 µg DDT/ml, but grown cultures showed enhanced death with only 1 µg/ml DDT (0.5 µg dry wt.). Mortality was time and dose dependent. Cell bound up to 1.7 µg DDT mg/cell dry wt. in membranes. Some conversion to DDE with faster cell release. REspiration not inhibited. Membrane appearance was altered.

Holden, A. V. 1962. A study of the absorption of <sup>14</sup>C-labelled DDT from water by fish. Ann Appl Biol. 50:467-477.

- Removes rapidly from H<sub>2</sub>O; stored in stomach, pyloric caeca, intestine, spleen, muscle and skin.
- Lipid expression best, may determine toxicity to fish, levels in reproductive organs are dangerous. Don't use static water

- (1) [Conc.] at 300X, 80-90% of DDT removed in 10 hr.
- (2) Blood-brain barrier held and no build-up there yet.
- (3) Don't use static water in experiments, for toxicity, because [conc.] DDT  $\downarrow$  too fast.

Hom, W., R. Risebrough, A. Sontar and D. Young. 1974. Deposition of DDE and polychlorinated biphenyls in dated sediments of the Santa Barbara basin. Science 184(4142):1197-1199.

PCB - 1945, DDE - 1952

Both  $\uparrow$  to 1967.

Deposition rates 1967, DDE =  $1.9 \times 10^4$  g/m<sup>3</sup>/yr; PCB =  $1.2 \times 10^{-4}$  g/m<sup>3</sup>/yr.

Hurtig, H. 1972. Long distance transport of pesticides. CEPPIEPO Bull. No. 4:5-25.

Residues in soil: volatilization, photo-decomposition, chemical decomposition, adsorption, leaching, dilution, erosion (mechanical, co-distillation, uptake by plants).

Not any data.

Ive, G. W. and J. Casida. 1970. Enhancement of photoalteration of cyclodiene insecticide chemical residues by rotenone. Science 167:1520-1522.

10 ppm to 100 ppm both compounds, sunlight for 1 hr.  
No DDT result of DDD.

Ivie, G. W. and J. Casida. 1971. Sensitized photo-decomposition and photosensitizer activity of pesticide chemicals exposed to sunlight on silica gel chromatoplates. J. Agr. Food Chem. 19:405-409.

Sunlight for 1 hr

Very slight action. Aromatic amines sensitize DDT photo-decomposition by formation of charge transfer complexes. Nothing quantitative.

2  $\mu$ g in 2 ml methanol of pesticide - in open air.

Jannasch, H. W., K. Eimhjellen, C. O. Wirsen and A. Farmanfarmaian. 1971. Microbial degradation of organic matter in the deep sea. Science 171:672-675.

Limited microbial degradative ability - 10-100X less than open water under same temperature.

5000 m depth

Jarvinen, A. W., M. J. Hoffman and T. W. thorslund. 1975. Significance to fat head minnows (Pimephales promelas) of food and water exposure to DDT. In press.

Higher DDT from water than diet. Diet and water residue were additive  
Conc. 1.2 times from diet and 100, 000 times from water. Residues were 4X in water exposed fish as dietary. Higher mortality from both exposures than from one or the other. Dietary DDT + PCO 0.025 survival  
DDT in water - estimated maximum toxicant 0.9  $\mu$ g/l  
DDT in diet and water (56.7  $\mu$ g/g) 0.4  $\mu$ g/l

Embryo and larval levels are 2X when parents have DDT in both water and food as when only to water.  
60% of mean total micrograms in fish exposed at 0.5 µg/l in water and diet was eliminated in 56 days. Virtually all if only dietary was used. None was eliminated with only water exposure.  
Clams X 25,000 from DDT-treated water.

Jensen, S., R. Gothe and M. -O. Kindstedt. 1972. Bis(p-chlorophenyl)-acetonitrile (DDN), a new DDT derivative formed in anaerobic digested sewage sludge and lake sediment. Nature 240:421-422.

1 l activated sludge and 100 mg pp DDT with 5 µCi <sup>14</sup>C-DDT with DDD and DDE, 8 days at 20°C.  
pp'DDT 1/2 life = 7 hr.  
DDE disappeared in 48 hr.  
DDCN was found in a natural lake sediment (Lake Malaren, Sweden, 0.6 ppm/dry wt.)  
Sludge from a treatment plant in Uppsala also contained DDCN (0.012 ppm/dry/wt.)

Johnson, B. T., T. Goodman and H. Boldberg. 1967. Conversion of DDT to DDD by pathogenic and saprophytic bacteria associated with plants. Science 157:560.

- (1) 23 of 28 microorganisms converted pp'DDT to pp'DDD, anaerobically 10 µg/ml DDT for 14 days.
- (2) Range of conversion was from trace to 5 µg/ml.
- (3) Most conversion occurred in last 7 days.
- (4) Other metabolites were present.
- (5) GLC analysis.

Johnson, B., C. R. Saunders and H. Sanders. 1971. Biological magnification and degradation of DDT and aldrin by freshwater invertebrates. J. Fish. Res. Bd Can. 28:705-709.

Freshwater aquatic crustacea and immature insects on continuous flow of <sup>14</sup>C-labelled aldrin and DDT to get magnification from water and degradation in invertebrates less than 100 ng/liter  
H<sub>2</sub>O - 3 days, no food.

Results - Rapid uptake without regard to surface/volume or taxonomy. Some of 100,000 magnif. No plateaus of uptake observed. Conversion to DDE, some shrimp also DDD, DTC, and DBP, aldrin and dieldrin

- \* invertebrates
- (1) contribute to rapid accumulation when DDT's present for only short time.
  - (2) when pesticides at constant rate, they magnify.
  - (3) also magnify degradation products.

Johnson, H. E. and R. C. Ball. 1972. Organic pesticide pollution in an aquatic environment. Great Lakes Res. Symp.:1-10.

General overview.

Jones, B. R. and J. Mogle. 1963. Population of plankton animals and residual chlorinated hydrocarbons in soils of six Minnesota ponds treated for control of mosquito larvae. Trans Am. Fish. Soc. 92(3):211-215.



Rice straw - 0.132 ppm pp'DDE, 0.464 ppm op'DDT, 0.66 ppm pp'DDT.  
Paddy soil - 0.030 ppm pp'DDE, 0.13 ppm pp'DDD, 0.105 ppm op'DDT,  
0.40 ppm pp'DDT.

Kearney, P.C., R. G. Nash and A. R. Iseuee. 1969. "Persistence of pesticide residues in soils" in Chemical Fallout (Charles C. Thomas, Pub., Springfield, Ill.) p. 54-67.

Persistence is a relative term. 75 to 100 bioactivity of control or 75-100% loss of pesticide.

Chl. Hydr. = 18 months and up for normal agricultural levels.

DDT = 4 years, when large quantities are applied, they last 2-3 times longer.

#### Disappearance

- (1) 1st order - the rate of loss is 1 to the amount in the soil.
- (2) Biological metabolism - delay before removed to food chain.
- (3) Levels with repeated application amounting to loss.
- (4) Mercury and arsenic levels are very complex depending on soil type, moisture, what compound is left. So their values are more complex.
- (5) If the pesticide is biodegradable, then it follows a significant curve.

Ko, W. H. and J. L. Lockwood. 1968. Conversion of DDT to DDD in soil and the effects of these compounds on soil microorganisms. Can. J. Microbiol. 14:1069-73.

Submerged soil with alfalfa residue

↑ conversion with ↑ alfalfa.

2 of 10, and 4 of 10 bacteria were inhibited by 10 ppm DDT or DDD in nutrient media.

DDD was more inhibitory than DDT on microorganisms.

This did not happen in soil.

Fungi were not affected even in nutrient media.

Kramer, R. E. and R. W. Plapp. 1972. DDT residues in fish from the Brazos River basin in central Texas. Environ. Entom. 1:406-409.

#### Streams

Agricultural > range land > recreational gar (*Lepesosteus* spp.) had highest levels (muscle)

None over 1 ppm.

Khur, R. J., A. Davis and E. Taschenberg. 1972. DDT residues in a vineyard soil after 24 years of exposure. BECT 8:329-333.

4-16 lb active DDT/acre/yr for 25 years; 164.85 lb/DDT/acre in 24 years; 54 lb/acre in 9 years

6 and 12 yr data - DDT in top 3", 1/2 life = 6 yr, 1/3 life = 12 yr, DDE only present.

Spring '71 - treated and control soil samples [average of 4 replicate plots].

[0-3" cores, 3-6" cores, center rows and drip place.]

