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MODELING THE ROLE OF PHYTOREMEDIATION IN MITIGATING GROUNDWATER CONTAMINATION IN INDIA

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ABSTRACT

Contamination of groundwater due to pesticides has become a major issue of concern in India. However, there are now attempts to contain and control this problem through phytoremediation, which is a very cost-effective and innovative technology. On the other hand, none of the hitherto developed models for groundwater contamination has incorporated an explicit role for phytoremediation. We have accordingly modified an earlier model used for studying groundwater contamination, and conducted sensitivity studies of the resulting model. It turns out that groundwater contamination has strongest dependence on the parameters, that represent the underground gradient of microbial population density.

INTRODUCTION

Groundwater is the main source for supporting domestic and various agricultural activities in India. However, a number of workers have now reported significantly high concentrations of toxic metals and pesticides in groundwater, mainly due to agricultural run-off and partly due to solid waste disposal [1-3]. At the same time, there is a general realization now that this problem can be controlled and mitigated through phytoremediation, which is a very cost-effective and innovative technology [4]. Phytoremediation (i.e., use of vegetation for extraction of metals and enhanced degradation of pesticide) is highly environment-friendly and removes contaminants from the soil, essentially through the following mechanisms:

1. taking up contaminants directly and subsequently accumulating non-phytotoxic metabolites into the plant tissues;
2. releasing exudates and enzymes that stimulate various microbial activities and subsequent biochemical transformations; and
3. enhancing mineralization in the rhizosphere (root-soil-interface).

Two important factors arise for the modeler: first, the fraction of contaminant which finally reaches a given soil depth; and second, the amount of time it takes. As far as different models used for groundwater contamination are concerned [5-7], they vary in their complexity and representation of specific underlying processes. In any modeling exercise, the choice of model should be determined not only by the objectives, but also by the availability of data [6]. Pesticide-degradation has been studied by various researchers [8, 9]. Diekkrüger et al. modeled the degradation rate, R (W, T) as a product of two functions R_1 (W) and R_2 (T), which respectively represented functionalities dependent on soil-water-content (W) and soil-temperature (T) [8]. Jury et al.'s treatment addressed pesticide-mobility through soil in order to arrive at a criterion for screening a range of local soil and environmental conditions for estimating which compounds may finally reach groundwater and thereby pose potential health hazards [7, 10].

However, none of these modeling exercises has incorporated the explicit role played by phytoremediation, i.e., remediation by plants (vegetation) and associated mycorrhizae. This comment holds true of the commercially available Groundwater Modeling System (GMS) software, e.g., MODFLOW, MODPATH, MT3D, FEMWATER, SEEP2D, RT3D, and BIOMOD3-D [5]. We modified the earlier model of Jury et al. [7] by incorporating depth-dependencies of various soil quality parameters [11] so as to incorporate the explicit role played by phytoremediation in the improvement of rhizospheric soil quality. The present work subsequently discusses two different approaches for sensitivity analysis. In the smaller ranges, the sensitivity has been studied by obtaining expressions for partial derivatives [12], whereas in the larger ranges, it has been analyzed through a computer simulation exercise, which was carried out by changing values of relevant parameters over a wider range, and graphically plotting the resultant changes in the total-underground-pesticide-concentration.

Atrazine was chosen as a case study pesticide, mainly because information on its biochemical half-life (Figure 1) and organic-C-partitioning-coefficient (K_{oc}) was already available in literature [7]. Depth-dependent model parameters have been estimated (Table 1) on the basis of data available [13] on the soil-ecosystem of the Kheda district in Gujarat state (India). Finally, we find that the groundwater contamination due to pesticides is most strongly dependent on those parameters which are linked to the underground-gradient of microbial population density.

PESTICIDES, GROUNDWATER CONTAMINATION, AND PHYTOREMEDIATION

Pesticides are widely used to control insects, weeds, and diseases. Moreover, in almost every country, there have been studies on the adverse effects of pesticides on human and environmental health. On the other hand, the problem of groundwater contamination due to pesticides is severe not only in India [1-3], but also in several other countries [6, 7]. A groundwater monitoring survey in California had identified (in 1979) about 11 pesticides present in groundwater, most of them having resulted from non-point agricultural sources [7].

