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ENVIRONMENTAL SIGNIFICANCE OF PESTICIDE[1] RESIDUES ASSOCIATED WITH AQUATIC SEDIMENTS

Key words: Pesticides, Environmental Hazard Assessment, Sorption

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ABSTRACT

In the U.S., water quality criteria and standards for pesticides in aquatic systems are generally equivalent to chronic exposure safe concentrations based on toxicity tests conducted in the laboratory where aquatic organisms are exposed to pesticides that are usually in soluble,

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generally more available forms. The water quality management agencies in the U.S. usually develop pesticide regulations based on the total pesticide concentration in water samples, using the worst case criteria for guidance or as the standard values. In natural water systems however, many pesticides tend to become strongly sorbed on particulate matter so that only a small part of the total pesticide concentration is available to aquatic life. Systems with large amounts of suspended sediments can thus often sustain larger total concentrations of certain pesticides without being harmful to aquatic life. Rather than assuming that all of the pesticide in a sample of lake, river, or ocean water is available to adversely affect aquatic life and using worst case criteria as enforceable limits, one should use the worst case water quality criteria as indicators of potential water quality problems. When the concentrations exceed the worst case criteria, a hazard assessment approach should be used to determine whether the apparent excessive concentrations represent actual environmental degradation. This approach more properly accounts for the availability of pesticides to aquatic life and the duration of organism exposure to the available forms. A recommended approach for establishing pesticide water quality standards and use regulations in Egypt is presented.

The large-scale pesticides use in some parts of Egypt may lead to the presence of high concentrations of pesticide residues in soils. These soils could be potentially significant sources of pesticides for surface and groundwaters. At this time it appears that there is limited information on pesticide residue concentrations in the surface or groundwaters, or in aquatic organisms. An approach is presented to define the significance of Egyptian soil pesticide residues. It involves collecting and critically evaluating existing residue data; developing a monitoring program to fill data gaps; development of Egyptian water quality criteria and standards, and organism tolerance levels; and comparing the critical concentration of pesticides developed for Egypt to existing concentrations. If excessive concentrations are found, then site-specific studies should be conducted to evaluate the role of soil pesticide residues in causing the excessive concentrations.

INTRODUCTION

The development of pesticide use regulations is an area of concern in developing countries in many parts of the world. A number of pesticides that have been banned from use in the United States (U.S.) and certain other countries, are being widely used in many developing countries. Does this mean that those responsible for environmental protection in these developing countries are not providing the same degree of protection that is afforded in those countries in which these pesticides are banned? Does it reflect unnecessary banning of certain pesticides in the U.S.? Perhaps it reflects differing needs and protection priorities in developing and developed countries.

About 20 years ago in the U.S., heralded by the publication of Silent Spring (Carson)[1], came a public awakening to the potential impacts of pesticides as used then, on "nontarget" organisms. During the past 20 years since this awakening, the almost indiscriminant use of pesticides has been replaced by the highly controlled and regulated manufacture and use of pesticides, with the complete banning of some pesticides from manufacture and/or use in the U.S. There are some, including the authors, who feel that this almost impulsive reaction has resulted in the unnecessary restriction of a number of pesticides.

There is no question that at the time that Rachel Carson wrote Silent Spring, there was a need to greatly strengthen regulations governing pesticide manufacture and use within the U.S. and elsewhere. However, little was known at that time about the hazards that chemicals in general, and pesticides in particular, represented to man and the environment. Since that time, knowledge in the fields of aquatic toxicology, and environmental chemistry and physics have made significant progress; considerable advances have been made in developing an approach for integration of the inputs from individual disciplines (the "hazard assessment approach"). Today, therefore, it is possible to determine with a high degree of reliability, the hazard that a particular chemical (such as a pesticide), or a combination of chemicals (e.g., in a wastewater discharge) represents to man and the environment in general, as well as at a specific site.

One of the primary areas of concern with pesticide use has been the transport of pesticides from their points of application to aquatic systems such as rivers, lakes, estuaries, or oceans. Many pesticides, especially those which have been banned and restricted, are persistent in aquatic systems such that their unrestricted use could be harmful to aquatic organisms or to man and other animals such as birds that use aquatic organisms as food. The biomagnification and bioaccumulation of a number of pesticides such as DDT and other chlorinated hydrocarbons in animals is well-known. However, the conditions that lead to the buildup of excessive concentrations of chlorinated hydrocarbons within fish are becoming sufficiently well understood that it should now be possible to allow the use of these types of pesticides in certain ways and yet minimize the hazard that their use represents to man and the environment. In order to do this it is necessary to understand and apply the principles of environmental hazard assessment in developing pesticide use regulations. Of particular importance is understanding the role of suspended and deposited aquatic sediments in influencing the availability of pesticides to aquatic life.

This paper presents a discussion of the general principles of hazard assessment as they may be applied to the development of site-specific pesticide use regulations. Emphasis is placed on the importance of aquatic particulate matter in influencing the hazard that a particular pesticide represents to a particular beneficial use of a particular aquatic system.

PRINCIPLES OF HAZARD ASSESSMENT

Hazard assessment, as it is becoming known in the water quality management area, has been developed to provide a technically valid basis for evaluating the impact of contaminants on water quality. It is a selective, sequential (tiered) testing scheme for the combined, coordinated development and use of aquatic toxicology and environmental chemistry-fate information.

Environmental chemistry-fate considers the transport pathways and ultimate disposition of the chemical in the environment, what transformations of the chemical occur and the rates of these transformations, and provides an estimate of the expected concentrations of the contaminant in various environmental compartments. Aquatic toxicology considers the concentrations of each potentially significant form of the contaminant being considered and its transformation products, that can be adverse to aquatic life. Emphasis is given to the potential impacts of their expected environmental concentrations. This evaluation is usually extended to include those terrestrial organisms, including man, that use aquatic organisms as food. A hazard assessment is made by proceeding through a series of testing levels or tiers which develop information on the environmental chemistry-fate and toxicology of the chemical until a decision can be made on whether the environmental risk associated with the discharge or use of the chemical is acceptable or unacceptable.