6, -12, -24 yr % DDE +. 6 yr = 12%, 24 yr = 27%, 24 yr loss of DDT = 22% recovered

Check plots near fields contained low levels of DDT (3) (1.4 lb/acre) and no DDE; in 24 yr the DDT had ↑ and moved down to 3-6" and DDE was contained in plots.

Kuwatuka, S. 1972. Pesticides in the soil. Kagaku Kogyo. 23(11):81-88.  
(Japanese)

75% of DDT remains for more than 6 months under aerobic condition.  
Anaerobic conditions or 1% alfalfa addition → 1% DDT in 12 weeks.  
General review.

Leland, H. V., W. Bruce and N. Shrimp. 1973. Chlorinated hydrocarbon insecticides in sediments of southern Lake Michigan. Environ. Sci. Tech. 7:833-838.

↑ organic carbon → ↑ DDT residue levels in ppb and general distributed and available to benthic organisms.

Lichtenstein, E. P. and K. R. Schulz. 1959. Persistence of some chlorinated hydrocarbon insecticides as influenced by soil types, rate of application and temperature. Econ. Ent. 52:124-131.

10 or 100 lb/acre - samples at 6, 12, 18, 24, 30, 36, 42 months  
Miami silh loam (organic = 3.8%) 22% of DDT recovered 42 months  
Muck soil (organic = 40.0%) 33% recovered 42 months.  
More original application → longer 1/2 life

Lichtenstein, E. P. and K. R. Schulz. 1961. Effect of soil cultivation, soil surface and water on the persistence of insecticidal residues in soils. J. Econ. Entomol. 54:517.

Persistence of DDT was not effected by the amount of water evaporated from soils on glass surfaces, or by surface enlargement.  
Field 4 lb/5" acre DDT with daily disking gave - 25% reduction in 3 months (24% nondisked, 44% disked)

Lichtenberger, J. J., J. W. Eichelberger, R. C. Dressman and J. E. Longbottom. 1970. Pesticides in surface waters of the United States - a 5 year summary, 1964-1968. Pest Monit. J. 4:71-86.

(1) Not applicable to model; stored values better

Lindquist, R. A., H. A. Jones and A. H. Maddeu. 1946. DDT residual type sprays as affected by light. J. Econ. Entomol. 39:55-59.

Nothing substantial, (1) wet more degradative than dry soil

Liu, H. J., P. Silk and I. Unger. 1972. The photodecomposition of an analogue of DDT. Can. J. Chem. 50(1):55-60.

1,1,1-trichloro-2,2-bis(5'-chloro-1'-methoxyphenylethane (MPA)  
light > 300 nm.

Solid → MPE and HCL, MPO, MPD and MPC

$O_2$   
Liquid → MPE and HCL, MPD, MPC and MPO

NO  
Liquid → HCL, MPD, MPC, and MPE; MPD and MPC were larger than MPE  
 $O_2$

Lloyd-Jones, C. 1971. Evaporation of DDT. Nature 229:65-66.

Vapor pressure =  $1.5 \times 10^{-7}$  mmHg 20 C  
Gas diff. coeff. = 0.05 cm<sup>2</sup>s<sup>-1</sup>

Still air layer thickness = 2 mm

∴ evap. rate at 20 C =  $3 \times 10^{-3} \text{ ug cm}^{-2} \text{ h}^{-1}$

Experimentally labeled  $\text{C}^{14}$ , on carbon rings → 0.5 ug cm<sup>2</sup>, several experiments with measuring label

Over time → a loss of evaporation rate of 2 ln/acre/yr in summer; 0.3 lb/acre/yr in winter or over half of the DDT applied.

Macek, K. J. and S. Korn. 1970. Significance of the food chain in DDT accumulation by fish. J. Fish. Res. Bd., Can. 27:1496-1498.

Food vs. water in DDT accumulation in fish

$3 \pm 0.3$  ppbtr. pp'DDT-labeled for 120 days in H<sub>2</sub>O

$3 \pm 0.15$  ppm  $^{14}\text{C}$ -pp'DDT

7% mortality in both groups - 120 days in H<sub>2</sub>O → 25.6 ppb, 120 days in feed → 1.92 ppm.

Uptake in both cases linear for 60 days, then leveled off a little.

Fish in H<sub>2</sub>O gained 3.55% of DDT available, fish in feed gained

35.5% of DDT available

At H<sub>2</sub>O rate, 12 yr to obtain wild levels, in food - 1 yr, so food levels were more important.

Macek, K. J., C. Rodgers, D. Stalling and S. Korn. 1970. The uptake, distribution and elimination of dietary  $^{14}\text{C}$ -DDT and  $^{14}\text{C}$ -dieldrin in rainbow trout. Trans. Am. Fish. Soc. 99(1):689-695.

<u>DDT</u>	<u>Dieldrin</u>	
0.2 mg/kg/wk 20-24%	1.0 mg/kg/wk 9-11%	equilibrium in 140 days
		portion accumulated
		shape of accumulation
160 days ↑ lipogenesis	40 days ↑ lipogenesis	time to eliminate 50%
(a) presence of dieldrin enhanced DDT uptake, (b) presence of DDT ↑ dieldrin uptake, (c) dieldrin inhibits DDT elimination, (d) DDT does not effect dieldrin elimination		

Meeks, R. L. 1968. The accumulation of  $^{36}\text{Cl}$  ring-labeled DDT in a freshwater marsh. JWM. 32:376-398.

DDT granules 1st to bottom, then DDT released and plankton and larger organisms removed. 1-3 days → max. producer levels (+ 1-3 days) → invertebrate max. through food web for levels separated.

Snakes more than 1 yr later = max.

Loss of total DDT throughout year from codistillation with H<sub>2</sub>O.

Soil got some and collections.

Some organism [conc.] DDT 200-500X, avg. = 50.

Fat good indicator in vert. tissues, not others.

Variation in accumulation at all levels is high.

Mendel, J. and M. Walton. 1966. Conversion of pp'DDT to pp'DDD by intestinal flora of the rat. Science 151:1527.

pp'DDT given rats intraperitoneally and by stomach tube varied as to pp'DDD in liver and feces. Stomach tube animals did, but not IP treated.

- (1) Coliform bacteria from feces could reductively dechlorinate pp'DDT to pp'DDD
- (2) ∴ site of pp'DDT conversion is not liver but G.I. tract.

Menzel, D. J., J. Anderson and A. Randhe. 1970. Marine phytoplankton vary in their response to chlorinated hydrocarbons. Science 167: 1724-1726.

Varying response, some insensitive, some lethal at 0.1 to 1.0 ppm DDT, intermediates exhibited + photosynthesis.

Metcalf, R. L., I. P. Kapoor and A. Hirwe. 1971. Biodegradable analogues of DDT. Bull. Wld. Health Org. 44:363-374.

All synthetic analogue data  
Review

Miller, L. L., R. Narange and G. Nordlom. 1973. Sensitized photolyses of DDT and decyl bromide. J. Org. Chem. 33(2):340-346.

Aromatic amines can break down alkyl halides. DDT broken down at 254 nm, especially in presence of oxygenated methanol. Sulfides inhibit this process, but direct photolysis is not effected in ethanol. At 310 nm photolysis is inhibited by oxygen but not at 254 nm. So not in sublight spectrum.

Mikus, R. P., D. Blair and J. Casida. 1965. Conversion of DDT to DDD by bovine rumen fluid, lake water, and reduced porphyrins. J. Agr. Fd. Chem. 13:481-483.

Incubated with (6 samples)  $^{14}\text{C}$ -DDT -0.01 ppm, 7 days, room temp. in stoppered flask, lake water Clear Lake, California

- (1) 80% of label was in DDD position on paper chromatography.
- (2) No good unity of conversion %; varied with  $\text{O}_2$  content and plankton count in water samples.
- (3) Boiled and distilled water under vacuum showed no conversion.
- (4) Rumen fluid converted 65% of  $\text{C}^{14}$ -DDT to  $\text{C}^{14}$ -DDD in 24 hr (0.04 ppm to samples 2 hr post feeding and strained)
- (5) No hemoglobin conversion unless under anaerobic conditions when porphyrins reduced.

Mosier, A. R., W. Guenzi and L. Miller. 1969. Photochemical decomposition of DDT by a free-radical mechanism. Science 164:1083-1085.

