

# ANALYTICAL TOOLS FOR GROUNDWATER POLLUTION ASSESSMENT

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## *Abstract*

This paper deals with the development of analytical screening-exposure models (indices) and their potential application to regulate the use of hazardous chemicals and the design of groundwater buffer strips. The indices describe the leaching of solutes below the root zone (mass fraction), emissions to the water table, and mass fraction of the contaminant intercepted by a well or a surface water body. The root zone is modeled separately from the intermediate-vadose zone, and the processes of crop uptake and volatilization from soil surface are incorporated in the root zone model. Other processes considered include (bio)chemical decay, adsorption, and percolation in the soil, and convective-dispersive and reactive transport in the aquifer. The methodology is applied to a list of pesticides, and their ranking scheme is compared to those based on some existing screening models. The potential use of the proposed indices for the design of groundwater/surface water buffer strips is also illustrated.

## *Introduction*

There is an increasing recognition that agricultural and municipal activities are contributing to the deterioration of the nation's water quality. Pesticides used in crop production and land disposal of hazardous organic waste are major source of non-point source pollutants and a serious contamination threat to groundwater, and aquatic and terrestrial ecosystems. Cost-effective tools are needed to identify areas which are potentially vulnerable to nonpoint-source pollution, so that management plans can be implemented to reduce exposure to soluble hazardous chemicals. Rather than relying on the often costly and prolonged field monitoring strategies, physically-based simple environmental simulation models can be cost-effective tools for resource managers to develop management plans.

Environmental fate and transport simulation models vary in their complexities from simple empirical or mass-balance to distributed parameters conceptual models. In general, conceptual models often account for the various physical, chemical, and biological processes that determine the environmental fate of hazardous chemicals in subsurface and surface waters. In this paper, mathematical expressions, hereafter referred to as indices, are presented to describe leached solute-mass fraction from the soil and convection past a given section in the aquifer normal and parallel to

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groundwater flow direction. The indices are derived from the analytical solutions of *Hantush and Mariño* (1996). Two distinct regions are modeled in the soil: the root zone and the intermediate-vadose zone. The models incorporate the processes of first-order (bio)chemical decay, passive root uptake, volatilization from soil surface, equilibrium adsorption, leaching rate, and convection and dispersion in the aquifer. The models are limited to steady flow and ignore dispersion in the soil. They may be applicable for regulating the use and exploring management alternatives of hazardous chemicals to reduce groundwater vulnerability and ecosystem exposure. The findings complement a class of models in the literature commonly referred to as screening models or indices: LEACH and VOLAT (*Laskowski et al.*, 1982), Travel Time (Tr) (*Jury et al.*, 1984), Attenuation Factor (AF) and Retardation Factor (RF) (*Rao et al.*, 1985). In general, these screening models assume homogenous soil profiles with some average properties. *Van der Zee and Boesten* (1991) and *Beltman et al.* (1995), however, showed that leaching increases when heterogeneity of the soil is taken into account.

The indices developed here are distinguished from previous ones due to the following factors. Firstly, the root zone is modeled for root uptake and volatilization. Secondly, the proposed aquifer index can be used to establish a less stringent regulation for the use of agricultural chemicals; especially, when groundwater quality down gradient from rather than underneath the agricultural field, is of a primary concern. The additional decay and dispersion of the soluble chemicals may further diminish their concentrations below hazardous levels before being intercepted by a well or discharged to a stream. Thirdly, the aquifer index can be used to estimate expected concentration in groundwater, and to provide a criterion for designing exclusion zones or buffer strips, which assure less than maximum contaminant levels (MCLs) in groundwater down gradient from the agricultural field.

### ***Leaching Below the Root Zone***

Figure 1a illustrates the conceptual soil and groundwater compartments in which fate and transport of a pollutant are modeled. We assume soluble-phase pesticide mass per unit area of soil,  $M_o$ , is mobilized by infiltrating water and introduced instantly into the root zone. This case is mathematically equivalent to a Dirac-delta pulse of input mass, and the mass of applied pesticide which leaches below the root soil compartment,  $M_r$ , can be obtained by integrating average solute concentrations in the root zone from  $t=0$  to  $t=\infty$ ,

$$M_r = \int_0^{\infty} v^* C_r(t) dt \quad (1)$$

in which  $C_r(t)$  is the average concentration in the root [ $M L^{-3}$ ] zone (see, *Hantush and Mariño*, 1996); and  $v^*$  is percolation below the root zone [ $L T^{-1}$ ] - equal to infiltration  $v$  minus evapotranspiration ET. The evaluation of the integral in (1) yields