Each successive tier is more sophisticated (and expensive) than the one before it. Each successive tier also defines more accurately the hazard of the contaminant. Relatively crude, inexpensive screening tests characterize the early tiers which are often sufficient to identify the highly innocuous chemicals, and also the highly hazardous ones that should not be discharged or used in the manner evaluated. The higher level tiers are thus reserved for those contaminants for which the potential impact is intermediate and for which a judgment needs to be made regarding the acceptability of the hazard associated with the use of the chemical under review.

AQUATIC TOXICOLOGY

The potential adverse impact of a pesticide or other chemical is judged primarily on the direct toxicity of the chemical to an organism, or the bioaccumulation of the chemical within an organism to the extent that it renders the organism unsuitable for use as food. The characteristics of both of these impacts as they relate to site-specific use regulations are discussed below.

Organism Toxicity

The toxicity of a chemical to an aquatic organism results primarily from a combination of the concentrations of the available forms of the contaminant and the duration of the organism's exposure. Figure 1 shows a generalized relationship between the concentration, duration of exposure, and "no impact" typical of many contaminants. It illustrates that the concentration of a pesticide, for example, can be elevated considerably without adverse impact on an organism provided that the duration of exposure is kept sufficiently short. However, as the duration of organism exposure to the pesticide is extended, the concentrations of available forms of the pesticide must be reduced in order to prevent adverse impact on aquatic organisms. The horizontal line in Figure 1 represents the chronic exposure safe concentration; at this concentration increased exposure duration will have no increased adverse impact on aquatic organisms. It is this concentration to which an organism can be exposed for its lifetime or during critical life stages without adverse impact to it. Critical lifestage refers to a period in an organism's life during which it is particularly sensitive to a contaminant. For many organisms, the lifestages of greatest concern are the larval or juvenile stages which can last for a period of days to weeks or months or more depending on

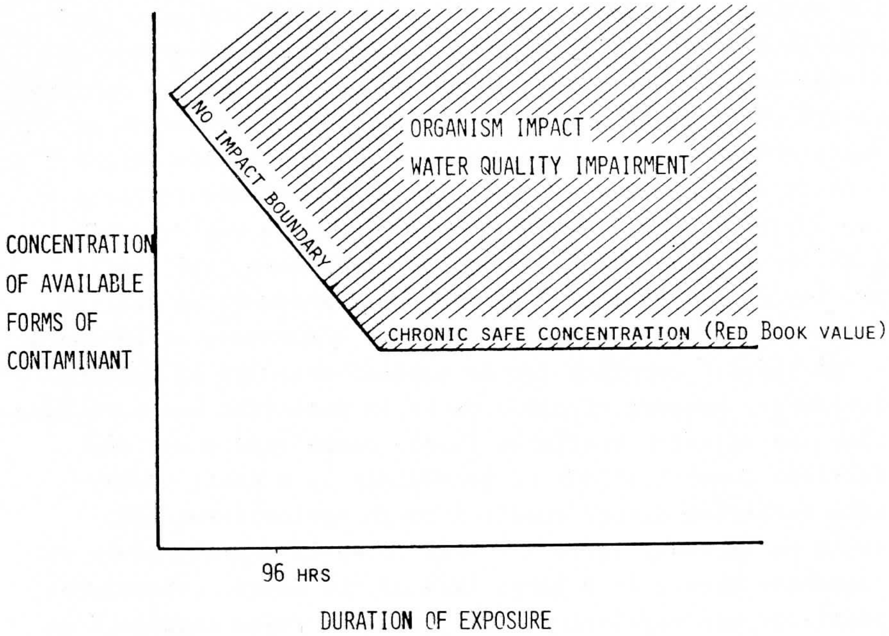


Figure 1. General Case Concentration of Available Forms - Duration of Exposure - "No Impact" Relationship for Contaminant Toxicity

the type of organism. A critical lifestage safe exposure concentration would be one to which the organism could be exposed continuously during this period without adverse impact. It is this concentration that is typically used by the U.S. Environmental Protection Agency (US EPA) as the water quality criterion for the total concentration of various toxic chemicals, including many pesticides, in the U.S.

The relationship shown in Figure 1 is of particular importance in developing site-specific pesticide use regulations because pesticides often move from their points of terrestrial application, into or through aquatic systems in pulses. The first rainfall runoff or irrigation water runoff following pesticide application will contain much higher concentrations of an applied pesticide than subsequent runoff. The presence of a pesticide at concentrations above its chronic safe level does not necessarily indicate that organisms in that area are being or could be adversely affected by the pesticide. Therefore, in most rivers or large waterbody nearshore waters, for example, the presence of total concentrations of pesticides at levels above their chronic safe concentrations must be interpreted in light of the duration of elevated concentrations and the exposure duration of the aquatic organisms of concern, the availability of the pesticide in the forms present, as well as the concentration of available forms - duration of exposure - "no impact" coupling for an exposed organism of concern. Obviously, because of differences in potential exposure duration and dilution available (i.e., concentrations), the critical concentrations of pesticides in a small fishing lake receiving direct runoff from an agricultural field would be markedly different from those in a swift river or nearshore waters of a large lake or the ocean. Therefore, pesticide use regulations must consider these couplings on a site-specific basis.

The aquatic toxicology testing portion of a particular hazard assessment defines the concentration of available forms - duration of exposure couplings for organisms of concern at a particular site, for the impact level that is acceptable (e.g., "no impact", an allowable impact on reproduction, bioaccumulation to just below the point at which the organisms are hazardous for use as human food, etc.). For a given exposure, the concentrations of available forms which are safe for one consideration (e.g., fish health) may not be safe for other uses (e.g., use of fish for food). Because this testing is site-specific, it can focus on those particular water uses and organism uses and hence potential impacts of concern for the particular waterbody at levels expected in the waterbody.