Solid and in hexane solution, 2537 Å (UV light), thin layers on inside of quartz tubing; 48 hr → 80% conversion to DDD, DDE, and DDC = 0  
No evaporation

Mosser, J. L., N. Fisher, C. Warster. 1971. PCBs and DDT alter species composition in mixed cultures of algae. Submitted to Science

Thalassiosira pseudonana - sensitive diatom, Dunaliella tertiolecta - resistant green alga.  
Each culture  $10^4$  cells/ml at zero time, mixed - 1:1 ratio

- (a) 25 ppb PCB and 100 ppb DDT inhibited T. pseudodonana, no effect on algae
- (b) Even at lower conc., T. p. did not compete with D. t. in mixed cultures.
- (c) Final cell counts were the same in all cultures; only species composition changed.

Murphy, P. G. 1971. The effect of size on the uptake of DDT from water by fish. Bull. Environ. Contam. Toxicol. 6:20-23.

Mosquito fish (Gambusia affinis)

41 ppt pp' DDT- $C^{14}$ , 19.5-21.0 C for 48 hr

Residues from field indicate that equilibria with the environment was reached by 150 mg in wt.

Small fish were more efficient than larger at DDT uptake (cut-off point = 200 mg) (mean conc. of small fish 4X that of large fish)  
70 mg → 36 ppb; 200 mg → 34 ppb, 300 mg → 28 ppb; 400 mg → 18 ppb;  
1000 mg → 10 ppb.

The fish (23) removed 21% of the DDT in the water in 48 hr.

Nash, R. G. and E. Woolson. 1967, Persistence of chlorinated hydrocarbon insecticides in soils. Science 157:924-926.

0-448 kg insect./acre throughout profile

<u>C.H.</u>	<u>Yr.</u>	<u>% Remaining</u>		<u>Yr.</u>	<u>C.H.</u>
Tech. Aldrin	14	40	10	14	BHC
Chlordane	14	40	45	14	Toxaphene
Cendrin	14	41	28	15	Par. aldrin
Heptachlor	14	16	31	15	Tech. dieldrin
Dilan	14	23	39	17	Tech. DDT
Isodrin	14	15			

Leaching, volatilization, photodecomposition, mechanical removal, biological decomposition were at a minimum. This may be an upper limit of persistence.

Nash, R. G., W. Harris and C. Lewis. 1973. Soil pH and metallic amendment effects on DDT conversion to DDE. J. Environ. Qual. 2: 390-394.

↑ pH → ↑ DDT to DDE

- (a) pH > 9, the conversion is enhanced by MgO
- (b) Temperature little effect.
- (c) Moisture does not affect pH effect.

Total residues were not effected by pH.

Newsom, L. D. 1967. Consequences of insecticide use on non-target organisms. Annu. Rev. Entomol. 12:257.

General review [soil, air, plant, animals (not complete)]  
to this time

Odum, W. E., G. Woodwell and C. Wurster. 1969. DDT residues absorbed from organic detritus by fiddler crabs. Science 164:576-577.  
DDT absorbed most readily to 250-1000 micron diameter particles.  
Fiddler crabs, Uca pugnax, fed 10 ppm DDT detritus of this size for

11 days showed altered behavior and DDT in muscle of claw increased 3-fold.

- (a) Size determined from screening field samples from a contaminated stream. Gas chromatography
- (b) Control claws - 0.235 ppm DDT, DDT - 0.885 ppm
- (c) Behavior alteration included incoordination causing loss of footing and lack of fear by day 5. Cause of disappearance from contaminated area.

Onsagu, J., H. Rusk and L. Butler. 1970. Residues of aldrin, dieldrin, chlordane, and DDT in soil and sugarbeets. J. Econ. Entomol. 63:1143-1146.

Residues in sugarbeets proportional to soil (of soil) residues at the time of planting. DDT (5.5%).

Patil, K. C., F. Matsumura and G. Bousch. 1971. DDT metabolized by microorganisms from Lake Michigan. Nature 230:325-6.

Isolated cultures (anaerobic) from Lake Michigan (24 sites on Wisconsin shore) water, silt, 6-12" below bottom.  
Approx. 300 microorganisms found; majority converted DDT to TDE

<u>Average</u>	<u>No.</u> <u>Cultures</u>	<u>No.</u> <u>Forming</u> <u>TDE</u>	<u>No.</u> <u>Forming</u> <u>DDNS</u>	<u>No.</u> <u>Forming</u> <u>DDE</u>
Water	68	54	34	15
Top silt	59	47	37	30
Bottom silt	35	27	17	13

Both TDE and DDNS are acricidal.

Patil, K. C., F. Matsumura and G. M. Boush. 1972. Metabolic transformation of DDT dieldrin aldrin and endrin by marine microorganisms. Environ. Sci. Technol. 6:629-632.

- (1) 30 days with  $^{14}\text{C}$ -DDT; seawater, bottom sediments from ocean and estuaries, surface films, algae and marine plankton.
- (2) 35 of 100 microbes degraded DDT to TDE.
- (3) No water samples degraded DDT by chemical or photochemical means, even polluted water
- (4) Surface films, sediments and plankton degraded DDT to TDE, DDNS and DDOH + (algae)
- (5) Sea sediments were very low in degradation.

Peterle, T. J. 1969. DDT in Antarctic snow. Nature 224(52919):620.

From snow melt -  $0.04 \times 10^9$  g/g from sample 6, 29.2 and 70.8% op'DDT pp'DDT respectively.

There could be as much as  $2.4 \times 10^6$  kg of DDT accumulated in the Antarctic snow.

Pfaender, F. K. and M. Alexander. 1972. Extensive microbial degradation of DDT in vitro and DDT metabolism by natural communities. J. Agr. Fd. Chem. 20:842-846.

Hydrogenomonas sp. converts DDT to DDD and DDMS, DBP under anaerobic conditions

Arthrobacter → same; ring cleavage there

(1) Natural samples → degradation, but slow by few organisms past DBP.

Pfaender, F. K. and M. Alexander. 1973. Effect of nutrient additions on the apparent cometabolism of DDT. J. Agr Food Chem. 21:397-399.

90% breakdown in polluted water to DDE, DDD, and DBP. Glucose enhanced DDD formation but slowed DBP biosynthesis. Diphenylmethane reduced DDD and DBP.

The number of microorganisms aboe to produce DDD and DBP ↑ with glucose and diphenylmethane. 7 wk 0.005% DDT

Pierce, R. H., Jr., C. E. Olney and G. T. Felbeck, Jr. 1971. Pesticide adsorption in soils and sediments. Env. Let. 1:157.

Reprint not available.

Plimmer, J. R., U. Klingebiel and B. Hummer. 1970. The collection and preservation of open ocean marine organisms for pollutant analysis. Science 167:67-69.

DDT - In methanol with bubbling nitrogen (photooxidation of DDT and DDE with O<sub>2</sub>)

Intermediates formed by free radicals of hydrogen from methanol → benzoic acids, aromatic hetones, and chlorinated phenols.

DDE - Undergoes photocyclization to dichlorofluorene derivatives.

Poirrier, M. A., B. Bordelon and J. Laseter. 1972. Adsorption and concentration of dissolved Carbon 14-DDT by coloring colloids in surface waters. Environ. Sci. Tech. 6:1033-1035.

Colored (Natural - humic or brown) colloids concentrate 0.168 ppb in natural surface water to 15,900X in 1 hr.

Colloids - 5-10 mm, 68% iron, fulvic acid - 68-78%, hymatomelanic acid - 16-28%, humic acid [this colloid can be precipitated to sediments by many aquatic changes] - 3.3-9.5%.

<sup>14</sup>C-technique.

Rautapaa, J. 1972. DDT, lindane, and endrin in some agricultural soils in Finland. J. Sci. Agr Soc. Finland 44:199-206.

21 sugarbeet fields; DDT residues average 0.73 ppm, 5% DDE of op'DDT + pp'DDT

21% of DDT applied in total was still present (Range = 2-65%).

Reinbold, K. A., I. Kapoor, W. Childers, W. N. Bruce and R. L. Metcalf 1971. Comparative uptake and biodegradability of DDT and methxocychlor by aquatic organisms. Ill. Nat. Hist. Surv. Bull. 30:405-417.

Couldn't get reference.

Reinert, R. 1970. Pesticide concentrations in Great Lakes fish. Pest. Monit. J. 3:233-240.

DDT and dieldrin in all fish. Lake Michigan contains 2-7x other Great Lakes.

↑ size → ↑ DDE within species on whole fish basis. On oil basis, the size diff. disappears.

Lab - pptr. H<sub>2</sub>O → ppm fish.

Risebrough, R. W., R. J. Huggett, J. J. Griffin and E. D. Goldberg. 1968. Pesticides: transatlantic movements in the northeast trades. Science 159:1233-1235.