On the other hand, using vegetation (phytoremediation) for enhanced degradation of pesticides is an emerging technology which is highly environment-friendly and cost-effective [4]. Poplar trees have already been used to remediate groundwater at various sites [14]. At Aberdeen, for example, the US-EPA is using them for controlling a groundwater plume contaminated with tetra-chloro-ethane [4]. In short, rhizospheric interactions have been found to control rates of two specific bio-processes: leaching and bioavailability of contaminants.

Mycorrhizal fungi associated with root systems act as nutrient or chemical traps and facilitate their recovery and retention within the ecosystem. Mycorrhizae are of three types: ectotrophic, endotrophic, and peritrophic (extramatrical). Ectotrophic mycorrhizae form root-like extensions that grow out from the cortex of the root; endotrophic mycorrhizae penetrate the cells of the root; and peritrophic

Table 1. Parameters Estimated for Kheda District of Gujarat State, India

S. No.	Description	Parameters	Values for Kheda District Gujarat, India
1.	Parameters representing the depth-dependency of the combined function of soil-bulk-density (SBD), Organic-C-fraction (OCF) and the organic-C-partitioning-Coefficient (K_{oc})	a_1 b_1	0.05 –0.20
2.	Parameters representing the depth-dependency of the soil-water-content (SWC)	a_2 b_2	33.32 0.16
3.	Parameters representing the depth-dependency of the microbial population density (MPD)	a_3 b_3	0.01 –1.73

