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PESTICIDES IN SURFACE AND GROUND WATER

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Summary

Pesticides have been detected in ground water, surface water, and drinking water samples from across the United States, indicating that some major water resources are contaminated. These detections are the result of extensive regional and nationwide studies often using analyses at very high sensitivity. Most of the detections involve a limited number of herbicides used extensively in corn and soybean production. Nationwide, the total number of detections is a few percent of the total analyses done, and in most cases the concentrations found are very small fractions of levels that are believed to be harmful to humans and aquatic life. However, there are problems in some areas of high pesticide use. Fish kills due to pesticides have been observed in several areas of the country and some water-supply systems, particularly in the Corn Belt, have pesticide concentrations that exceed human health based drinking water standards.

A large scientific/regulatory system has evolved to attempt to balance the benefits and risks of pesticides. The system is imperfect. Much improvement is needed, especially in our knowledge and prediction of risks of long-term exposure to low levels of pesticides, to both humans and ecosystems. However, the system appears to be capable of maintaining overall risk at acceptably low levels, because of the use of safety factors which are thought to be conservative. After the registration of a pesticide, if its subsequent use results in unacceptable adverse effects, a system of “special review” is initiated which can result in use restrictions or cancellation. Pesticides in water resources can be decreased through the application of scientific knowledge, in a case-by-case process, that can provide reasonable protection to humans and the environment.

Introduction

Of all human activity, agriculture most alters our global environment. Converting native forest or prairie to cultivated fields entails massive and irreversible changes in the life present. A much different ecosystem is produced, which must be maintained artificially. Adjacent soil, water, and air are contaminated by dust, sediments, fertilizers, animal wastes, and pesticides.

In the 1950s, the environmental effects of persistent organochlorine insecticides such as DDT began to be observed. These chemicals, a revolutionary breakthrough in crop and human protection, were used in vast quantities (by today's standards) all over the world. But they were so persistent and so strongly dissolved into animal fat that they concentrated as they moved up the food chain, causing damage, especially to bird populations. These compounds are now banned in the United States. A new pesticide with the same combination of very high persistence and very high food chain accumulation would be unlikely to receive registration today. But every pesticide has risks of environmental side effects, and these must be understood and considered before it may be used.[1] The compounds replacing organochlorine insecticides have their own risks. These include, sometimes, greater hazard to applicators and farm workers, fish and bird kills and poisoning of other wildlife, and crop and other plant damage. As another example, pesticides are present in trace amounts in many of the foods that we eat, and in many instances such traces are unavoidable if the pesticides are used. Thus, to receive approval for use on a crop, experiments are conducted in which the crop is treated with the pesticide, and the amounts of pesticide in the harvested crop are measured. These amounts must be shown to be well below levels that would lead to unacceptable risks.

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In an attempt to avoid harm by pesticides, a vast, intertwined scientific enterprise and regulatory system has evolved. Discovery or hypothesis of adverse health effects has resulted in additional testing requirements, changes in use patterns, complete bans of some compounds, and research for improved ways of predicting problems before they happen. The philosophy of this system is that these chemicals are permitted to be deliberately introduced into the environment only if, for every use of every chemical, estimated risks are not unreasonable and are balanced by the benefits of the pesticide—benefits that extend beyond agriculture to all of society.

But the risk is never zero. Discoveries of environmental effects have occurred and will continue to occur (though less frequently, it is hoped, as the science improves). Whenever such discoveries occur, the risk assessment process is called into question.

The Issue

The most important recent test of the pesticide regulatory system was the discovery that some heavily used pesticides can be found in important drinking water sources. In the early 1980s, traces of pesticides began to be detected in drinking water wells in areas of the country where ground water lies relatively close to the surface and pesticide use is intense (i.e., a large percentage of the overlying land is treated with a particular pesticide). Areas of the Corn Belt and the southeastern coastal plain were particularly affected. The compounds most often detected included atrazine, aldicarb, DBCP, EDB, and dacthal. Although most of the pesticides detected had been in use for decades, it is not known how long they have been in ground water and the drinking water drawn from it. Ground water was not widely analyzed for pesticides until new, very sensitive and relatively inexpensive analytical techniques became available.