Air transport (1) codistillation with H<sub>2</sub>O detection in air and rainwater, (3) atmospheric dust from Texas → Ohio, (4) mineral talc, DDT carrier occurs in rain in much higher degree than expected, in airborne particulate matter over the sea.

- (1) Total conc. of C. H.'s in air more in winter, overall pesticides did not change.
- (2) No correlation with pesticides and plants or minerals.
- (3) 41 ppb in dust - wind currents and dispersal in agricultural areas.
- (4) No PCB from Calif. but probablu in vapor and transported same way.

Robinson, J. A., A. Richardson, A. Crabtree, J. Conlson and G. Potts. 1967. Organochlorine residues in marine organisms. Nature 214: 1307-1311.

Many organisms and trophic levels.

Saito, M. and M. Kitayama. 1973. BHC and DDT residues in arable soil Hokkaidoritsu Eisei Kenkyushoho 23:116. (Japanese)

(1 yr after DDT ban)

<u>Paddy Fields</u>	<u>Arable Land</u>	
0.051-0.232 ppm	0.135-0.1845 ppm	pp'DDT
0.009-0.045 ppm	0.018-0.59 ppm	pp'DDE

This shows a decrease in paddy fields, 1969 - 0.036 pp'DDT  
arable, 1969- 1.272 ppm pp'DDT

Shtannikova, Ye. 1972. Decontamination of water contaminated with DDT and BHC. GigSanit. 37(9):97-99. (Russian)

2 mg DDT - Coagulate with sodium carbonate → 75-99% removal  
All artificial

Spencer, W. F. and M. M. Cliath. 1972. Volatility of DDT and related compounds. J. Agr. Food Chem. 20:645-9.

op'DDT's (7.5) are more volatile than pp'DDT (1)

At 30 C - atm contains 62% op'DDT, 16% op'DDE, 14% pp'DDE and 8% pp'DDT.

Technical DDT up to 20 mg/g ≈ equal op and pp DDT in soil and atm, but at higher conc. op'DDT in the atmosphere increases more than

pp'DDT.

Dieldrin did not effect volatilization.

Air drying + volatilization.

pp'DDE has a higher volatilization rate.

pp'DDT vapor pressure were  $1.52 \times 10^{-7}$  mm - 20 C

sand  $7.26 \times 10^{-7}$  mm - 30 C

$33.2 \times 10^{-7}$  mm - 40 C

Stadnyk, L., R. S. Campbell and B. T. Johnson. 1971. Pesticide effect on growth and  $^{14}\text{C}$  assimilation in a freshwater alga. Bull. Envir. Cont. and Toxicol. 6(1):1-8.

Evaluate in terms of changes in growth and metabolism rather than death - cell biomass, cell number and carbon-14 assimilation.

Cultured in an equivalent to a eutrophic lake - Duiron, carbaryl, 2-4D, DDT, dieldrin, tixaphene, and diazinon were investigated.

Results - diuron (herbicide) - + biomass: severe for 8 days and

+ carbon assimilation

carbaryl - exact opposite effect.

2-4D - less severe duiron effect DDT 925-51), toxaphene

and dieldrin (22-32) all + cell numbers at all concentrations and cell biomass (toxaphene only 3-4%.

DDT - Day 2 - 75% + C-14 assimilation

toxaphene - Day 2 450% + C-14 assimilation

+ algae + energy throughout ecosystem

Stenersen, J. H. V. 1965. DDT metabolism in resistant and susceptible stable flies and in bacteria. Nature 207:660-661.

in	<u>Serratia marcescens</u>	Anaerobic and aerobic
resistant	<u>Alcaligenes faecalis</u>	cultures with $^{14}\text{C}$ -DDT
fly feces	+ one other	25 and 37 C
	<u>E. coli</u>	24 or 72 hr ( $\text{H}_2\text{SO}_4$
	<u>B. brevis</u>	added)
	<u>A. aerogenes</u>	

(1) Anaerobically, S. marcescens, E. coli and other + 90% TDE (DDD) and 5% DDE; nothing in aerobic.

(2) There was no difference in rate of absorption, detox. or excretion of DDT in susceptible and resistant flies.

Stenersen, J. and J. Kvaloy. 1972. Residues of DDT and its degradation products in cod liver from two Norwegian fjords. BECT 8:120-121.

(Gadus morrhua L.) cod that are stationary in fjords

No Fruit Growing		Fruit Growing
Sample Size	19	5
DDT	0.5 ppm	5.05 ppm
DDE	0.27	2.67
DDD	0.42	1.85
	1.28 ppm	9.57 ppm

At low levels DDT in liver is dependent on liver wt.

Swoboda, A. R., G. Thomas, F. Cady, R. Baird and W. Knisel. 1971. Distribution of DDT and toxaphene in Houston Black Clay on three watersheds. Environ. Sci. Technol. 5:141-5.

10 yr - less than 16% of the DDT recovered in the top 5 ft of soil. 60-70% of that recovered was in the top 12". Leaching and erosion of top soil from abnks caused downward movement.

Tabor, E. 1965. "Pesticides in Urban Atmospheres," Paper No. 65-30 at 58th Ann. Meeting of Air Pollution Control Assoc., Toronto, Canada, June 20-24.

Mean DDT in air, agricultural 5 ug/1000 mm<sup>3</sup>  
Range up to 23 ug/1000 mm<sup>3</sup> DDT

Tarrant, K. R. and J. O'G. Tatton. 1968. Organochlorine pesticides in rainwater in the British Isles. Nature 219:725-727.

Up to 400 ppb in rainwater; high in London because of carbon particles.

12 months in 7 areas in England → rainwater in amber colored glass to prevent photodegradation.

Samples analyzed after 3 months. TLC on silica gel with hexane, then GLC.

- (1) Vary throughout yr. but pp'DDT, pp'DDE, pp'TDE always there, in ppb quantities, no matter what is the use in specific areas. So world-wide distribution is supported.

Tatton, J. O'G. and J. H. A. Ruzicka. 1967. Organochlorine pesticides in Antarctica. Nature 215:346-348.

McMurdo Sound DDT may be due to human activities, not weather, wind, water (ocean currents, etc.)

More remote birds and their prey were sampled and analyzed for several insecticides.

- (1) All remote penguins contain at least traces of BHC isomer, dieldrin, pp'DDT and pp'DDE in their liver, blubber and fat.  
(a) heptachloroxide and pp'DDE were also present.
- (2) Kill their major prey had lower levels of all compounds.

Trofimova, M. G. and A. Mitrofanov. 1972. Effect of granulated DDT, used for mosquito control, on aquatic organisms. (preliminary report) Med. Parazitol Parazit Bolez. 41(5):620-622. (Russian)

Surface and bottom water; aquatic plants, sediments (reservior)

5 kg 10% granulated DDT/ha - aerial

1-30 days - surface water and aquatic plants - no DDT

10, 20, 30 days - benthic water - 0.001, 0.003, and 0.007 mg/l

1, 10, 20, 30 days - benthic silt - 0.5, 0.8, 1.1, 0.9 mg/kg

Benthic pop. of Chironomidae deid after application, but surface organisms lived. TLC

Vrochinskiy, K. K., I. V. Grib and A. V. Grib. 1970. Organochlorine insecticide residue levels in aquatic plants. Gidrobiol. Zh. (Kiev) 6(6):107-109. (Russian)

## DDT

Lemna minor L.  
Spirodela polyrrhiza 2-3.8 mg/kg for  
Nymphaea abba L. 11.5 mg/kg other species  
Acorus calamus L.  
Potamogeton pectinatus L.

Water = 1 mg/kg, so they concentrate  
Benthic = 1.4 mg/kg DDT, DDE and DDD from plant rot.

Warner, K. and O. C. Fenderson. 1962. Effects of DDT spraying for forest insects on Maine trout streams. JWM. 26:86-93.

+ populations, especially young of year class., but didn't persist into 1959.  
Caddis fly larvae were affected.

Waybrant, R. C. 1973. Factors controlling the distribution and persistence of lindane and DDE in lentic environments. Purdue University Ph.D. thesis. Hamelink, J. L. - Major Professor.