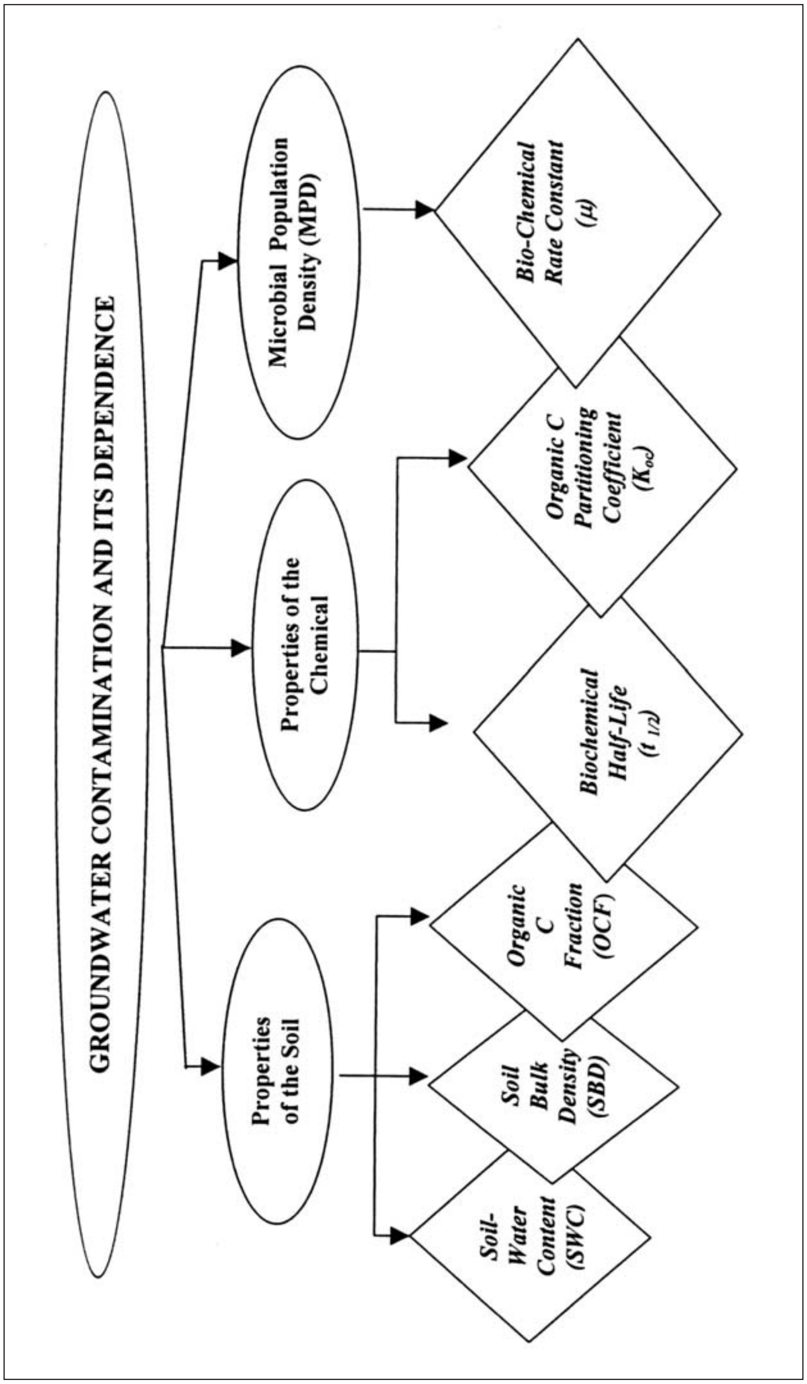

Figure 1. Groundwater contamination and its dependence.

mycorrhizae form mantles or clusters around the roots. The mycorrhizae are thought to be very important in creating a favorable biochemical “rhizospheric environment” that transforms insoluble or unavoidable chemicals to forms that can be taken up by the roots [15].

Essentially, phytoremediation plays two key ecological roles: on one hand, it enhances the microbial population density and thereby the bioavailability and uptake of contaminant through various ecological interactions; and, on the other, it modulates and alters the soil-quality by affecting organic-C-fraction of the soil and its water-holding-capacity. Moreover, in a highly interactive manner, it controls the leaching rate too. These are the parameters on which attention has been focused under sensitivity analysis so as to find out the relative strengths by which they affect the total-underground-pesticide-contamination.

MODEL MODIFICATIONS AND SENSITIVITY ANALYSIS

The present article stresses modeling of the ecological role of phytoremediation in controlling groundwater contamination, mainly by modeling the depth-dependencies [12, 16] of soil-bulk-density (SBD), organic-C-fraction (OCF), soil-water-content (SWC), and microbial-population-density (MPD) (Figure 2). Subsequently, these depth-dependent models are interfaced with the earlier model of Jury et al. [7] by making the following substitutions:

$$\text{(SBD) (OCF) (}K_{oc} = a_1 \exp(b_1 z) \tag{1}$$

$$\text{(SWC)} = a_2 \exp(b_2 z) \tag{2}$$

where K_{oc} is organic C partitioning coefficient for the pesticide (contaminant) under consideration, and (a_1, b_1) and (a_2, b_2) are the parameters which were estimated [11] on the basis of available site-specific data on SBD, OCF, SWD, and their variations with respect to depth [13]. Values of these parameters, however, will change from one soil-type to another, as the depth dependencies are going to be different in different ecosystems. As far as pesticides’ biodegradation is concerned, biochemical decay is a very important parameter [7]. It is essentially dependent on microbial population density (MPD), which has been taken to be of the form a_3 exp (b_3z), i.e.:

$$\text{MPD} = a_3 \exp(b_3 z) \tag{3}$$

In fact, a_3 is analogous to exp(γL) and b_3 to the depth constant ($-\gamma$) of Jury et al.’s model [7]. L is the length of the surface zone within which the biological decay constant $\mu(d^{-1})$ and the microbial population density (MPD) are both constant. μ, in fact, can be expressed as:

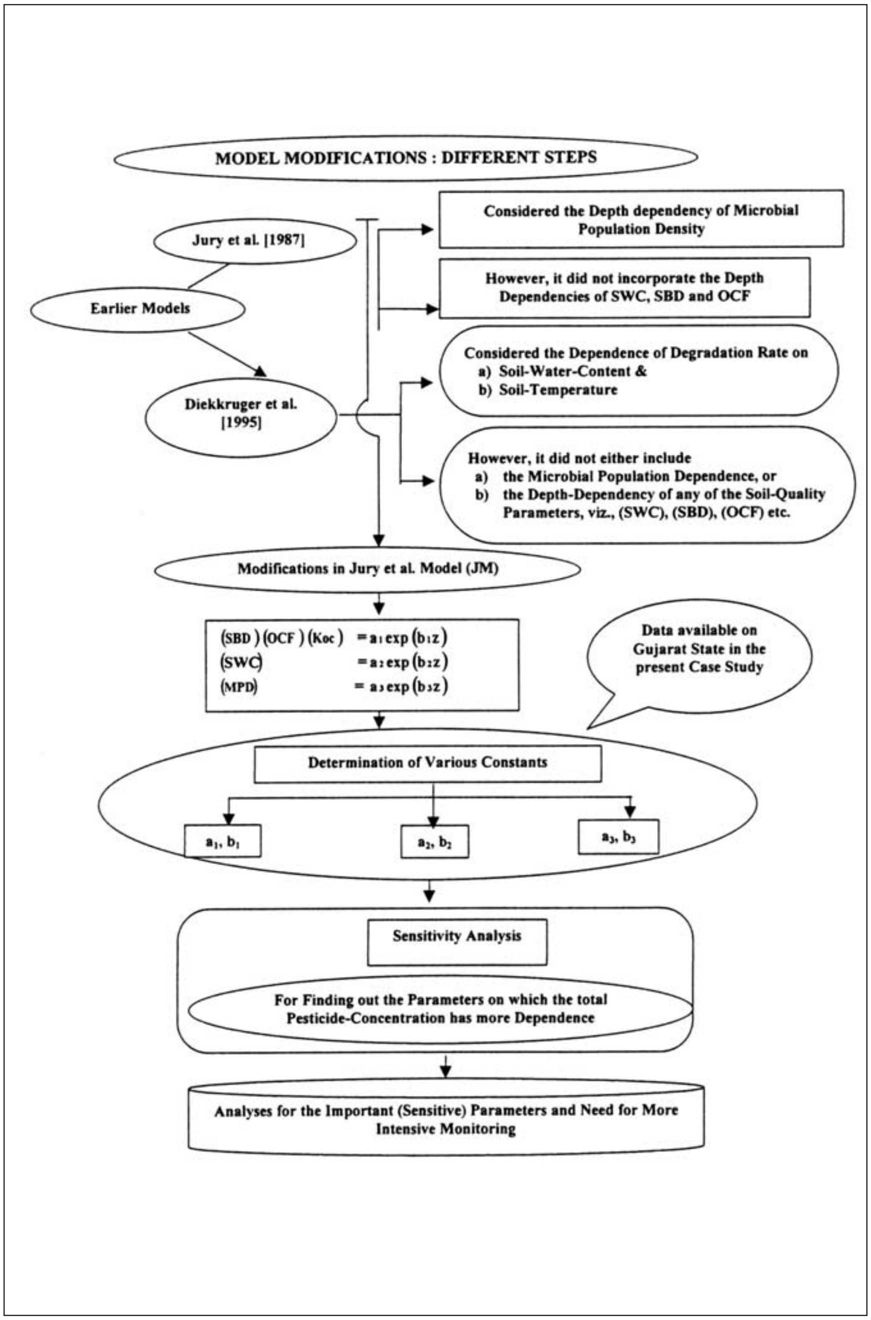

Figure 2. Model modifications: different steps.