Bioaccumulation

The above discussion on "critical" concentration - duration of exposure couplings was directed toward toxicological impacts in which the health and welfare of aquatic organisms themselves are the point of primary concern. In addition to impacts of this type, consideration must be given to bioaccumulation of the pesticide within the aquatic organism's tissue to such an extent that the organism becomes unsuitable as food for man or other organisms. There appears to be considerable confusion in the water quality management field about critical concentrations of pesticides within aquatic organisms. At this time little is known about the critical body burden of a chemical to aquatic life, i.e., the concentrations in tissue which will impair the organism. It is generally known, however, that the critical concentrations for contaminants in aquatic organisms are considerably greater than the critical concentrations (Action Limits) established by the U.S. Food and Drug Administration (FDA) for the use of these organisms as human food. Until November 1980, the only reliable critical concentrations for pesticides and other chemicals in human food were the US FDA Action Limits, such as 5 ppm DDT in edible portions of fish. Regulatory agencies should not use the 5 ppm DDT Action Limit established for human food as a critical concentration in lower trophic level organisms such as aquatic worms, however; the FDA Action Limits do not necessarily translate to other such organisms even if they are used directly as food by fish or other organisms. As discussed in a subsequent section, there is a wide variety of factors that must be considered in evaluating the uptake of pesticides and other chemicals by higher forms of aquatic life that leads to excessive concentrations in the higher forms.

A key aspect of the bioaccumulation of pesticides in aquatic organisms is their depuration. A fish or other aquatic organism can accumulate what might be considered an excessive concentration of pesticides within its tissue as a result of exposure to elevated concentrations of pesticides in the week or so following runoff from an agricultural field and thereby at that time be unsuitable for use as food. However, within a few weeks, as a result of depuration, as the concentrations of the pesticide in the water decrease, the excessive pesticide concentration within the fish may be reduced to below FDA Action Limits. It is conceivable that regulations could be developed which would prohibit the use of fish and other aquatic organisms as a source of human food during periods of time when the highest concentration of pesticide in runoff from agricultural fields usually occurs. This approach could readily be used by regulatory agencies in those situations where the increased concentrations of pesticides in fish are associated with increased turbidity. Also of potential concern would be the release of pesticides during the dredging of a river to maintain channel navigation depth. For some pesticides there may be a period of time during or immediately following dredging when fish located near the dredged material disposal site may accumulate "excessive" pesticides within their tissue, but a few weeks later pesticide concentration would be back to normal within the fish due to depuration. It is important to emphasize that the bioaccumulation of pesticides and many other chemicals that accumulate within fish tissue is also governed by concentrations of available forms - duration of exposure couplings. This phenomenon can be illustrated with a diagram similar to Figure 1. A several-week period is usually required for fish tissue to come to equilibrium with concentrations in the water.

In November 1980, the US EPA released a set of water quality criteria for 64 "toxic" chemicals (US EPA)[2]. A number of the chemicals on this list are pesticides. Associated with the release of these criteria was the introduction of a new approach for establishing criteria for hazardous chemicals such as some of the chlorinated hydrocarbon pesticides that have been found to be carcinogenic to test animals and, by association, to man. Using what the US EPA considered to be the best information available, it has established critical concentrations for chemicals in water which would not be expected to lead to cancer development in man, associated with the consumption of aquatic organisms and water. The US EPA assumed that a person consumes 2 L of water per day and 6.5 g of fish per day and that the fish

tissue that is consumed contains the pesticide or other chemical at a concentration that would occur under worst case conditions, i.e., that the fish tissue has come to equilibrium with the chemical in the water, which for many chemicals would result after two to three weeks of continuous exposure. The US EPA has established a water quality criterion for DDT under these conditions of 0.0024 ng/l. With DDT at that level and under the fish and water consumption rates assumed, the US EPA predicted that one additional cancer would be experienced in every 11 million people because of the DDT. If the water concentration were 0.024 ng/l, the number of additional cancers for an 11 million population would be increased to 10.

It is important to emphasize that these criteria and their associated risks are based on U.S. conditions and may not be applicable to other parts of the world. Further, if a particular population of people consumed more or less water or fish than the amount assumed by the US EPA, then the risk of obtaining cancer from this water or fish would have to be changed accordingly. As discussed below, the worst case nature of these criteria - the assumption that the total concentration of the pesticide in the water is available - makes it highly improbable that the critical concentration criterion for water established by the US EPA would actually result in a human health risk as great as that estimated.

The magnitude of the difference between the criterion value and the total concentration of the chemical in a particular waterbody that would cause the "worst case" impact would depend on the amount of the contaminant that was in available forms. It is generally found that the availability of pesticide forms that are associated with suspended particulate matter such as algae, silt, clays, and other erosion-derived material is different from, and for many aquatic life forms of concern, less than that of dissolved forms. Therefore, the enforceable pesticide concentration limit for water should be established on a site-specific basis in light of the availability of the forms present to the organisms of concern. Lee and Jones[3] have recently reviewed the problems of translating worst case laboratory bioassay toxicity and bioconcentration data to field conditions. They have recommended approaches that can be used to detect situations where worst case laboratory data may not be directly applicable to field situations and to use such data in the hazard evaluation and standards-setting processes.

Another problem with using the US EPA criteria directly as standards and a problem that may be encountered in establishing standards for Egypt is that for certain pesticides, levels which are known to bioaccumulate in aquatic life are below reliable analytical detection. Under these circumstances it is better to base the standards on concentrations within organisms of concern in relation to FDA or other suitable limits. This approach is more technically appropriate than water content-based standards because it measures tissue residue which is the focal point of concern; and problems of assessing pesticide availability and organism exposure are eliminated.