200 pptr. in the epilimnion or 50 pptr. of the whole lake in a thermally stratified ultra-oligotrophic flooded limestone quarry.  
(a) Persistence controlled by absorption on suspended particles. DDE with 15X the absorption disappeared 15X faster. In 3 months, 85% of DDE was in the sediments, 72% of lindane was still in water.

e.g., Stand 1

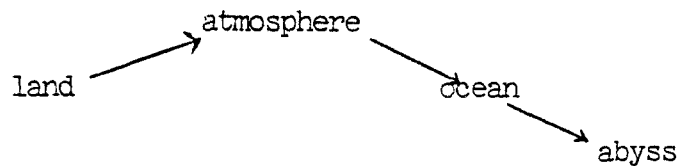
<u>Year</u>	<u>DDT</u>
1958	.409 + 0.80 kg/hectare
1960	1.496 ± .360 kg/hectare
1961	1.622 kg/hectare

Woodwell, G. A., C. Wurster and P. Isaacson. 1967. DDT residues in an East Coast estuary: A case of biological concentration of persistent insecticide. Science 156:821-824.

Larger animals in higher trophic levels had most residues.  
0.04 ppm in plankton → 75 ppm herring gull.  
DDT → DDE → DDD as move up trophic levels.  
+ repro. in shrimp, amphipds, blue crab, toad, woodcock.  
Variability in the amounts among a species leads to continuous cropping of higher individuals and no spectacular kill.

Woodwell, G. M., P. Craig and H. Johnson. 1971. DDT in the biosphere: Where does it go? Science 174:1101-1107.

Physical properties - (1) lipid soluble and ... attract to biological material, (2) persistence, (3) high vapor pressure.  
Avg. DDT/acre = 1.50 in U.S. agricultural soils - other stat. of DDT use, etc.  
DDT reservoirs - land surface, trophosphere, mixed layer of ocean, the abyss.  
Major effects as in British Isle captors comes from local contamination, not world-wide spread, and will respond to change.



Wurster, C. 1969. DDT reduces photosynthesis by marine phytoplankton. Science 159:1474-1475.

1-2 ug of pure DDT (pp')/culture. 20-24 hr → add  $^{14}\text{C}$ -bicarbonate, and let run for 4-5 hr. Radioactivity measured and taken as an index to photosynthetic rate. Cell conc. about equal at start. Dark uptake was subtracted from all values.

↑ Effect at ↑ cell conc. for low soluble DDT in  $\text{H}_2\text{O}$  is greatly attracted to biological material.

Typical dose response curve in photosynthesis rate. But sensitive even to very low levels.

Repres. natural levels for DDT in phytop. are not known.

Greatest effect at low cell concentrations, so selective effect and shifting pyramid base of food chain is possible.

Young, R. H. F. 1972. Effects on groundwater. J. WPCF 44(6):1208-1210.

Just a few references; the best is Swoboda.

Young, O. S., J. J. Chodan and A. R. Wolcott. 1970. Adsorption of DDT by soils, soil fractions and biological materials. J. Agric. Ed. Chem. 18:1129-1133.

pp'DDT - incubated in soil with aqueous medium to determine adsorption isotherms, to see if DDT adsorption is directly related to organic content. It was not. It does depend on

- (1) structural and water repellent effects of lipid deposits on sorptive surfaces,
- (2) differences in mineral structures and the way organics bond with them,
- (3) nature and proportion of non-humic and humic portions of organics in soil.

Yule, W. N. 1973. Intensive studies of DDT residues in forest soil. BECT 9:57-64.

6,000 tons/10 million acres in 16 yr - all forested.

(1) All in top 6" - 0.63 ppm was top mean sample for transect

10.79 oz/zcre left in 1968 from application

Disappearance curves, 1/2 life of 10 yr without vertical runoff

1968-71 - pp'DDT ↑ while pp'DDE ↑

Zabik, M. J. 1969. The contribution of urban and agricultural pesticide use to the contamination of the Red Cedar River. Mich. Inst. of Water Research, Prlj. No. A-012, Michigan.

DDT saturated all year

↑ on sediments and downriver

Bottom → water is rapid → more downstream.

APPENDICES

3 and 4

APPENDIX - 3

## APPENDIX - 3

### Lake Compartment

#### Foreword

Meadows and Randers<sup>1</sup> constructed a model of DDT transport in the global environment in 1971. We extended Meadows and Randers' model and evaluated the accuracy and scope of their model. This report examines a facet of the extension of Meadows and Randers' DDT model.

#### Introduction

In Meadows and Randers' model of DDT transport in the environment, they neglected to include lakes as a DDT pathway or sink. We feel that this is a shortcoming in the model. The impact of DDT in lakes on man is probably greater than the impact of DDT in oceans because of the proximity of lakes to man, and the available drinking supply in lakes.

Although lakes comprise only .1 to .2% of the earth's surface area and contain .015% of the total water volume on Earth, lakes could be reservoirs of DDT. Even a minute fraction of the total DDT production which reaches the lakes has the potential to produce harmful effects on the lake ecosystems. High concentrations of DDT (DDT concentrations of lake fish have been as high as 13 ppm: Reinert 1965-1968) can reduce food webs and eliminate carnivores (Woodwell 1971). The destruction of food webs can intensify pollution problems, particularly in lakes that receive mineral nutrients in sewage or in water draining from heavily fertilized farm lands. The plants, which are no longer consumed by animals, sink to the bottom to decay, producing noxious gases and further deteriorating the environment (Woodwell 1967: Scientific American Vol. 216, No. 3, P. 24) It is important in a global model of DDT transports to include lakes in order to comprehend the total impact of DDT on the global environment. Thus we feel it is justifiable to incorporate a lake compartment in our DDT mathematical model.

<sup>1</sup>Meadows and Randers' Sample Study of DDT movement is the first entry in the bibliography.

## DDT in Lakes and Lake Biota

Several studies have been made of DDT concentrations in lakes and lake fish.

The following are some of the results:

- .29 -13.28 ppm DDT residues in Lake Michigan fish
- .02 - 8.61 ppm DDT residues in Great Lakes fish  
(1965-1968 Reinert: Pesticides Monitoring Journal, Vol. 3, No. 4, p. 233)
- 1 -11.17 ppm DDT residues in Lake Superior lake trout (1969)
- Not Detectable - 15.7 ppm DDT residues in Lake Michigan lake trout  
(1965, 1966) (Great Lakes Fishery Laboratory: Progress Report for Annual Meeting, June 1970).
- .16 -11.79 ppm DDT and metabolites in Great Lakes fish  
(1967-1968 Henderson, Inglis, Johnson: Pesticides Monitoring Journal, Vol. 3, No. 3, p. 145)
- .74 -8.61 ppm DDT and metabolites in Great Lakes fish  
(1969 Henderson, Inglis, Johnson: Pesticides Monitoring Journal, Vol. 5, No. 1, p. 1)
- 9.3 ppb p,p<sup>1</sup> DDT<sup>1</sup> in Southern Lake Michigan surficial sediments  
I p,p<sup>2</sup> DDT are DDT metabolites  
(1969-1970 Leland, Bruce, Shimp: Environmental Science and Technology, Vol. 7, No. 9, p. 833)
- .1 -4.1 ppb DDT-type compounds in the Utah Lake drainage system
- 79 ppb DDT in catfish in Utah Lake
- 123-956 ppb DDT in carp in Utah Lake (1970-71 Bradshaw, Loveridge, Rippee, Peterson, White, Barton, Fuhrman: Pesticides Monitoring Journal, Vol. 3, No. 3, p. 166)
- .01 ppm DDT residues in lake biota (1971 Woodwell: Science Vol. 174, December 10, 1971, p. 1101)

100 ppb DDT<sup>2</sup> in Lake Michigan sediments (1971 Schact)

These figures may not be of significance until compared with other DDT concentrations. For example, the concentration of DDT in the oceans has been estimated at .005 ppb (Meadows, Randers 1970) and at .00015 to .0056 ppb (Portmann 1974) compared with the value of .1 to 4.1 ppb DDT in the Utah Lake (1970-1971). The concentration of DDT in ocean fish has been estimated at .1 to 1 ppm (Meadows, Randers 1970) and at .0006 to .004 ppm (Portmann 1974) compared with the values of .123 - .956 ppm DDT in carp in Utah Lake (1970-1971) and .74 to 8.61 ppm DDT in Great Lakes fish (1969). Thus, the observed lake concentrations are of the same magnitude or even higher magnitude than the observed ocean concentrations. Even though DDT is present in larger quantities in the oceans, DDT may have a greater impact on the lakes. Therefore, the DDT rates and routes in and out of the lake compartment should be explored further.

#### Chosen Parameters

There was a lack of information and research on exact rates and routes of DDT transport in and out of lakes. For this reason, we could only use very crude estimates of average rates in our DDT mathematical model. These chosen values are very likely not accurate, since there are no data to support precisely correct rates. But other values can be almost effortlessly inserted without altering the structure of our global model. Assuming exponential decay, rates are represented in terms of half lives.