A number of large (regional- or national-scale) well-water quality surveys have been conducted to as-

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[1] The issue, of course, is that we never can be absolutely certain that we know what all the side effects will be. Technical arguments over pesticide risk assessment are about how much testing is needed to provide reasonable confidence that no human or ecosystem damage will occur, and how best to estimate exposure and to develop a weight of evidence approach. Currently, it takes about 7 to 10 years and $30 million worth of testing before a new pesticide can be used.

sess the extent of this largely invisible pollution. In the most ambitious nationwide attempt, the U.S. Environmental Protection Agency (EPA) analyzed samples from 540 community water wells and 752 rural household wells for 126 pesticides and pesticide metabolites. The wells were carefully selected to statistically represent all U.S. water supplies. Fourteen pesticides and metabolites were found and the percentage of contaminated wells, when extrapolated to the country as a whole, indicated that between 0 and 750 community systems (0–0.8%) and between 9,000 and 200,000 rural household wells (0.1–1.9%) will have at least one pesticide above a human-health-based drinking water standard, such as the maximum contaminent level (MCL) set by the EPA. As many as 14% of all wells may have detectable residues, generally in the range 0.1 to 0.2 part per billion (one millionth of a gram per liter of water; ppb for short) of some pesticide.

The EPA also has data from numerous other ground water studies conducted form 1971–1991. In this database, of a total of 65,865 wells sampled, 14.4% or 9,509 had concentrations of one or more pesticides in excess of health standards. This high percentage is a reflection of sampling bias—many of the wells sampled were selected because they were located in areas where pesticide leaching was known to be occurring.

More recently, the U.S. Geological Survey used the same analytical techniques to demonstrate that surface waters, including major rivers and lakes in the Corn Belt, also contain some of the most used pesticides in the United States: herbicides used in corn and soybean production, including atrazine, alachlor, and cyanazine. During the 2 to 3 months in spring and early summer immediately after these herbicides are applied on farms, pesticide concentrations in surface waters can be much higher than in ground water. In some instances, human health standards are exceeded and concentrations of 1 to 10 ppb are common; occasionally, concentrations exceeding 100 ppb are observed. Concentrations in rivers and streams decrease to < 1 ppb by mid-fall, but elevated concentrations may persist in lakes.[2] This seasonal peak concentration of pesticides in rivers and lakes in the period following their use on fields indicates that *runoff*, the drainage of excess rainfall from the surface of fields, is responsible for much of the pollution.

If one sums all detections of all pesticides in all surface and ground water samples analyzed in the last decade and divides the sum by the number of analyses, the fraction is small: on the order of a few percent. But hundreds of thousands of analyses have been conducted, almost every state has had pesticide detections somewhere, and most of the important pesticides in use have been detected somewhere. In some surface water studies in the Midwest, pesticides were detected in a majority of samples. Although some detections are due to spills or to other sources of direct contamination, clearly, the large-scale use of pesticides by agriculture almost inevitably will produce instances of detectable residues of those pesticides in adjacent ground or surface waters. This is because combinations of weather, site, and pesticide characteristics leading to pesticide transport to water resources, although they can be minimized by good practice, still are likely to occur somewhere. And analytical sensitivity to pesticides has increased to the point that vanishingly small amounts can be detected.

This report describes how pesticides enter water resources, summarizes the risk implied for both human and aquatic ecosystem health, and discusses what the authors believe to be the most appropriate responses.

Pesticide Varieties, Uses, and Resulting Pollution Potential

The term "pesticide" includes any chemical used to kill any pest species, including insects, weeds, disease-causing organisms, etc. In the United States, herbicides now account for at least three-fourths of the total synthetic pesticides used in commercial agriculture

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[2] Peak concentrations during storm runoff events, shortly after pesticide applications, frequently exceed drinking water standards. However, the standards actually are set for annual-average concentrations. When river waters are analyzed year-round, the annual averages are occasionally above MCLs, but only slightly above. Recent data indicate that above-MCL annual averages may occur more frequently in lakes and reservoirs due to a lack of flushing. A number of water supply systems in the Corn Belt are out of compliance with respect to the 3 ppb MCL for atrazine.

and are the major current concern as pesticide water pollutants. Insecticides, which are sometimes thought of as synonymous with "pesticides," are a distant second in usage, with fungicides, nematicides, and other products even further back.