A number of attempts have been made to predict the impact of pesticides and other chemicals using laboratory microcosms in which fish and/or other aquatic organisms are placed in an aquarium containing sediments and other "natural" materials, including aquatic plants. The pesticide or chemical of interest is added to the system and after a period of time its distribution among the various components of the system - fish, water, sediments, etc. - is determined. While experiments of this type are of interest, they have limited capability to predict what might happen in the real world with respect to the bioaccumulation of the pesticide in fish. The problem with this approach is that the amount of pesticide that accumulates in a particular sink, i.e., aquarium component, is dependent on the size of the sink, and the pesticide partitioning between fish and other components such as sediment in proportion to the amount of the component present in the test system. The appropriate approach when estimating the environmental behavior of a pesticide with respect to its bioaccumulation potential is either deterministic modeling or investigation of actual behavior on a site-specific basis.

ENVIRONMENTAL CHEMISTRY-FATE

The second key component of an environmental hazard assessment for pesticides is the investigation of the aqueous environmental chemistry-fate of the pesticide. Through this testing, the transport and transformations that the pesticide may undergo between its point of entry and exit from the compartment of concern are defined. Since for many pesticides, movement with suspended sediment is the dominant transport mechanism, the environmental chemistry-fate evaluation must consider both dissolved and particulate transport.

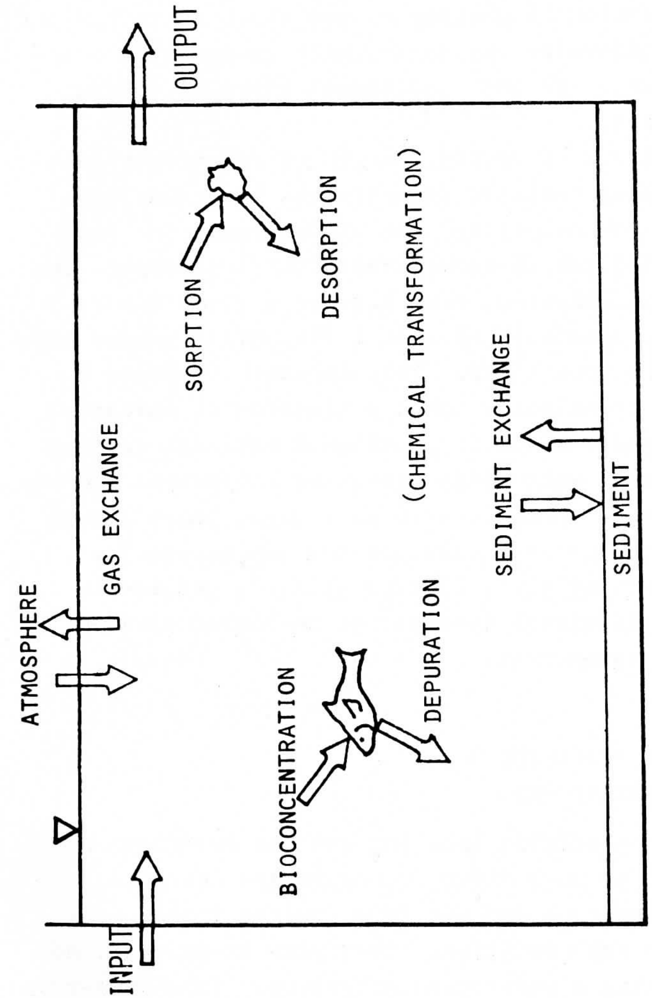
The forms of the pesticide or other chemicals present are governed by the kinetics and thermodynamics of the chemical reactions that may take place in the aquatic system. These reactions include acid-base, precipitation, complexation, oxidation-reduction (redox), hydrolysis, photolysis-phototransformation, volatilization, and sorption. Sorption reactions include uptake both by organisms (biotic) and by non-living natural water particulate matter (abiotic). While some of the above-mentioned reactions can lead to the formation of new chemicals which are more toxic than the parent compounds, generally the transformation of pesticides results in the formation of less toxic chemicals.

Of particular importance for pesticides are the photolysis, hydrolysis, and sorption reactions. Sorption generally does not result in a transformation of the chemical to a new chemical species. It does, however, significantly influence the availability of the chemical to aquatic organisms. It may also promote certain types of reactions which would not take place to the same extent or at the same rate in the absence of particulate matter. The increased concentrations of the pesticide and bacteria that occur at the surface of the particle may enhance the rates and extent of pesticide reaction. The various reactions which a pesticide may undergo in an aquatic system are illustrated by the model in Figure 2. If properly developed, this model will describe, for any aquatic system and given pesticide input rate, the concentrations of the available forms of the pesticide at any point, and the time - concentration distribution for the pesticide. With knowledge of organism behavior patterns, the concentration - duration of exposure relationships can then be developed for the aquatic organisms of concern.

Based on this model then, and the aquatic toxicology information obtained, it is possible to determine through a hazard assessment, how a particular pesticide will or may affect aquatic life in a system, or man. Once the technical question of what the expected impact will be, then a "risk assessment" or a determination of the acceptability of the hazard is made. This assessment addresses the social, economic, political, and legal aspects of the situation based on the technical information provided by the hazard assessment, and will call for a societal decision as to whether the use of the pesticide represents a sufficiently significant risk to man and the environment to justify altering the pesticide use pattern. For almost all pesticides there will be conditions under which their use in a certain manner would represent an unacceptable risk.