The mass of lake fish consumed by man was estimated to be almost one-half of the total mass of fish (15,000,000) with birds consuming another two-tenths. The values for the lake fish - the body weights eaten per year. Degraded fraction, excretion half life and fish half life - were taken to be the same as in seafish. Therefore, Meadows and Randers' values for ocean fish were employed. The volume of lakes in 125,000,000,000 cubic meters

<sup>2</sup> tDDT includes all of the DDT residues

(Encyclopedia Britanica). The lake fraction was chosen to be .05 and the lake basin fraction was chosen to be .05 in order to magnify the effect of DDT on lakes. The precipitation half life and evaporation half life were chosen to be the same as the values used in the ocean compartment of our model. The ocean and soil fractions of the earth were changed in order to make room for a lake compartment. The lake plankton concentration factor was estimated from data of DDT concentrations in marsh biota (Perterle 1967) to be approximately 1000.

Soil to lake transfer includes leaching into the underground water table and direct run-off into lakes occurring in the lake basin portion of the earth. Leaching was found to be a contributing factor to DDT concentration in depths of soil below one foot (Swoboda, Thomas, Cady, Baird, Knisel: Environmental Science and Technology, Vol. 5, No. 2). We did not incorporate a lake to soil transfer rate though it is possible for the DDT to leach from the lake sediments back into the soil. This is probably not a significant process, since DDT residues in the sediments of Southern Lake Michigan were found to be concentrated in the upper 2 centimeters (Leland, Bruce, Shimp 1973). Lake to river transfer includes leaching from the sediments into the ground water to the rivers, as well as DDT that's transported by water currents from lakes that feed rivers. River to lake transfer included DDT that leach into the ground water to the lakes, and DDT from rivers that enters directly into lakes. Of course, these rates are very small fractions of the total DDT production, but they do represent actual transfers in and out of the lake compartment. Very crude estimates (river to lake half life- 1000 yeats, lake to river half life - 2000 years) were chosen, with a relatively short half life (5 years) selected for the soil to lake transfer in order to clearly observe the impact of a lake compartment in the DDT model.

The sedimentation half life was estimated to be on the order of 5 years, resolving reports of little downward transport of DDT (Eberhardt, Meeks, and

Pertle 1971) and sedimentation as fast as one month in ponds (Bridges, 1963 Trans. American Fisheries Society, Vol. 92). Water in lakes that contain only a trace of DDT can continuously transport it from bottom sediments to organisms (Woodwell 1967). If the benthic organisms in lakes can obtain much DDT from bottom sediments, this could contribute to the existence of high DDT concentrations in fish in lakes for many years since such benthic organisms are an important food source for aquatic predators. (Leland, Bruce, Shimp 1973). Taking into account turbulence and resuspension of DDT residues in lake sediments, and fish feeding on the lake bottoms, a substantial fraction (.8) of the sedimented DDT residues is estimated to re-enter the lake fish.

#### Results

The DDT model with the lake compartment was written in Dynamo language, and run and compiled in a Dynamo II<sub>F</sub> system using a Univac 1108 computer. The total amount of DDT applied to the biosphere in our model system was 1,000,000 tons. The DDT in lakes reached a peak of approximately 325 tons and DDT in lake fish reached a peak of about 14 tons. Although the application rate reaches zero in about 55 years, the DDT in lakes and lake fish does not approach zero until more than 100 years after the first application.

Concentration of DDT in lakes reaches a peak of 2.56 ppb fifty years after the first application. Concentration of DDT in lake fish reaches a peak of 944 ppm fifty years after the first application. The ocean, air and soil concentrations all reach their peaks thirty or thirty-five years after the first application.

The concentration in ocean fish reaches its peak at 634 ppb, almost three orders of magnitudes lower than the concentration in lake fish. The concentration in oceans reaches its peak at .077 ppb, about one or two orders of magnitudes lower than the concentration in lakes. At the end of a century after the first application of DDT, the concentration in lake fish is 778 ppm, the highest concentration of any part of the biosphere at that

period of time. Concentration in seafish is only 58.45 ppb after a century. After a hundred years, concentration in lakes is 2.11 ppb compared with .007 ppb of DDT in the oceans.

#### Analysis and Conclusions

We have successfully incorporated a lake compartment into our DDT global model. The parameters used were certainly not precise, but they served a purpose. The purpose was to show the potential impact DDT could have on lakes and lake biota. Although our analysis and estimation of parameters was not as detailed or exhaustive as Meadows and Randers' analysis, our results are exaggerated conclusions, they are nevertheless meaningful conclusions. Actual calculations of lake concentrations and lake fish concentrations have been reported up to three orders of magnitude higher than concentrations in oceans and seafish, which is comparable to our outcomes. The DDT in lakes in our model has been shown to persist longer in greater concentrations than in any other compartments of the models. This agrees with the assumption that recycling of DDT sediments in lake food webs is of significance. Our model can be of great use in portraying DDT flows into and out of lakes, so that we can determine the total biological effects that can occur.

DDT may not only affect the lake biota, but also humans. In the United States, lake waters provide 98% of the surface waters available for drinking purposes and provide 7,400,000 tons of fish for human consumption. The inhabitants of the United States have already absorbed some of the DDT circulating in the world (11 ppm DDT residues in fat tissues, Woodwell 1971; 6.6 - 12 ppm DDT residues in fat tissues; Metcalf 1973: Journal of Agriculture and Food Chemistry, Vol. 21, No. 4). Although DDT is not known to present a health hazard in the current concentrations, there may be disastrous results if DDT is present in higher concentrations in humans, or is mixed with other toxic chemicals in the body.

Of course, the peaks of DDT production and usage have passed, and all this speculation and modelling of DDT transports may be irrelevant now. But DDT is still being used in other parts of the world such as India (India's inhabitants have absorbed 12.8 to 31 ppm of DDT-Woodwell 1967). With DDT's well-documented extensive half life in nature, we could still be feeling the adverse effects of DDT for years to come. Peaks of DDT concentrations can re-occur in local areas because of turbulence in surface waters causing resuspension and release of previously unavailable DDT to the biota. DDT sediments may also be oxidized (Woodwell 1971) and re-enter the food chain. Benthic organisms in lakes may also consume the DDT sediments and this will cause the recycling of DDT into the food web. So high concentrations of DDT could exist in lake fish for years to come.

Once again, we would like to stress that these parameters are very crudely estimated, and in some cases, magnified in order to emphasize the importance of introducing a lake compartment into a DDT global model. In spite of this magnification, our results were similar to actual observations. This indicates that further study of DDT in aquatic environments is needed. And once again, let us let of stress that even though very little DDT reaches lakes, judging from the residues in lakes and lake biota, it has had quite an impact on lake ecosystems. Of course, this may all be irrelevant since DDT usage has declined. But this model can serve as an example for transport models of other toxic chemicals that man introduces to the environment, and can hopefully predict the flows and impacts of other toxic chemicals in the global environment.

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APPENDIX - 4

September 10, 1975

Academician Yuri Antonievich Israel  
Chief, Main Administration of Hydrometeorological  
Service of the USSR  
Moscow, pereulok Pavlika Morozova, 12  
USSR

Dear Academician Izrael:

As you can see from the enclosed we have a U.S. Government-wide program to develop models to describe the fate of pesticides on the globe. The first trial run is being done on DDT and as you might guess the model would like to be fed more data than we have. The problem does seem to fit nicely under the category of "Comprehensive Analysis of the Environment." I am therefore writing to ask if you would be interested in helping with the data requests listed on the sheet entitled Specific Data Needs.

I think that these modelling efforts could turn out to be very instructive and useful in performing comprehensive environmental assessments, and that such an area is an excellent one for US/USSR cooperation. Should such a joint effort look attractive to you, I suggest that the appropriate Soviet specialist establish direct contact with:

Dr. Padma R. Datta  
Chairman, Interagency Ad Hoc  
Committee on Mathematical Modeling  
U.S. Environmental Protection Agency  
Room 809, Crystal Mall Building #2  
1921 Jefferson Davis Highway (WH-568)  
Arlington, Virginia 20460

I look forward with great anticipation to seeing you again on October 19.