> "... DETECTIONS ARE NOT TO BE IGNORED. INDEED, THEY PROVIDE A USEFUL EARLY WARNING OF POTENTIAL PROBLEMS. MITIGATION SHOULD BE UNDERTAKEN TO MINIMIZE OR TO ELIMINATE SUCH EXPOSURE—IN EFFECT, TO WIDEN SAFETY MARGINS."

A large variety of chemicals are used as pesticides. In the 1970s one could refer to 25 or so "classes" of pesticides, e.g., the organochlorine insecticides or triazine herbicides. But a constant search by the pesticide industry for unique proprietary products has diversified the list. A recent compilation contains about 130 "chemical families." At the same time the chemical variety of pesticides has increased, however, the total number of different individual chemicals in wide use has decreased because registrations have expired, compounds have been banned, and the costs of developing new pesticides has increased. The number of compounds in wide use today, at levels that make them a general concern as water pollutants, is probably less than 100. These are also compounds that are very important to agriculture.

This relatively small number of different pesticides, and their great chemical variety, means that we can and should deal with each pesticide, and its pollution risk, on its own merits. Whether a problem is observed for a chemical already in use, or the risks of a new experimental chemical need to be predicted, the many factors in each case that affect the likelihood of pollution must be considered. The technology and knowledge are available to do this and the complexities of each individual pesticide use pattern offer many opportunities to make that use safer.

In an agricultural crop system, there are three compartments where pesticides may be applied and these compartments become the source of pesticide losses to water. These are vegetation, the soil surface, and the soil below the surface. Each of these compartments can lose pesticides by degradation, evaporation, and other "dissipation" processes. If rainfall contacts these compartments before much dissipation occurs, transport of the pesticides from plant foliage and across and through the soil occurs. *Pesticide leaching*, the process that may contaminate ground water directly, occurs as water percolates down through the soil carrying those pesticides that are "leachable" with it. *Pesticide runoff*, the process that may contaminate surface water directly, occurs if rain falls faster than it can be absorbed by the soil, thereby generating flow across the soil surface, which picks up soluble pesticides or pesticides attached to eroding soil particles.

Surface water also can be contaminated directly by pesticide spray *drift*—the travel and deposition of fine pesticide spray droplets away from their intended target—when the spray is applied too close to water. Drift incidents can result in greater surface water contamination than either runoff or leaching. Obvious, acute effects such as fish kills can occur. However, these incidents should be considered mostly preventable and will not be discussed further.

Leaching and runoff are *nonpoint* pollution processes that depend on five sets of factors, some of which are controllable and some not.

1. **Application Factors**. These include the application site (crop or weed plants or soil surface or subsurface), the formulation (e.g., granules or suspended powder or liquid), and the application amount and frequency.
2. **Pesticide Persistence and Mobility**. Some pesticide-soil combinations result in such strong binding of the pesticide to soil particles that the pesticide is moved only if the soil is moved, i.e., if erosion occurs. Many pesticides now in use are degraded so

quickly on soil and crop surfaces that rainfall must occur within a few days after application for significant transport to occur. Pesticides must be relatively persistent and mobile to leach to ground water because the travel time for water to percolate to deep aquifers can range from months to years. However, once a pesticide has leached into subsurface soils, the biological activity and binding capacity there are often less than in soils near the surface. Thus, the pesticide becomes more persistent and mobile.

Persistent and mobile pesticides also are more of a threat for runoff. However, that part of pesticide residues which is most available for runoff—the part at the topmost surface of soils—is the part most rapidly dissipated by evaporation and photodegradation. Moreover, runoff transport can be complete in hours, and erosion can transport immobile pesticides attached to soil. Thus, pesticide runoff is less dependent on pesticide properties than pesticide leaching, and much more dependent on how soon runoff occurs after application.