$$\mu = \left(\frac{\ln 2}{t_{1/2}}\right)(\text{MPD}) \tag{4}$$

where $t_{1/2}$ is the half-life of the pesticide concerned. Values of a_3 and b_3 have been estimated on the basis of data available in [16]. With the above substitutions (i.e., (1), (2), and (3), dissolved-pesticide-concentration CL (z) in soil-water at depth z assumes the following form:

$$CL(z) = \frac{CT(z)}{[a_1 \exp(b_1 z) + a_2 \exp(b_2 z)]} \tag{5}$$

where CT (z) is the total pesticide concentration at the depth z. The steady state solution for the mass-balance equation, therefore, yields the following expression for CL (z):

$$\text{CL}(z) = [\text{CL}(0)]\text{A} \tag{6}$$

where

$$\text{A} = \exp\left[\left(\frac{1.0}{\text{Le}}\right)(\text{A}_1\text{A}_2 + \text{A}_3\text{A}_4)\right] \tag{7}$$

$$\text{A}_1 = \frac{(\text{a}_1)(\text{a}_3)}{\text{b}_1 + \text{b}_3} \tag{8}$$

$$\text{A}_2 = [1.0 - \exp(\text{b}_1 + \text{b}_3)] \tag{9}$$

$$\text{A}_3 = \frac{(\text{a}_2)(\text{a}_3)}{(\text{b}_2 + \text{b}_3)} \tag{10}$$

$$\text{A}_4 = [1.0 - \exp(\text{b}_2 + \text{b}_3)] \tag{11}$$

Le is the leaching rate (meter per day) and CL (0) is the dissolved concentration of the pesticide in soil-water just below the surface, i.e., at z = 0, i.e.:

$$\text{CL}(0) = \left[\frac{\text{CT}(0)}{(\text{a}_1 + \text{a}_2)}\right] \tag{12}$$

CT (z), therefore, can easily be obtained from (5):

$$\text{CT}(z) = [\text{a}_1\exp(\text{b}_1 z) + \text{a}_2\exp(\text{b}_2 z)]\text{CL}(z) \tag{13}$$

The expressions for sensitivity have been derived in the form (y_x), where x is the independent variable with respect to which sensitivity is being studied, and y is the dependent variable, in which the consequent changes need to be analyzed [13].

RESULTS AND DISCUSSION

In a smaller range, expressions for sensitivity have been computed by taking the partial derivative of the dependent variable with respect to the independent variables. However, in a bigger range they are studied through a computer simulation exercise, whereby independent variables are varied one at a time, keeping the other variables constant. The resultant changes in the dependent variable (total pesticide concentration in the soil) are then analyzed and studied.

Sensitivity expressions given in the Appendix have been quantified through a computer program written in "Turbo-C." As far as sensitivity of total pesticide-concentration is concerned, the largest sensitivity values (Figure 3) are with respect to a_3 (–154.7), b_3 (–61.7), b_2 (–59.3), and Leaching rate (Le) (49.5). The negative values show that if a_3, b_3, and b_2 increase, the value of total pesticide concentration at a given depth decreases. a_3 and b_3 are parameters linked directly with the microbial population density (MPD). While b_2 is the parameter linked with soil water content (SWC). For all the parameters considered, these sensitivity values represent changes in very small ranges only.

For larger variations in independent variables, one has to keep other parameters constant and simulate the consequent changes in the dependent variable (total pesticide concentration) due to changes in the independent variable under consideration. In the present case, values (a_1, b_1), (a_2, b_2), (a_3, b_3), and Le (Leaching rate) were changed through computer simulation in the appropriate steps and consequent changes in CT(z) were plotted (Figures 4a through 4g). These computations were done for a specific depth of z = 3.5 m. Maximum variations (taken as gradients in different graphs) in CT(z) were observed with respect to a_3 (–69.6), Leaching rate (63.4), and b_3 (–0.78) (Figures 4e through 4g), while variations with respect to a_1 (–0.12), b_1 1.3×10^{-4}), a_2 (–0.03), and b_2 (0.50) were found to be minimum (Figures 4a through 4c).

Since the total-pesticide-concentration (in the soil) has maximum sensitivity with respect to parameters which represent depth-dependency of microbial-population-density (MPD), the importance of monitoring MPD very carefully with respect to depth (at a given site) especially needs to be stressed.