$$\frac{M_r}{M_o} = \frac{1}{1 + (T_r / \lambda)[\ln(2) + \mu]} \quad (2)$$

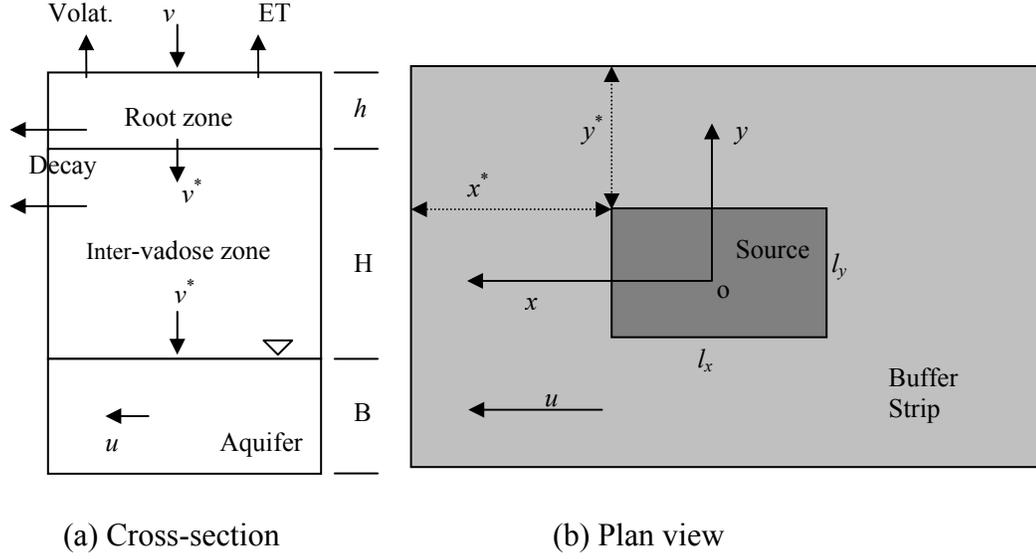


Figure 1. (a) Side view of soil-aquifer model. (b) Top view of source area (dark shade), and protection buffer strip (light shade).

in which  $T_r$  is the residence time in the root zone [T],  $T_r = h R_r / (v^* / \theta_r)$ ;  $\mu = (F S + \sigma / h) \lambda / (R_r \theta_r)$ ,  $R_r$  is the liquid-phase partition coefficient,  $R_r = 1 + (\rho_b K_d + \kappa K_H) / \theta_r$ ;  $\sigma = \kappa K_H D_g / d$ ;  $\theta_r$  is the average volumetric water content in the root zone;  $h$  is the depth of the root zone;  $\rho_b$  is bulk soil density [ $M/L^3$ ];  $\lambda$  is the pesticide half-life [ $T^{-1}$ ];  $K_d$  is distribution coefficient [ $L^3/M$ ];  $\kappa$  is volumetric air content;  $K_H$  is dimensionless Henry constant;  $S$  is transpiration rate [ $T^{-1}$ ];  $F$  is transpiration-stream concentration factor;  $D_g$  is gaseous diffusion coefficient [ $L^2/T$ ]; and  $d$  is thickness of air boundary layer on soil surface – suggested value is 0.5 cm (*Jury et al.*, 1983). Equation (2) describes the fraction of  $M_o$  that leaches below the root zone and enters the intermediate-vadose zone. The essence of equation (2) are: i) well-mixed root zone; ii) volatilization from soil surface occurs through an air boundary layer of thickness  $d$ ; iii) first-order rate reaction; and iv) passive plant uptake – rate of uptake is proportional to soluble-phase concentrations.

### ***Emissions to Groundwater***

Similarly, total solute mass loading to the water table,  $M_u$ , from the inter-vadose zone, can be obtained by integrating average solute concentrations convected to the water table from  $t = 0$  to  $t = \infty$

$$M_u = \int_0^{\infty} v^* C_u(t) dt \quad (3)$$

in which  $C_u(t)$ , is the average concentration in the inter-vadose zone resulting from a Dirac-delta pulse of input mass [ $M L^{-3}$ ] (see, *Hantush and Mariño*, 1996). The evaluation of (3) is straightforward,

$$\frac{M_u}{M_o} = \frac{1}{[1 + (T_r / \lambda)(\ln(2) + \mu)][1 + \ln(2) T_u / \lambda]} \quad (4)$$

in which  $T_u$  is the residence time in the inter-vadose zone in the form similar to that of  $T_r$  in the root zone. Note that mass fraction loading to the water table (4) is a function of the individual resident times in the root and inter-vadose zones rather than their cumulative.