Sincerely yours,

Roger S. Cortesi  
Acting Director, Criteria Development  
and Special Studies Division

### Specific Data Needs

1. Photodegradation of DDT in air (a) over the ocean surface particularly from Arctic Ocean and (b) land mass in Siberia or agricultural land mass.
2. Concentration of DDT or its major metabolites DDE and TDE in aquatic organisms and terrestrial organisms particularly birds, shrews, and similar insect-eating mammals.
3. Concentration of DDT and degradation products in Benthic organisms or suspended particles in Benthic regions of oceans.
4. The data of Nos. 2 and 3 are needed to determine the actual "sink" of DDT and its metabolites.
5. The rate of dispersion from soil to air and rate of redeposition to the soil.
6. Agricultural "runoff" to freshwater lakes, estuarine and marine estuarine (Caspian Sea).
7. The bioconcentration or bioaccumulation if fish (edible and non-edible) and plankton different species.
8. The biochemical effects of DDT in low concentration (pp, ppt) in photosynthesis organisms (phytoplankton).
9. The rate of degradation (kinetics) of DDT on the ocean surface and the concentration of its degradation product(s).
10. The "terminal" residue levels of DDT, degradation products and metabolites (DDE and TDE) in food and fiber.
11. The concentration of DDT and its metabolites in ice core samples before 1940 and up to the present.
12. The rate of movement of DDT and its metabolites from ocean air, ppt in soil.
13. The rate of accumulation and dissipation from various ecosystems (tundra, taiga, estuaries, etc.).

14. The available data for the rate of uses or total production of DDT in Russia and other countries.
15. Solutions to mathematical differential or difference equations for diffusion and absorption/adsorption processes in the environment.

A Compendium of Matters of Interest  
to the Ad Hoc Committee on Mathematical Models

The current thrust of our activity is the treatment of the disposition of DDT in the biosphere as a paradigm for the study of pesticides. The vehicle for our investigation is a version of a computer model proposed in 1970-1971 by D. Meadows and J. Randers, based loosely on the techniques of J. W. Forrester's "Systems Dynamics" and cast in the associated DYNAMO simulation language. The model is documented in J. Randers' "DDT Movement in the Global Environment," Chapter 3 of Toward Global Equilibrium: Collected Papers (ed. by D. L. Meadows and D. H. Meadows, Wright-Allen Press, 1973).

The model uses a set of linear difference equations to trace over the flow and accumulation of DDT in a system consisting of five major ecological compartments ("soil," "air," "rivers," "ocean," and "fish") each considered as a homogeneous worldwide aggregate. Very large fresh water bodies are considered integral with the "ocean," while all other fresh water is subsumed under "rivers."

Life-forms higher than fish are excluded from the model, except to furnish a "sink" for some portion of the systems DDT, as noted below.

The driving force for the system is the rate of application of DDT. Because in reality, most application is assumed to occur as crop dusting of cultivated land areas, the model splits application into "air" and "soil" components to represent convective dispersion during the dusting process.

The model explicitly identifies the following flows:

- (1) from soil-to air by evaporation, to rivers by solution percolation and washing (not separately distinguished) and out of the system by bacterial and chemical (not distinguished) degradation.
- (2) from air-to soil and oceans by precipitation and out of the system by photochemical degradation.
- (3) from rivers-to the ocean by runoff.
- (4) from the ocean-to air by evaporation, to fish by ingestion

through plankton, and out of the system through sedimentation, i.e., settling into the abyssal depths.

- (4) from fish-into the ocean by excretion and morbidity and out of the system through destructive metabolism (labelled "harmless excretion") and by trophic predation by higher life forms.

The decay and growth used in the model are all "average" exponential rates, i.e., linear functions of the levels of various quantities at a given time. The level of precision can be inferred from the fact that the basic units are tons/year.

Most of the assumptions in the model were made by Randers and Meadows on the basis of a fairly exhaustive literature search at the time of the construction of the basic model, and are they subject to drastic revision. The terms describing photochemical action, evaporation from the ocean, and sedimentation were added by us later and the associated parameter values are even more crudely approximative than the others.

There are obviously many directions in which refinements could be attempted, but some questions which we consider critical at present involve actual rates of photodegradation of DDT (if they are indeed not negligible) over land and over water, the fate of particulates in the upper atmosphere, the absorption, ingestion by plankton (DDT is lipophilic), whether there really is substantial sedimentation and whether DDT reaching benthic levels below the "well mixed layer" in the ocean can readily be transported back out of the abyss, or if such DDT is essentially removed from the potentially damaging pool in the biosphere, and of course, the broad questions of transfer rates through the interface between this limited system and one including birds and mammals, and whether or not there is any validity at all in considering systems as highly aggregated as the one we have at hand.

We append into an internal memo from two mathematician members of the ad hoc committee on Mathematical Models, outlining the substantive questions resulting from an introductory rather rapid consideration of the technical problems to be addressed in constructing a broad scale pesticide model. It's purpose was and is to stimulate dialogue.

Finally, there is a short list, in no particular order, of published studies on ecological models and modeling.

## 1. INTRODUCTION

We now have the DYNAMO simulation-language compiler up and running on the NBS computer. We have set up the model, and checked its outputs on our machine against those reported for the same cases in the Randers-Meadows (R&M) paper. Furthermore, we have developed a corresponding differential-equation version, and are proceeding to derive its closed-form solution in various parametric regimes; this should permit more efficient analysis than does simulation.

What else can and should we be doing with this model? Our present ideas can be grouped under the following 5 headings:

- (a) Update Data. The R-M model was developed in 1970-1971. One should by now have better data on the "preferred" values of the various parameters, and/or on their reasonable upper and lower limits, as well as production and/or application data for 1970-1974.
- (b) Update Structure. New data insights may be available to guide changes in the structure of the model. Have additional propagation paths been observed? Have some "inter-sector" transfer rates, previously thought negligible, been found appreciable (or vice versa)? Linear kinetics are assumed throughout the present model; are there physical considerations (e.g., encapsulation of remaining DDT, by reaction products, away from other reactants) which suggest modifying this, and how?
- (c) Further Sensitivity and "Predictive" Runs. Once the model is updated as indicated by (a) and (b) above, additional runs to ascertain sensitivity to various uncertainties may be in order. Are there particular patterns of combinations of parameter-levels which the Committee would like us to run, or shall we make these selections? Various scenarios as to future rates of application should be run' which would the committee recommend? For both sensitivity and "predictive" runs, what outputs would the committee like emphasized, say for grouping to facilitate comparison of different cases?

(d) Model Refinement. It is mainly disaggregation that we have in mind here. In the time domain, this might represent annual differences (due to malaria epidemics, crop-pest plagues, meteorological abnormalities, etc.), or seasonal cycles. Other plausible areas for disaggregation include spatial, soil-type, river-type, etc. Suggestions? From a mathematical viewpoint, the crux is that a combination of exponential decays with different half-lives is not equivalent to any one exponential decay with some intermediate half-life.

(e) Model Extension. This has three possible aspects. First, to extend the model up the chain-of-life from the "fish" level at which it presently terminates. Second, to pass from "concentration" outputs to mortality/morbidity/disreproduction rates in the affected species. Third, to evaluate the resultant "impacts" -- in part, in economic coin, but also trying to deal with the "Cost to Man" if some species is lost from viewing and from Earth's ecological pool. These three aspects are progressively more difficult, and we trust it is clear that our role in any of them (NBS is not a life-science or economic-science institution) would rely principally on initiatives by inputs from the other agencies represented on the Committee. Yet the desire that our joint efforts be policy-relevant does seem to demand some efforts in these directions. Indeed, since the "third aspect" above refers to cost impacts of DDT usage, one should also have available models to estimate and evaluate benefit impacts (on public health and agriculture) of such usage -- but this seems to me beyond our Committee's charter.

Specific questions relative to (a) - (e) above, and keyed to successive sections of the R-M paper, are given in (2)-(10) below. Some of them may be answered in documents available to us, but not yet digested. The questions pertain to improving the model's inputs and structure; they say nothing about direct or indirect validation of its (intermediate or final) outputs. The latter seem so aggregate as to defy checking, obviously a situation of grave concern for any modeling or model-evaluating effort. Suggestions?