TIERED TESTING

If the hazard assessment is to be cost-effective, it is important that the information-gathering process be tiered in such a way as to permit termination of the process without going through the complete testing sequence. There has been a tendency in pesticide evaluation to require that a complete set of tests be run on each, even though some of the tests are not appropriate for a particular pesticide. An example of this type of superfluous testing would be requiring chronic-lifetime toxicity tests for a pesticide which hydrolyzes so rapidly in aquatic systems that a chronic



$$\frac{D(\text{AVAIL. FORM})}{DT} = K_1(\text{GAS EXCHANGE}) + K_2(\text{BIOCONCENTRATION}) + K_3(\text{SORPTION}) + K_4(\text{CHEMICAL TRANSFORMATIONS}) + K_5(\text{ETC.})\ldots$$

Figure 2. Components of Aquatic Chemistry of a Pesticide

exposure of organisms of concern would be virtually impossible. The site-specific hazard assessment should consist of a series of tiers, each including an aquatic toxicology and an environmental chemistry-fate component. At the end of each tier, the individual or group making the hazard assessment faces a decision of whether or not there is sufficient information to determine the hazard with an acceptable degree of confidence. If not, additional tiers of testing would be indicated.

The early tiers of testing should be relatively inexpensive screening tests to identify the innocuous and highly hazardous chemicals and use situations. For such chemicals, testing can be terminated after this tier. The higher, more sophisticated, more expensive tiers are reserved for those chemicals with an intermediate hazard that may or may not be acceptable. This approach provides a cost-effective, technically sound evaluation of potential environmental impact since it provides a rational testing sequence, beginning with rough screening procedures and becoming increasingly specific with each tier, which can be carried out to the degree necessary for any particular situation. Cairns et al.[4], Dickson et al.[5], and Lee et al. provide additional information on tiered environmental hazard assessment.

IMPLICATIONS FOR PESTICIDE USE AND LABELING RESTRICTIONS

The current pesticide labeling and use restrictions in the U.S. as well as some other countries are designed to protect the environment and man from adverse impact of pesticides under any condition. They were in general, developed by assuming a worst case situation. This conservative approach leads to unnecessary restrictions being placed on the use of some pesticides. During the late 1960s and early 1970s when the current approach was formulated, the "cost" of this approach was generally accepted as being appropriate. Today, however, many question the need for and

the general appropriateness of the worst case condition assumptions applied to chemicals in the environment. The basic issue in the U.S. that is left unresolved in this regard is whether the citizens will make use of the technical information provided by site-specific hazard assessment to develop cost-effective, technically sound, yet environmentally protective pesticide use regulations. While the social and political atmosphere in the U.S. is such that bans on the use of certain pesticides will not likely be reversed, in developing countries where such pesticides are being used, it should be possible to formulate use restrictions which would allow their continued use in those situations where they do not represent significant hazards to man or the environment.

SIGNIFICANCE OF SEDIMENTS IN HAZARD ASSESSMENT

The primary factor governing the availability, and therefore the water quality significance, of pesticides is the presence of particulates. Many of the more persistent pesticides tend to become strongly attached to suspended and settled sediment particles and are thereby transferred primarily with particulate matter in aquatic systems. In the past few years, significant advances have been made in predicting the transport of suspended and "settled" particulate matter such as silt-sized and especially sand-sized particles. While this type of work is important in predicting erosion and scour, it is of limited value in predicting pesticide transport since pesticides tend to be associated with even finer-sized particles which become cohesive upon settling. There is limited information at this time on scour and transport of particles of this type.

There have been a number of studies devoted to pesticide - particulate matter interactions. Many of these studies such as that of Karickhoff et al.[7] have shown that the organic content of particulate matter is often a major factor influencing the amount of pesticide sorption that will occur. Lee et al.[8] and Jones and Lee[9] discuss the results of their comprehensive study of the release of selected pesticides from U.S. waterway sediments. Table 1 presents a summary of these results. Sediments from a variety of fresh and marine water systems were subjected to the "elutriate test." This "test" is actually a leaching procedure designed for dredged sediment evaluation, in which one volume of sediment and four volumes of water (site water, collected from near the region from which the sediment was obtained) are vigorously mixed under oxic conditions for a period of 30 min. The mixture is allowed to settle for one hour and centrifuged to remove particulate matter. The centrifugation was such that it did not remove colloidal matter. As shown in Table 1, some of the sediments studied contained relatively large amounts of certain pesticides; however, usually only a small amount of this sediment-associated pesticide was released in the elutriate test. Table 1 also presents the polychlorinated biphenyl (PCB) release found, which was also generally low; for some sites, concentrations in the elutriate were less than those in the site water.

It appeared, as shown in Table 1, that the primary factor governing chlorinated hydrocarbon release from the sediments was their organic content as measured by oil and grease, or total organic carbon (TOC). The greatest release of these compounds occurred from those sediments with the lowest oil and grease levels. These sediments also tended to have somewhat lower pesticide levels compared to levels in other sediments taken from the same general areas. For some sediments, the total iron content also played a role in controlling pesticide uptake, through the formation of ferric hydroxide which tends to be an efficient scavenger for many chemicals. Since most aquatic sediments tend to be anoxic just below the surface, the iron in the sediments would be in the reduced (ferrous) form. Upon suspension of the sediment into the water column, the ferrous iron would be oxidized to the ferric (oxidized) form which would precipitate as ferric hydroxide, scavenging trace chemicals such as

some pesticides from the water column. Sridharan and Lee[10], and Lee[11], provide more detailed discussion of this phenomenon.

It is clear from the studies of Lee et al.[8], and Jones and Lee[9], that there is no relationship between the total concentration of a pesticide in a sediment and the tendency for that sediment to release pesticides upon suspension in the water column.

These results have important implications for the development of pesticide use regulations. The pattern and extent of the "safe" use of a persistent pesticide in an area depend in part on the amount of particulate matter in waterbodies receiving runoff or other input from the area. In a system with large amounts of suspended sediment, much of the pesticide content would be sorbed on particulates and would thus be less available, in general, to affect aquatic life. As discussed earlier, most water quality criteria and standards developed for pesticides have been based on sediment-free systems. The introduction of sediment into the system almost always tends to greatly increase the amount of total pesticide that may be present without being toxic to aquatic life. In some instances, however, sorbed pesticides may be available to certain kinds of organisms such as filter-feeders. Water quality criteria such as those developed by the US EPA, should not be used to establish absolute limits for pesticide concentrations in a water sample. They should be used to indicate areas in which there are potential water quality problems from pesticides; a hazard assessment of the type described above would have to be made to determine whether or not the pesticide in the particular system could impair the beneficial uses of that system.