### **Loading to External Water Body**

A stream or a well intercepting the groundwater flow is often termed as the external water body. The fraction of total applied mass,  $M_o l_x l_y$ , convected past an aquifer section, of infinite length and normal to the flow direction, can be obtained by the integration of groundwater concentration  $C$  (Hantush and Mariño, 1996),

$$M_g(x) = n B \int_0^{\infty} \int_{-\infty}^{+\infty} \left( -\frac{D_x}{R} \frac{\partial C}{\partial x} + \frac{u}{R} C \right) dy dt \quad (5)$$

in which  $x$  is the longitudinal distance measured from the center of the field (Fig. 1b);  $n$  is the aquifer porosity;  $B$  is the aquifer thickness [L];  $D_x$  is the longitudinal dispersion parameter [ $L^2/T$ ];  $u$  is the average aquifer pore-water velocity along the  $x$  axis [L/T]; and  $R$  is aquifer retardation factor. The integral in (5) can be evaluated, albeit lengthy procedure, for  $x > l_x/2$

$$M_g(x) / (M_o l_x l_y) = \frac{M_u}{M_o} \frac{\sqrt{\gamma} + u \sinh \rho}{2\sqrt{\gamma} \rho} e^{-2\rho x/l_x} \quad (6)$$

where  $\gamma = u^2 + 4D_x R k$ , and  $\rho = [(\sqrt{\gamma} - u)/(2D_x)] (l_x/2)$ , in which  $k$  is decay-rate coefficient in the aquifer [ $T^{-1}$ ]. By virtue of symmetry, equation (6) can also be used to infer the total pesticide mass fraction past an aquifer section parallel to the flow direction, by substituting zero for  $u$  and switching  $l_x$  with  $l_y$ .

### **Application to Screening**

Table 1 lists chemical properties for six pesticides. The chemical data includes solubility,  $S$  [ $\text{kg}/\text{m}^3$ ], organic carbon partition coefficient,  $K_{oc}$  [ $\text{m}^3/\text{kg}$ ], dimensionless Henry's constant,  $K_H$ , vapor pressure,  $V_p$  [Pa], and half-life,  $\lambda$  [days]. Table 2 compares ranking schemes using (2), (4), and (6) to those obtained using: 1) Travel-time index,  $Tr = L R \theta/v^*$ , 2) Attenuation Factor,  $AF = \exp\{-\ln(2) Tr/\lambda\}$ , and 3) Leach index,  $LEACH = (S \lambda) / (V_p K_{oc})$ .  $L$  is the distance from the soil surface to the water table [L];  $R$  is an average retardation factor; and  $\theta$  is the average field capacity. A hypothetical well and stream are assumed to be located at distances 100m and 200m, respectively, downgradient from the center of 1 ha ( $10,000 \text{ m}^2$ ) source area. The indices (2), (4), and (6) are applied to the pesticides in Table 1 using a hydrological and climatic data that are typical for the Locust Grove site in Kent county, Maryland. The resulting rankings are compared to those obtained using  $Tr$ ,  $AF$ , and  $LEACH$  methods. Loamy sand is considered for which depth of the root zone  $h$  is chosen to be 1 m (typical for corn). The depth from the soil surface to the water table  $L$  is assumed to be 6 m. Percolation below the root zone  $v^*$  is estimated to be 34.5 cm/yr, and groundwater velocity of 100 m/yr is considered.

In Table 2  $M_r$  ranks the chemicals relative to the potential for contamination of the soil below the root zone. Whereas,  $Tr$ ,  $AF$ , and  $M_u$  rank them relative to the potential to contaminate the water table at depth 6 m below the source area.  $M_g$  achieve the same objective at  $x = 100 \text{ m}$  (aquifer) and  $x = 200 \text{ m}$  (stream) downgradient

from the center of the field. Note that  $M_g$  integrates the effects of the length of the source area parallel to flow and natural attenuation in the aquifer (i.e., dispersion and decay), which affects the ranking of the pesticides relative to their potential to pollute

**Table 1. Chemical properties.**

Chemical	Solubility (Kg/m <sup>3</sup> )	K <sub>oc</sub> (m <sup>3</sup> /Kg)	K <sub>H</sub>	V <sub>p</sub> (Pa)	λ (days)
Atrazine	0.03	0.16	2.5× 10 <sup>-7</sup>	4.0× 10 <sup>-5</sup>	71
Bromacil	0.82	0.07	3.7× 10 <sup>-8</sup>	3.3× 10 <sup>-5</sup>	350
Chlordane	0.001	38.0	2.2× 10 <sup>-4</sup>	1.3× 10 <sup>-3</sup>	3500
Heptachl.	5.6× 10 <sup>-5</sup>	24.0	1.45× 10 <sup>-1</sup>	5.3× 10 <sup>-2</sup>	2000
Cyanazine	0.17	0.17	1.2× 10 <sup>-4</sup>	2.0× 10 <sup>-1</sup>	108
Metolachl.	0.53	0.2	9.84× 10 <sup>-7</sup>	4.18× 10 <sup>-3</sup>	90

an external water body.