APPENDIX

$$CT(z)\_a_1 = (Y9)\ [CL\ (z)\_\ a_1] + [CL\ (z)]\ [\exp\ (b_1 z)] \quad (1)$$

$$CT(z)\_a_2 = (Y9)\ [CL\ (z)\_\ a_2] + [CL\ (z)][\exp\ (b_2 z)] \quad (2)$$

$$CT(z)\_a_3 = (Y9)\ [CL\ (z)\_a_3] \quad (3)$$

$$CT(z)\_b_1 = (Y9)\ [CL\ (z)\_\ b_1] + [CL\ (z)](a_1)\ (z)[\exp\ (b_1 z)] \quad (4)$$

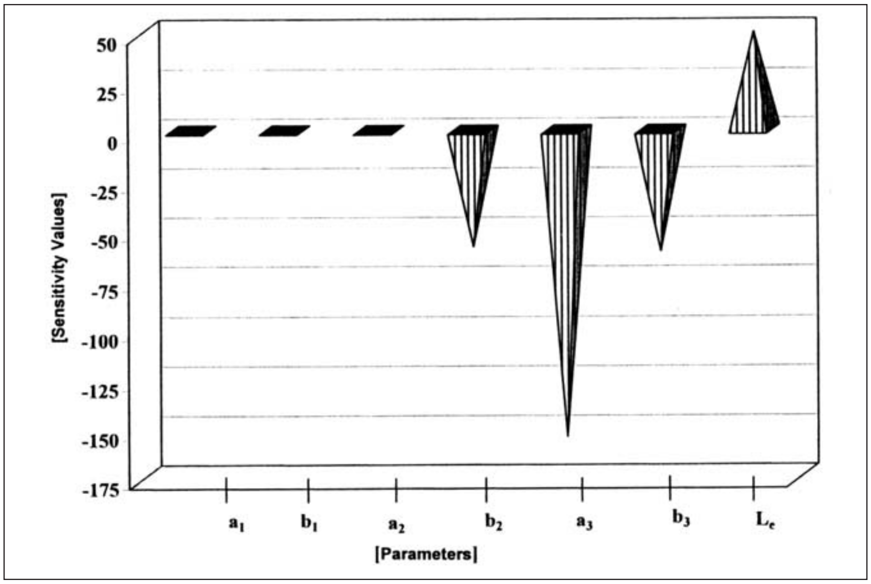

Figure 3. Sensitivity values (computed on the basis of partial derivatives shown in the Appendix. For all computations z = 3.5 m).

$$CT(z)\_ b_2 = (Y9)\ [\ CL\ (z)\_ b_2] + [CL\ (z)](a_2)\ (z)[\exp\ (b_2 z)] \quad (5)$$

$$CT(z)\_ b_3 = (Y9)\ [CL\ (z)\_ b_3] \quad (6)$$

$$CT(z)\_(Le) = (Y9)\ [CL\ (z)\ (Le)] \quad (7)$$

$$\text{Where, } Y9 = a_1\exp(b_1 z) + a_2\exp(b_2 z) \quad (8)$$

$$CL(z)\_a_1 = [CL\ (0)]\ [A]\ [(Y16)(Y12)(Y3)] \quad (9)$$

$$CL\ (z)\_a_2 = [CL\ (0)\ [A]\ [(Y16)\ (Y13)\ (Y6)] \quad (10)$$

$$CL\ (z)\_a_3 = [CL\ (0)][A][(Y16)\ \{(Y14)\ (Y3) + (Y15)\ (Y6)\}] \quad (11)$$

$$CL\ (z)\_b_1 = -\ [CL\ (0)Y16]\ Y1\left[\left(\frac{Y3}{Y4}\right) + Y5\right] \quad (12)$$