The work of Lee et al.[8], and Jones and Lee[9], included bioassays in which selected aquatic organisms were exposed to the settled (unfiltered) elutriates containing the settled sediments. In general it was found that under the worst case test conditions, the test systems showed little or no toxicity to aquatic life. Normally under a

Table 1. Results of Chlorinated Hydrocarbon Analyses - Content of and Release from U.S. Waterway Sediments

Study Site	Test Ratio Percent Sediment	Oil and Grease Sediment (mg/kg)	Oil and Grease Water (mg/l)	Oil and Grease Elutriate (mg/l)	Total Fe Sediment (mg/kg)	TOC Sediment (mg/kg)	Total PCBs Sediment (μg/kg)	Total PCBs Water (ng/l)	Total PCBs Elutriate (ng/l)	Total Pesticides Sediment (μg/kg)	Total Pesticides Water (ng/l)	Total Pesticides Elutriate (ng/l)
Rodeo Flats	5	2227	NT	NT	1,350	NT	90	85	25	B	B	B
Mare Island	5	3120	NT	NT	1,380	NT	95	225	21	B	B	B
Oakland 1	20	1168	< 0.5	36.3	37,300	24,000	600	B	ND	148	3.3	20.2
Oakland 2	20	1436	< 0.5	95.0	37,300	25,000	360	B	20	135	3.7	B
TCC 1	5	304	NT	NT	23	NT	7426	130	150	15.5	1.4	5.1
TCC 4	20	533	0.9	14.7	NT	8,000	3010	52	9619	12.5	2.4	28.1
GBEC Buoy 1	5	24	NT	NT	41	NT	192	210	170	5.5	11.8	10.5
Galveston Channel	20	437	NT	NT	NT	9,200	33	171	261	6.7	10.3	49.4
Los Angeles A7*	20	2438	NT	NT	17,478	30,800	4430	B	36	675	15.6	10.7
Newport, R.I.	20	168	NT	NT	885	12,000	50	B	B	B	B	B
Stamford W	20	1877	< 0.5	0.9	9,531	32,000	2064	7	26	341.7	B	8.0
Norwalk S	20	2506	< 0.5	1.8	9,387	44,000	2820	B	104	320.9	4.2	94.8
Apalachicola 1*	20	345	NT	NT	18,800	29,000	13	24	14	8.4	15.6	4.4
Apalachicola 3*	20	423	NT	NT	9,648	49,000	454	38	B	10.6	4.7	14.0
Duwamish River	20	702	< 0.5	< 0.5	16,079	36,000	406	12	33	32.2	2.8	6.8
Perth Amboy Channel	20	4044	< 0.5	< 0.5	13,900	35,000	1078	B	69	104.2	B	B
Perth Amboy Anchorage	20	2091	0.7	1.3	14,800	31,500	1760	17	81	71.5	B	34.9
Bay Ridge Channel	20	826	< 0.5	3.6	15,900	31,800	1820	8	86	184.4	14.2	15
HSC 1	20	5868	< 0.5	54.7	19,045	6,000	5325	B	11,755	578.5	32.6	417.2
HSC 2	20	3634	< 0.5	47.0	20,055	4,900	7918	64	872	695.8	33.0	170.1
Upper Mississippi R.	20	60	0.5	2.0	11,820	3,300	7	B	11	3.3	5.7	10.4
James River	20	471	< 0.5	0.6	NT	27,000	45	B	B	23.6	B	37.3
Bailey Creek	20	1059	< 0.5	0.9	NT	21,000	235	B	34	1093.5	17.6	34.5

Study Site	Test Ratio Percent Sediment	Total DDT Sediment (μg/kg)	Total DDT Water (ng/l)	Total DDT Elutriate (ng/l)	Total Aldrin-Dieldrin Sediment (μg/kg)	Total Aldrin-Dieldrin Water (ng/l)	Total Aldrin-Dieldrin Elutriate (ng/l)	Heptachlor Sediment (μg/kg)	Heptachlor Water (ng/l)	Heptachlor Elutriate (ng/l)	Lindane Sediment (μg/kg)	Lindane Water (ng/l)	Lindane Elutriate (ng/l)
Rodeo Flats	5	B	B	B	B	B	B	B	B	B	B	B	B
Mare Island	5	B	B	B	B	B	B	B	B	B	B	B	B
Oakland 1	20	148	B	13.7	B	B	B	B	B	6.5	B	3.3	B
Oakland 2	20	135	B	B	B	B	B	B	1.6	B	B	2.1	B
TCC 1	5	8.4	B	B	6.1	1.4	3.6	B	B	B	1.0	B	1.5
TCC 4	20	9.5	B	17.6	2.6	1.4	8.9	B	B	B	0.4	1.0	1.6
GBEC Buoy 1	5	2.2	5.2	5.2	2.5	4.1	2.8	B	B	B	0.8	2.5	2.5
Galveston Channel	20	5.4	B	B	0.9	6.9	35.1	B	B	B	0.4	3.4	14.3
Los Angeles A7*	20	675	B	6.2	B	B	B	B	B	B	B	15.6	2.5
Newport, R.I.	20	B	B	B	B	B	B	B	B	B	B	B	B
Stamford W	20	322.2	B	8.0	7.6	B	B	11.9	B	B	B	B	B
Norwalk S	20	215.3	B	67	70.3	B	12.6	23.1	B	9.0	12.2	4.2	6.2
Apalachicola 1*	20	5.6	B	B	B	B	B	B	B	B	2.8	15.6	4.4
Apalachicola 3*	20	6.6	B	B	B	B	B	3.2	2.4	7.7	0.8	2.3	7.0
Duwamish River	20	30.4	B	2.8	B	B	B	1.8	2.8	4.0	B	B	B
Perth Amboy Channel	20	66.1	B	B	26.4	B	B	5.9	B	B	5.8	B	B
Perth Amboy Anchorage	20	34	B	25.8	20.3	B	B	9.9	B	4.5	7.3	B	4.6
Bay Ridge Channel	20	130	B	5.2	22.7	9.2	B	14.6	B	5.3	16.7	5.0	4.5
HSC 1	20	413.4	B	316.2	132.2	B	78.0	B	B	B	32.9	32.6	23.0
HSC 2	20	515.8	B	117.1	110.6	7.8	31.7	50.8	5.8	13.2	18.6	19.4	8.0
Upper Mississippi R.	20	1.6	B	6.0	0.7	3.4	1.3	B	B	B	1.0	2.3	3.1
James River	20	20	B	17.3	B	B	B	B	B	B	3.6	17.6	20.0
Bailey Creek	20	1085	B	22.8	B	B	B	B	B	B	8.5	17.6	11.7

