

Use of physical and chemical properties to assess environmental transport and fate*

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Abstract

A full Environmental Assessment (EA) is required under 21 CFR Part 25.31a for proposed actions to approve food/color additives, drugs, biological products, animal drugs and Class III medical devices. The heart of the EA is found in Sections 6, 7, and 8, which addresses, in order, the introduction of substances into the environment, the fate of emitted substances, and the effects of released substances on the environment. The major goal is to prevent harmful environmental effects from the projected use of a new drug substance. Simulation or field experiments, while useful, cannot be used to evaluate environmental migration and depletion for every possible situation. It is much easier to project environmental movement from an analysis based on chemical and physical properties of the chemical(s) introduced, then proceed to simulation experiments when confirmation is required.

1. Introduction

The process for estimating environmental fate can be iterative. The first step is to generate needed chemical properties, then combine this information to estimate concentrations in environmental compartments. Depletion mechanisms that may be expected to be operative in the most significant environmental compartments are then identified. Depending on suitability of measured depletion rates, it may be advantageous to evaluate additional/related chemical properties, or to address the assumptions made in developing the initial environmental scenario.

Chemical and physical properties that are essential to estimate environmental distribution are (1) water solubility, (2) vapor pressure, and (3) one or more distribution ratios: air/water; soil/water; wastewater treatment

*Paper presented at the Symposium on the Role of Environmental (Ecological) Assessment in the Management of Chemical Pollution, American Chemical Society 204th National Meeting, Division of Industrial & Engineering Chemistry, Washington, DC, August 26–28, 1992.

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sludge/water; manure/water; and air/soil. This information allows the estimation of the most appropriate release mechanisms. For animal discharges which are direct to the environment, typical release mechanisms are to ground water, surface runoff, volatilization, and fugitive dust.

Given reasonable rates of chemical transport between compartments, the major depletion mechanism depends on the potential for chemical transformation. The tendency for air oxidation, photolysis, microbial transformation, and for hydrolysis is generally determined first. Where there are multiple depletion mechanisms, the most important of them is frequently the one that is operative in the environmental compartment that contains most of the released substance.

Our approach for predicting environmental transport and fate is illustrated here for a cattle feed additive. Some background information is presented first to develop a realistic analysis.

2. Case study

For the beef cattle industry, the 80/20 rule applies, in that >80% of the beef fattened in the United States takes place at <20% of the cattle feedlots [1]. Many of the lots are located in arid to semi-arid areas of the southwestern U.S. Large scale drug use is therefore centered at relatively few feedlots. Since cattle discharge directly to the environment, migration and fate naturally invite environmental concern. Few realize the complexity of managing a large feedlot. The inputs of feed and water, and discharge of waste matter on a per animal-day are measured quantities [2], and their control is of critical importance to the economic success of the operation.

Consider first the release of excreted chemical, either drug substance or metabolite, from excreta to rainfall runoff and groundwater. The typical feedlot has an even dirt surface, covered with a manure pack of variable thickness, which is removed infrequently [3]. A water impermeable "slime" layer forms at the waste/soil interface [4]. This layer effectively inhibits water percolation through the feedlot surface, so that the direct release to groundwater is insignificant. A large portion of the rain is absorbed by the solids on the lot. In this situation, the equation for rain runoff is $R = 0.345 P - 0.309$, where P is the amount of rain in inches [5]. A major runoff (1" or more) does not normally occur until more than 3 inches of rain have fallen [6], which may be a once in a year event at most feedlots. The concentration of released material in runoff may be estimated from its known concentration in manure and manure/water partition coefficient, using the assumption that the runoff has equilibrated with the solid waste. The percent of released chemical that leaves the lot may be obtained from the estimated concentration and volume of runoff. It should be apparent that runoff is normally an insignificant release mechanism unless the released material is exceptionally water soluble.

Volatilization from the feedlot surface is a factor that has not been studied in detail, but it is possible to estimate an upper limit from the maximum rate of evaporation [7]. The maximum rate of evaporation, $N_{\text{mol/s}}$, requires data for the vapor pressure, P_{Torr} , and the fraction of surface covered, F_{cov} , as shown in the following expression

$$N_{\text{mol/s}} = 3.52 \times 10^{22} P_{\text{Torr}} F_{\text{cov}} / (MT_K)^{1/2} \quad (1)$$

Various combinations of P_{Torr} and F_{cov} may be utilized. One can estimate P_{Torr} from the fraction of aqueous saturation and assume F_{cov} is unity. Where the released substance is slightly volatile, $P > 10^{-7}$ Torr, one may use P_{Torr} vs. concentration data, where P is the measured vapor pressure at the released concentration over a manure or feedlot waste matrix.