3. **Soil and Field Topography**. Soils differ greatly in their capacity to absorb water. The slope and drainage pattern of a field or a watershed greatly affect its potential to generate runoff water. Fast-draining soils such as sands and sandy loams have the greatest leaching potential; slow-draining clays and silty clays have the greatest runoff potential. Watershed size has an important effect on runoff pesticide concentration patterns: small streams adjacent to treated fields can have very high peak concentrations of hundreds of ppb, but concentrations decrease quickly to low values. In large rivers, peak concentrations are much lower but concentrations may be elevated longer.
4. **Weather and Climate**. Climate affects the type of crops grown, the intensity of pest problems, and the persistence of pesticides used. The intensity of rainfall and its timing with respect to pesticide application determines how much pesticide transport occurs. While these factors are not controllable, probabilities of pesticide runoff and leaching can be estimated, and avoiding pesticide application when rain is imminent is often possible.
5. **Farmer Decision Making**. Federal and state agencies and pesticide manufacturers are making an effort to provide farmers with the information needed for pollution prevention. The farmer has considerable control over the pollution probabilities: knowledge of erosion control and of best application techniques, and an eye on the weather, are the first lines of defense against pollution.

What Do These Detections Mean? Relating Concentrations in Water Resources to Human and Ecosystem Risk

Pesticide risk assessments for both humans and ecosystems are the same in principle. Two factors are involved: the *hazard*, or toxicity of the chemical and the *exposure*, the concentration of the chemical that will occur in food or water or some other environmental component. Hazard is determined using “indicator” species—a series of animal and plant species for ecosystems, other mammals for humans. The indicator species are exposed to the chemical in air, food, or water over a range of concentrations, and the toxicity of the chemical at each concentration is observed. Both *acute* (short-term, high exposure) and *chronic* (long-term, low exposure) studies are conducted. Since individual members of a test species exhibit a range of sensitivities to chemicals, in most experiments a “median lethal concentration” is determined or LC_{50}—the concentration that is lethal to half the test population. The more hazardous the chemical, the smaller the LC_{50} and the smaller the amount required to be toxic—obviously, “toxic” is a relative term. Since humans may be more sensitive than the test species, a safety factor ranging from 1/10 to 1/1,000 is used (depending on how good the test data is and other factors). “No effect” levels for long-term exposures and effects such as birth defects and cancer are more difficult to estimate, and safety factors are increased. If toxicology studies suggest that a pesticide is a probable human carcinogen, a “negligible additional cancer risk” level is estimated rather than a no effect level. The EPA considers added cancer risks of one in a million in a lifetime to be a negligible added risk.

Toxicology tests give a hazard measurement. The next step is to compare the resulting “levels of concern” to measured or predicted pesticide concentrations in water and food likely (or even unlikely) to occur in the environment when the pesticide is used. During the pesticide registration process, if “estimated environmental concentrations” (EECs)[3] for aquatic ecosystems exceed 1/2 LC_{50} for the most sensitive test species, risk is of high concern. If the EEC is more than 1/10 the LC_{50}, registration as a restricted-use pesticide is considered. If EEC is less than 1/10 LC_{50}, risk is considered small. In the case of chronic concentrations, comparison with a “lowest effect” level is made.

Once the pesticide is put in use, incidents of observed toxic effects may trigger further assessments and are analyzed on a case-by-case basis.

The same principles are applied by the EPA to develop MCLs for chemicals (not just pesticides) for drinking water. An additional five-fold factor is included in the MCLs because water is only one potential source of pesticide intake.

The procedures by which both the toxicity and the likely concentrations of a pesticide in food and water are estimated are inexact, indeed. Controversial assumptions are used. Criteria are used that are negotiated compromises. Nevertheless, the system seems to work, probably because of the multiplication of the conservative safety margins used in both hazard and exposure estimates. The pesticide uses allowed by the current regulatory system appear, with occasional exceptions, to keep U.S. water and food within established safety limits and there is no conclusive evidence that allowed concentrations are the source of any human health effects.

There is more concern with effects on aquatic ecosystems and on wildlife. Biologists at the EPA are collecting a database on “incidents”—reports (mainly from the states) of fish kills, bird kills, etc., which are due to pesticides, and they suggest that such incidents are much more widespread than generally thought. Some fish kills have occurred at quite low (ppb) levels of some pesticides. While there is no conclusive evidence that such damage is more than localized and transitory, it must be emphasized that our knowledge is very incomplete. Ecosystems are very complex and interdependent systems, and little has been done to determine the potential for subtle damage resulting from long-term exposure to chemicals at concentrations of a few ppb. In some instances, pesticide breakdown products are more widespread contaminants than their “parents,” and less is known about the toxicology and fate of these chemicals. The effects of pesticides in sediments (where they often are concentrated in aquatic ecosystems) generally have not been evaluated due to a lack of sediment toxicity and residue data. Few epidemiological studies have been conducted to determine whether low levels of pesticides in food and drinking water exert chronic effects on humans. It is not clear how to consider exposure to multiple chemicals, each of which is separately below any effect level.