NT = Not Tested
ND = No Data
B = Below Detection Limit
*Indicates elutriate test run with Reconstituted Sea Water.

20% V/V sediment test condition, only one or two of the test organisms out of 10 died in four-day test periods. Since these conditions grossly exaggerated what would happen in the real world both in terms of the amount of sediment present and the duration of organism exposure that would be encountered by water column organisms, it was concluded that, in general, pesticides associated with dredged sediments did not represent a significant threat to water column aquatic life. It should be noted that the toxicity that was found under worst case conditions in the studies by Lee et al.[8], was probably not due to pesticides; the sediments also contained a wide variety of other contaminants such as heavy metals and ammonia that can be highly toxic to aquatic life. It is important to emphasize that even the toxicity found in the sediments due to all causes would not represent a hazard to aquatic life present in the water column where suspension of the sediment takes place. Jones and Lee[9], and Jones et al.[12], provide a more in-depth discussion of the results of these studies including the toxicity testing, and their implications for water quality.

In addition to toxicity to water column organisms, consideration must be given to the impact of sediment-associated contaminants on benthic and epibenthic organisms as well. In the toxicity tests performed during the Lee et al.[8] studies, the test organisms, because of their epibenthic behavior, had the opportunity to obtain pesticides as well as other potential toxicants directly from the settled sediment particles. While their studies on the direct uptake of pesticides and other contaminants from these sediments was not as comprehensive as their water column work, it appeared that in general (except for situations in which sediments contain massive concentrations of pesticides such as from industrial waste discharges associated with pesticide manufacture), it would be rare that pesticides in sediments would cause significant toxicity to benthic or epibenthic organisms. This is an area, however, that needs additional attention and must be evaluated on a site-specific basis.

A related area that needs research on a site-spec basis is the bioaccumulation of pesticides by benthic and epibenthic organisms. These organisms can accumulate chlorinated hydrocarbon pesticides within their tissues. The significance of such accumulation to man and the environment, however, must be determined. As discussed earlier, this accumulation is only of readily discernible significance if the concentration of the pesticide is above the established limit for the use of the organism as human food. This does not mean that there are no other impacts associated with bioaccumulation of pesticides in higher trophic level organisms. However, at this time the relationships between the concentrations of pesticides within the organism and those which are known to cause these "other" problems are poorly understood; where studies have been conducted they have generally found these "other" problems occur at higher concentrations than those which would render fish and other aquatic life unsuitable for use as human food based on U.S. Food and Drug Administration Action Limits.

The approach that should be used to evaluate the potential for bioaccumulation of existing pesticides in a particular system would be to measure the concentrations of the pesticides of concern in the flesh of fish and other organisms that are used for human food. From data of this type, coupled with information on pesticide usage in the watershed, it should be possible to develop load - response relationships which provide guidance on how a pesticide may be used in a particular system without causing excessive bioaccumulation in human food organisms. If some animal other than man, such as a fish-eating bird, is the point of concern, then similar kinds of relationships can be developed for it. This may require that work be done to determine the critical concentrations of the particular pesticide in the animal's diet which could adversely affect the bird population of a region.

For new pesticides, deterministic models of pesticide behavior would have to be developed in order to estimate the concentration of the pesticide in water and sediments in a particular system. This information would then be used in a hazard assessment evaluation to determine whether the concentrations in the systems would likely result in excessive concentrations within the organisms. Since it is difficult at this time to make a reliable model of the bioaccumulation of a chemical when the mode of accumulation is through the food web involving benthic and epibenthic organisms' uptake of the chemical from the sediments, it is probably best to neglect this route of bioaccumulation in the deterministic modeling effort. If the deterministic model without this route included shows that there is little likelihood of the bioaccumulation of the pesticide in this system, then limited use of the pesticide should be allowed while conducting an intensive monitoring program to determine actual environmental behavior of the pesticide. Such information could help establish specific use restrictions for that system.

COST-EFFECTIVENESS OF SPECIFIC HAZARD ASSESSMENT VS. WORST CASE REGULATIONS GOVERNING PESTICIDE USE

The hazard assessment approach discussed in this paper requires site-specific evaluations of the hazard that a pesticide represents to a particular use. The cost-effectiveness of the lower tier screening tests has already been touched upon. The hazard assessment approach allows in the early screening level(s), the relatively easy and inexpensive identification of those contaminants which will cause insignificant environmental impact. The early tiers also allow ready identification of many of the contaminants that would cause severe and highly undesirable environmental impact. The higher tiers of these evaluations, however, are expensive to conduct and require highly skilled technical assistance. Further, they will normally require a several-year effort. The cost-effectiveness of this approach must be weighed for each site of concern, against that of the worst case approach that is generally used in the U.S. and

in some other countries. For highly productive agricultural regions such as a valley with a single-river drainage system for example, it could be very cost-effective to do a hazard assessment study to establish pesticide use regulations rather than to assume that worst case regulations should apply throughout the system. As more is learned about site-specific use regulations, it should be possible to significantly reduce the cost of hazard assessment studies. It is important that all sites for which use regulations were based on a site-specific hazard assessment, be carefully monitored to determine what actually happens within the system. Eventually, as experience is gained from this approach, it will be possible to reduce the magnitude of the monitoring program as well.