Release by fugitive dust is generally not important as a release mechanism, but it may be important to estimate an upper limit in order to reduce the concern about airborne material. Generation of dust over cattle feedlots is a cyclical, daily event with a maximum about sunset [8]. Dust loads can reach 9 mg/m^3 , and visibility can be significantly reduced. The concentration in air is simply the product of dust loading and concentration of released material in dry waste.

Depletion of released material in the feedlot may occur by several mechanisms. Photolysis may play a major role in the "inactivation" of released chemical. There is always a high potential for microbial transformation. Even though the lot surface may appear dry, there is from 20-25% water in air dried waste [9], and microbial degradation, while slow, may significantly reduce the average concentration of chemical. Microbial degradation of the organic component in waste is a mixed blessing. On one hand, this process greatly reduces the cost of lot cleaning and waste disposal. On the other hand, the concentration of a recalcitrant chemical may actually increase over time as microbial activity reduces the amount of accompanying organic matter.

Waste removed from feedlots may or may not be composted before application to agricultural land as a final means of disposal [10]. Manure is not eagerly sought by farmers, and the cost of hauling and application is significant. Where applied, rates vary from 10-15 tons per acre of irrigated land, to 5-10 tons for dryland farming. Waste is generally plowed in to reduce fly and odor problems, as well as to reduce potential damage from the high salt content [11].

Depletion in amended soils is essentially limited to microbial transformation. Rapid biotransformation may occur, however, and where fast, obviates the need for further environmental analysis. When kinetic data can be obtained for the transformation, it may be possible to understand what takes place by comparison with known decay curves for various microbial processes [12]. Clearly, a material that binds tightly to the clay or organic matter of soil is going to exhibit a reduced biotransformation rate. Characteristics of waste from beef and dairy cattle, hogs, and poultry that may influence the rate of biodegradation have been described [13].

Release after land application is practically limited to surface runoff, to percolation into groundwater, and to volatilization. Soil sorption and desorption measurements give a good indication of the extent of release to surface runoff. Here also, binding of the released material to soil components reduces the potential for removal by runoff. Rainfall and runoff data for various regions of the U.S. may be obtained from the 1983 National Water Summary [14].

Release to groundwater may be significant for persistent chemicals. While simple chromatographic models may be used to gain an appreciation of the rate of movement, a more comprehensive analysis may be required [15]. One predictive method is the Pesticide Root Zone Model (PRZM), which makes use of many physical properties of soil, but requires no additional chemical/physical properties of the released material [16].

Release by volatilization may be significant for a compound that has a low vapor pressure if the water solubility is also low. Water adsorbed by soil plays a major competitive role, and the vaporization from dry soil may be markedly enhanced by rain [17, 18]. In many instances, it may be sufficient to show that the maximum rate of evaporation is too slow for the release to be significant. Equation (1) developed for feedlots may also be used to estimate the upper limit of transfer from soil to atmospheric compartments when the chemical does not irreversibly bind to soil. The following example of the volatilization of 10 ppm of dieldrin in soil illustrates how this estimation is performed.

The dieldrin vapor pressure at a concentration of 10 mg/kg in soil is about 7×10^{-7} Torr [19], so that the only unknown in eq. (1) is the extent of surface coverage. An approximate value for the fraction covered, F_{cov} , may be obtained from the density of dieldrin, the thickness required to exhibit bulk properties of dieldrin (about three monolayers), and the approximate surface area of soils (about $10 \text{ m}^2/\text{g}$) [20]. Using these assumptions, the calculated rate of evaporation, $7.5 \times 10^{-7} \text{ g/cm}^2 \cdot \text{day}$, agrees well with several measured rates that range from $(3.50\text{--}3.90) \times 10^{-7} \text{ g/cm}^2 \cdot \text{day}$ [21]. The close agreement is much better than expected, and may be the result of an underestimate of the fraction of surface covered.

3. Summary and conclusions

An approach has been described for modeling the environmental migration and fate of a chemical introduced into the environment by beef cattle confined to the feedlot. In practice, this would be a "worst case" scenario arising from the use of a medicated product by the feeder cattle industry. The approach has general applicability, since information for feedlot practices and waste characterization have been reported for dairy cattle, hogs, and for poultry [1, 14]. The key element for modeling migration is, in every case, an adequate knowledge of the distribution of chemical between the various components that are defined by a typical feedlot operation. For those compounds that are designed to be

stable in air and water, which includes most veterinary drugs, the key element required for modeling fate is the rate of microbial transformation. Specific and sensitive analytical methods for following the rate of biotransformation(s) of chemicals in excreta, or systems receiving excreta as a means of waste disposal, are now commonplace. These methods should be used in preference to older, non-specific methods based on the rate of mineralization to CO₂.

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