The crux of the current pesticide water-quality issue, however, is that the presence of residues at any level is, for many, unacceptable. Of course, the only way to meet such a standard would be to discontinue pesticide use entirely. The presence of detectable pesticide residues in drinking water should not be taken out of its toxicological context. Residues of pesticides in drinking water should be held to the same standard as residues in food, i.e., a no-effect level is established and intake held below that level by a wide safety margin.

Risk Mitigation: A Framework

In response to detections of pesticides in well water in Europe, European Community regulators originally decided, based on the rationale that ground water contamination was potentially irreversible, that a zero tolerance for pesticides in ground water that is used to produce drinking water would be set. When it was rec-

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[3] An adequately accurate prediction of the likely worst case concentration of a pesticide in runoff or leachate, ground water or surface water, is no simple task. Such predictions generally are based on a combination of monitoring studies and predictive calculations. The methodology is undergoing intense scrutiny, because the current revolution in computer simulation modeling offers opportunities to greatly improve the procedures.

ognized that this was an impossible requirement (one can only analyze to the detection limit of analysis) the limit was set at 0.1 ppb for each compound and 0.5 ppb for all pesticides. This concentration was below or near the detection limits for the best analytical techniques of the time.

Since then, a 0.1 ppb detection limit has become (almost) routine for pesticide laboratories. Certain U.S. Geological Survey methods used in Midwest river/lake studies had reporting limits of 0.01 ppb or less. The EPA National Pesticide Survey of drinking water wells had minimum reportable levels of 0.1 to 1 ppb for most pesticides surveyed. But the *lifetime* exposure limits for pesticides in drinking water (i.e., a level of concern if a person drinks water containing that level every day for his or her entire lifetime) and the MCLs for public drinking water for pesticides are on the order of a few ppb to 100s or 1,000s of ppb.[4] Thus, analytical sensitivities are such that detections of pesticides can occur at concentrations of hundredths to thousandths of toxicologically significant levels.

Such detections are not to be ignored. Indeed, they provide a useful early warning of potential problems. Mitigation should be undertaken to minimize or to eliminate such exposure—in effect, to widen safety margins. But such mitigation, in the absence of evidence of risk, should be a result of case-by-case cooperation among agriculture, the pesticide industry, and the regulatory community, with opportunities for input from any other concerned sectors of society.

Levels of pesticides in water resources can be reduced by such a process in an orderly manner with maximum protection of humans and the environment and minimum disruption of food and fiber production. The process is already in operation. Some mitigation measures in use for individual pesticides include

- reductions in maximum recommended application rates or in the number of applications per season,
- elimination of specific high-rate, high-risk uses,
- reclassification of pesticides into the "restricted use" category,
- buffer zones between application areas and water bodies and wells,
- user (farmer) education about safe application technology and timing,
- banding and other methods of more efficiently targeting pesticide sprays,
- definition and protection of sensitive ecosystems and water resources,
- pairing of soils having high leaching or runoff potential with pesticides having low leaching or runoff potential, respectively, and
- adoption of soil conservation practices that can decrease pesticide runoff in some cases, especially in the Corn Belt.

Monitoring of the environment (including food, water, biota, soil, and air) for pesticide residues must continue. We need to know what pesticides are found, where they occur, and what the trends in their concentration are. We must be vigilant for early warning signs of damage to ecological systems. We must seriously consider every claim of human illness. Finally, the science of pesticide safety, and the regulatory system based on that science, must continue to advance. Much improvement is needed. Many assumptions made, though reasonable given the knowledge base we have, are still questionable.

We may have some confidence that the pesticide regulatory system that is in place is protecting the planet and ourselves. We reasonably can hope that few new unpleasant surprises will occur. But an important task of agricultural science, both public and private, is to continue to try to improve the record.

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[4] While this is true for human toxicity, there are exceptions for some other species. Some insecticides, for instance, are toxic to some aquatic invertebrates at less than 0.01 ppb.

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