## 2. APPLICATION OF DDT

- (a) Do we have any better data now, on world or U.S. production of DDT during 1940-1970? How about 1971-74? What about the future, with its pressures of population on food supply? Do we have better data on the amount used, year by year, for malaria control? Is there information, on yearly outbreaks of malaria or particular large programs of malaria control, which could be used to refine the model's implicit "20% per year" to a time series?
- (b) The model implicitly assumes that each year's application amount of DDT is equal to that year's production level. Is this reasonable, or are there inventory/reserve-stock considerations? For example, if pest infestations or malaria outbreaks have a known cyclical pattern, one might stock DDT to await the "danger year".
- (c) The model assumes in effect that each year's application of DDT occurs uniformly over the year. This seems dubious, in view of the seasonal cycle of agriculture, pest life-cycles, and perhaps (?) malaria. Please advise. The model's time-scale (presently 0.02 yr.) is more than fine enough to permit representing seasonal effects. This might require spatial disaggregation, say of the Northern and Southern Hemispheres, or perhaps of temperature zones.
- (d) Re the fraction (ABF) of applied DDT that remains airborne: any reason to change past or current values? Are technological improvements to reduce this, in mode of delivery or delivered form, likely? Would changes of the latter type, i.e. in particle size or accessibility to reactions, affect other model parameters?

## 3. DDT IN SOIL

- (a) What if any are the significant seasonal effects? For example, is the fall-down to change the assumption that the amount of DDT removed by harvesting is negligible?

- (b) Any better estimates on degradation rates? Any reason to expect significantly nonlinear decay?
- (c) Does erosion or wash-off lead anywhere except rivers? Significant take-up by birds, animals, insects, worm-?
- (d) Is it plausible that the substantial amount of DDT on walls (which the model includes in variable S) has the same degradation rate as that really in soil? That wall-DDT has the same rates of loss by evaporation and by movement to rivers as does soil-DDT? Similarly re plant-DDT?
- (e) Can we make a coarse disaggregation into 2-3 classes of soils? How is application divided among them?

#### 4. REMOVAL THROUGH RIVERS

- (a) Any better data bearing on solution half-life in soil prior to suspension in rivers? Is it reasonable to model this as a linear process?
- (b) Similarly for run-off rate (river-to-ocean movement). Any evidence counter to the assumption of negligible degradation while in rivers? What about deposits of soil on land, from rivers?
- (c) What are the significant seasonal effects?
- (d) Is it worthwhile to try using some crude classification of rivers, perhaps by flow speed?

#### 5. EVAPORATION FROM SOIL

- (a) Has there been confirmation of the R-M paper's tentative conclusion that this must be a significant mechanism for removal of DDT from soil? If not, what other explanation of its disappearance rate has emerged?
- (b) Better data on rate? Reason to introduce nonlinearities? Seasonal effects? Some useful spatial or soil-type disaggregation?

#### 6. PRECIPITATION FROM ATMOSPHERE

- (a) Are the particle sizes right for using data on a "radioactive debris"? Anything new on precipitation half-life? Why treat this as a linear process?
- (b) Any reason to doubt the assumption of negligible degradation while in the atmosphere? Might volumes and precipitation half-lives over land differ

systematically from those over seas?

(c) Significant seasonal factors? One would expect them for rain, though not for gravity-induced precipitation.

#### 7. DDT IN OCEANS

(a) Any further evidence on the assumption that almost all ocean DDT dissolves rather than settles?

(b) Any further evidence on the assumption that evaporation from the ocean is negligible? Sensitivity to this would be easy to test.

(c) Might there be significant differences between oceans in degradation rates say due to differences in temperature or salinity? If these match differences in distributions of plankton and/or fish, then this is a plausible area for disaggregation.

(d) Any better information on the "mass of the mixed layer"? Apparently it was not varied in the R-M runs. Is a separation into upper and lower layers worthwhile?

#### 8. DDT IN PLANKTON

(a) Is the concept of an ocean-plankton concentration factor acceptable? Any new evidence about its value?

#### 9. UPTAKE IN FISH

(a) Any new evidence on the assumption that uptake direct from water is negligible relative to that from food? That representation as a 2-level food chain (fish eat plankton) is adequate?

(b) Any new data on total fish mass and feeding rate? Seasonal effects? Does DDT harm plankton or fish, tending to reduce their populations?

(c) Is there some useful disaggregation by fish type to be made because of either non-uniformities at this point in the model or differences in uptake by higher life forms?

## 10. ELIMINATION FROM FISH

- (a) Any new information on excretion half-lives? Is a disaggregation on this basis worthwhile? (The R-M paper mentions some evidence for two superimposed processes.)
- (b) Anything new on fraction of excreted DDT which is degraded form?
- (c) Any new data or trends re level of fish removed from ocean (by birds or man)? Is stock-fish supply negligible? Future shift to more fish in world diet?
- (d) New data or disaggregation re half-life of fish? Is exponential decay a reasonable way to model deaths of fish?

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Summary of the Ad Hoc Committee's Activities As Report  
to the FWGPM by Committee Chairman Dr. P. R. Datta  
of EPA on 5/21/75

This interagency, interdisciplinary ad hoc Committee on Mathematical Models of Pesticide Behavior in the Environment was charged (1) with evaluating all available mathematical model(s) capable of predicting the fate and movement of pesticide(s) in the environment and (2) with devising a working mathematical model or models.

The committee selected DDT as a model compound due to the voluminous data in the literature and the opportunity to determine the fate and movement of residual DDT in the continental United States since the banning of its use here in 1972.

The Action Program (December 1973) was submitted by this ad hoc committee and finally approved by the FWGPM and other federal agencies. The program consisted of an evaluation of the intrinsic and extrinsic merits of the various predictive mathematical model(s) by computer simulation test runs using the DYNAMO simulation language compiler. EPA (OPP/TSD) has now accepted the lead in implementing this interagency effort. The ad hoc committee's activities are as follows:

- a. NBS of the Department of Commerce, in cooperation with NIH computer division of DHEW, is currently evaluating the various predictive mathematical model(s). Most of the published mathematical model(s) based on system dynamics are of the DYNAMO model type. To date, 45 different computer simulation DYNAMO model test runs have been conducted to evaluate the mathematical properties of the linear, non-linear functions of the system parameters in each compartment and sensitivity analysis using differential and/or difference equations at various steady-state equilibriums. The results indicate that there is a

paucity of data on several model compartments of critical importance, for example, data on the ocean water surface, ocean mixed layer and ocean abyssal layer. Due to this paucity of data, coupled with low mean residence time of DDT in the atmosphere (30-40 days) and the extremely low concentration of DDT in the ocean (ppt), the assumption that oceans act as a "sink" for DDT as postulated by the published model(s) cannot be ascertained as the true fate of DDT in the environment at this time. The committee, therefore, requested: (1) Lamont Geographical Laboratory of Columbia University to supply a few ocean bottom core samples (both pre- and post 1942) for analysis of DDT by a member of the committee of NOAA. (2) Ten principle investigators of the NSF International Decade of Ocean Exploration of Pollutant Transfer Program to supply existing data on DDT or to obtain samples for analysis of DDT in the ocean's water surface, mixed layer, and abyssal layer. (3) The International Activities Office of EPA's Administrator to help this committee in obtaining data on DDT or samples for analysis of DDT in the water surface, mixed layer and abyssal layer of the world's oceans. (4) Army's AIDZEC project and CRREL project to obtain a few ice core samples from Greenland, Antarctica, and the North Pole (both pre and post 1942) for analysis of DDT by NOAA's Bauefort Laboratory.

- b. To update the data on DDT, a literature search will be conducted by a graduate student working half-time in Dr. Peterle's Ecology Department at Ohio State University under the supervision of this Committee through TSD/OPP/EPA who will supply the graduate student with an on-line computer system (desk model). This literature search program will be supported financially along with Dr. Peterle's

work on behavior of DDT in fresh water marshes and terrestrial organisms by ERDA/Environmental Safety Division.

- c. The evaluation and validation of the updated data before input into the model(s) will be conducted by committee members versed in specific disciplinary areas of the model parameters.
- d. After completion of the simulation test runs with updated data using the DYNAMO simulation language compiler, the committee may consider changes in the DYNAMO model(s) structure, refinement (disaggregation), extension (propagation pathways), and predictive runs having various scenarios.
- e. The committee intends to identify the type of data needs, knowledge gaps, research priorities, etc., during the model evaluation efforts and sensitivity analysis (absolute and/or relative sensitivity) in each compartment of the DYNAMO Model(s) so as to improve the model's input and structure and validation of its output (final, intermediate, etc.). The committee will also evaluate cost to man, resultant impact in socio-economics and health effects, etc.
- f. The committee is also considering the purchase of an 1108 DYNAMO compiler from Pugh Roberts Associates providing the justification is substantial.

The committee has requested figures of the world product of DDT since 1942 from World Health Organization. Dr. Whittemore, operations Division/OPP/EPA, made available to the members of the committee the latest report on production of DDT by FAO. It appears that the estimated world production of DDT in 1975 will be about 100,000 metric tons.

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