In general,  $M_r$  and LEACH produced relatively comparable results among the different ranking schemes, in contrast to Tr and AF, which do not account for volatilization and root uptake. Tr and AF produced ranking schemes that are significantly different than that of  $M_u$ . In contrast to Tr and AF, which ignore volatilization and root uptake,  $M_u$  accounts explicitly for the effect of the different processes in the soil. Comparison among the last three columns demonstrates how decay and dispersion in the aquifer alter the rankings. The  $M_r$  index ranked heptachlor with the least potential to contaminate the soil, whereas  $M_u$  ranked chlordane with the

**Table 2. Comparison of ranking schemes.**

Chemical	Tr	AF	LEACH	$M_r$	$M_u$	$M_g(x)$	
						(100 m)	(200 m)
Atrazine	2	4	2	1	1	4	3
Bromacil	1	1	1	3	3	1	1
Chlordane	6	5	5	5	6	5	6
Heptachl.	5	6	6	6	5	6	5
Cyanazine	3	2	4	4	4	2	4
Metolachl.	4	3	3	2	2	3	2

least potential to contaminate groundwater. This exercise illustrates the importance of taking into account the integral effect of the different physical and (bio)chemical processes, rather than addressing them individually. The results in the last four columns in Table 2 indicate that ranking schemes differ in the soil and with distance downgradient from the center of the source area. Hence, a pesticide-use regulation is useless unless it is associated with a particular environmental compartment.

### ***Design of Protective Buffer Strips***

Regulating authorities may be interested in concentrations rather than a fraction of a dose given by (6). An estimate of expected solute concentration can be obtained using the approximate relationship:  $C \approx M_g/(n b l_x l_y)$ , in which  $b$  is the plume thickness in the aquifer [L]. Substituting  $C$  into (6) and solving for  $x$  yields

$$x = (l_x / 2\rho) \ln \left\{ \frac{M_u}{nbC} \frac{\sqrt{\gamma} + u \sinh \rho}{2\sqrt{\gamma} \rho} \right\} \quad (7)$$

Average plume thickness  $b$  in groundwater can be estimated on the basis of transverse-vertical dispersivity  $\alpha_z$ ,  $b \approx (\alpha_z x)^{1/2}$ , which requires an iterative solution for (7).

If we substitute  $C$  with MCL, which is EPA-enforced drinking water standard, then (7) can be used to design a buffer strip of size  $x^*$  (see Fig. 1b), within which less than MCL may be attained. For example, the MCL for atrazine is 3  $\mu\text{g/L}$ , and assuming that  $\alpha_z = 1.5$  cm, then for a dose of  $M_0 = 1 \times 10^{-4}$   $\text{Kg/m}^2$  (1  $\text{Kg/ha}$ ), (7) can be solved iteratively to yield  $x^* = 10.8$  m, for an estimated plume thickness of  $b \approx 1$  m. Thus, a stream or a drinking water well may require monitoring if it is within a distance of 67 m downgradient from the center of a rectangular field should atrazine be applied at a dose of  $1 \times 10^{-4}$   $\text{Kg/m}^2$  (1  $\text{Kg/ha}$ ). If  $M_0 = 2 \times 10^{-4}$   $\text{Kg/m}^2$  (2  $\text{Kg/ha}$ ), then  $x^* = 27.8$  m, for an estimated plume thickness of  $b \approx 1.1$  m.

### Conclusions

Simple analytical models were developed for screening agricultural chemicals and the design of protective buffer strips. The root zone was modeled for volatilization and crop-root uptake. Percolation, decay, and adsorption were also accounted for in the soil, while convective-dispersive and reactive transport was considered in the aquifer. The development may be used for regulating the use of agricultural chemicals relative to their potential to pollute the subsurface environment, and for designing protective buffer strips against potential contamination of wells and surface-water bodies.

***This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.***

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**Key words:** Groundwater hydrology, Contaminant hydrology, Transport processes in soils, screening models, volatilization, crop uptake, Transport models, Transport in aquifers, non-point source, and pesticides.