SUGGESTED APPROACH FOR EVALUATING THE WATER QUALITY SIGNIFICANCE OF PESTICIDE RESIDUES IN EGYPTIAN SOILS

The intensive use of pesticides in Egypt creates the potential for significant human health and environmental quality problems. The existence of pesticide residues in soils itself, does not mean that there are environmental quality problems. Further, finding a problem in one area for one type of residue pesticide and a certain type of soil does not mean that the same pesticide residue in another part of Egypt with a different type of soil will cause the same type of problems. As discussed above, there is a wide variety of factors that govern the hazard that a particular pesticide residue present in a particular soil represents to man and the environment. Each situation must be examined to evaluate whether or not real problems exist.

The approach that should be followed to evaluate the environmental and human health hazard that soil-associated pesticide residues present in Egyptian surface and groundwaters represent should involve collection of all existing data on the pesticide content of water, fish, and other aquatic organisms and aquatic sediments. These data should be critically reviewed for their reliability. Attention should be given to the analytical methods used, especially the cleanup procedures employed. A compilation of the reliable data should be prepared.

A report should be developed presenting and discussing the compiled data. Also, an attempt should be made to identify time trends in the pesticide residue data. The existing data plus information from the literature should be used to design a national pesticide monitoring network. This network should consider any on-going studies by governmental agencies, universities, etc., in this area. It should also be designed to fill gaps in the current data base and detect time trends in pesticide residues in water and fish in various parts of Egypt. All groups that participate in the national monitoring program should participate in annual round robin - ring tests to assess the precision and accuracy of pesticide analyses made by the laboratories.

A national committee representing Egyptian governmental agencies, industries and universities should be organized to develop Egyptian pesticide residue criteria and standards for surface and groundwaters that are used as individual and domestic water supplies and for irrigation. Also, pesticide tolerance levels should be established for fish and other aquatic life used for human food in Egypt. These criteria, standards, and tolerance levels do not necessarily have to be identical to those developed for use in North America, Western Europe, or Japan. The markedly different social, cultural, and economic conditions and indigenous organisms that exist in Egypt compared to those of many other countries justify, and in fact require, that Egypt develop its own pesticide residue criteria, standards, and tolerance levels.

Because the development of these criteria, standards, and tolerances is likely to take a number of years, it is suggested that as a starting point for evaluating the potential environmental significance of pesticides within Egypt's water and aquatic life, studies be initiated to compare existing residue data to US EPA water quality cri-

:eria for pesticides. It is important to emphasize again, :hat these criteria are based on worst case assumptions. :herefore a residue above a US EPA criterion should not be :nterpreted to mean that there is an environmental problem. :lso, it is suggested that the U.S. FDA Action Limits for :esticides in fish and other aquatic life food be used as :n initial starting point for existing residue data review. :f the existing water and aquatic life residues exceed the :S EPA water quality criteria and/or FDA Action Limits, :hen studies need to be initiated to determine the source(s) :f the pesticides that are the primary cause(s) of the :ituation. Of particular significance may be the pesticide :esidues that have accumulated within the Egyptian soils. :t is important to clearly distinguish between the relative :oles of freshly-applied pesticides as potential sources of "excessive" residues within water and fish, and "aged" pesti:ide residues in soils. It could be that the aged pesticide :oil residues are playing a relatively minor role as a cause :f "excessive" concentrations within water and fish. It is :lso likely that there are insufficient data at this time :o determine whether or not there are "excessive" amounts of :esticide residue in the Egyptian environment. It would, :hen, be at least a year before sufficient amounts of data :ould be gathered as part of the monitoring program to :scertain whether there are excessive amounts of pesticides :n Egyptian water and fish. During that time the pesticide :esidue criteria and tolerance committee should be in a :osition to make initial recommendations on the appropriate :riteria and tolerances for Egypt. If it becomes established :hat there are excessive amounts of pesticides in Egyptian :ater and fish, then control programs specifically designed :o control those kinds of pesticides that are creating the :roblems, should be formulated and, where possible, put into :ractice. It is important to emphasize that the approaches :hat have been used in the U.S., involving the large-scale :anning of certain pesticides for use throughout the coun:ry, may not be in the best interest of Egypt. The hazard :ssessment approach discussed in this paper should be used on a site- or area-specific basis to formulate the approach to be used in developing control programs for any excessive pesticide concentrations that are found.

CONCLUSIONS

The typical approach used in the U.S. and some other Western countries for pesticide use restrictions may not be the best overall regulatory approach for developing countries. Rather than assuming that worst case conditions prevail everywhere, site-specific hazard evaluations should be conducted in which aquatic toxicology and especially environmental chemistry-fate information is used to evaluate the potential hazard that a pesticide use represents to man and the environment. This approach would be a cost-effective method of regulating pesticide use while at the same time providing protection for man and the environment which equals that achieved through adoption of worst case pesticide use restrictions. Site-specific pesticide use restrictions developed through the hazard assessment approach should be considered for all aquatic systems which tend to be highly turbid, i.e., have large amounts of particulate matter suspended in the water. These systems can have a much higher load of certain pesticides than less turbid systems because of the sorption of the pesticides on the particulate matter, with a generally concomitant reduction of the bioavailability of the pesticide.

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