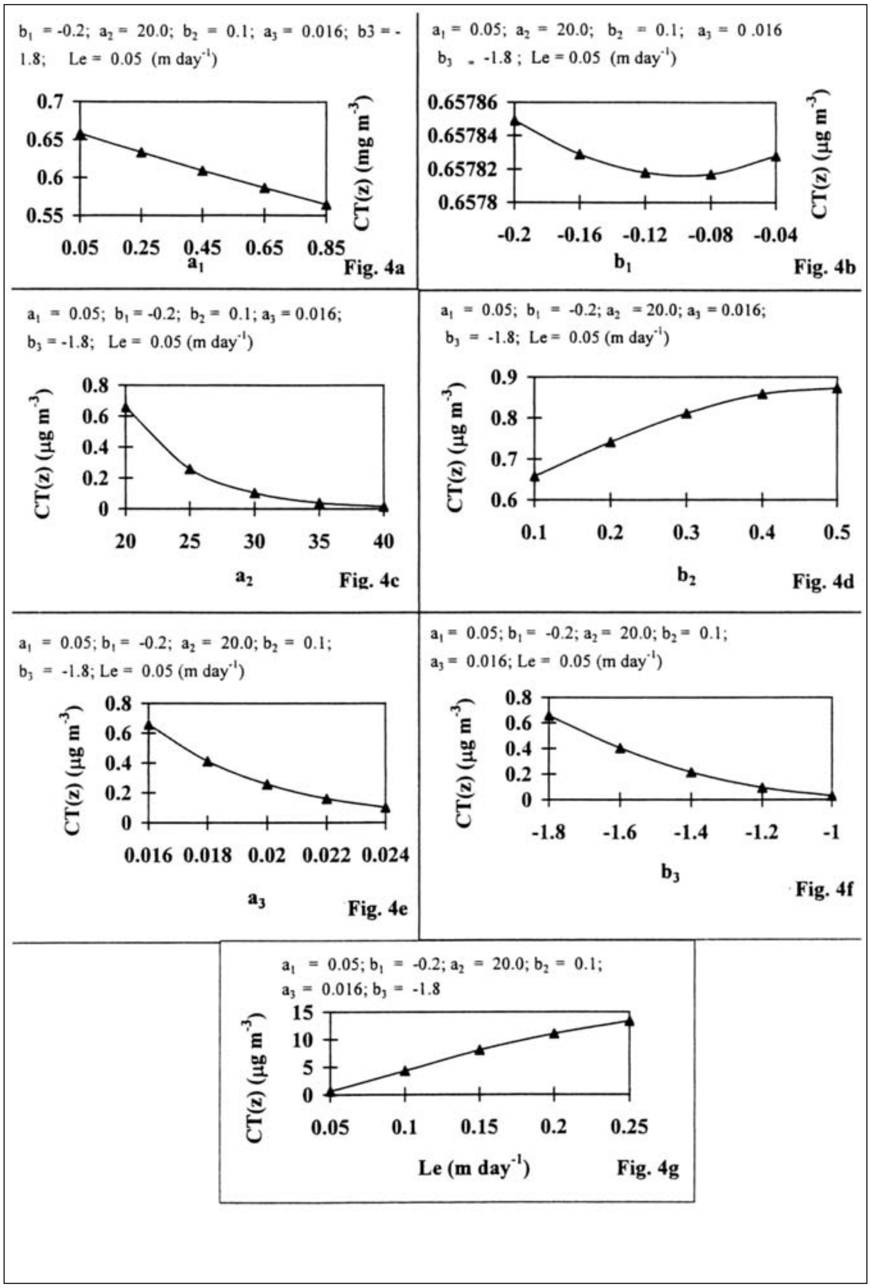

Figure 4. Computer simulations: variations in CT (z) (μg m^{-3}) w.r.t. larger changes in different parameters. For all computations z = 3.5 m).

$$\text{CL (z)\_b}_2 \quad = -[\text{CL (0) Y16] Y2}\left[\left(\frac{\text{Y6}}{\text{Y7}}\right) + \text{Y8}\right] \tag{13}$$

$$\text{CL (z)\_ b}_3 \quad = -[\text{CL (0)Y16] [A1\_b}_3 + \text{A}_2\text{\_b}_3] \tag{14}$$

$$\text{CL (z)\_(Le)} \quad = -\text{CL (0)}\left[\frac{\text{A}}{\text{Le}}\right][\log(\text{A})] \tag{15}$$

$$\text{A1\_b}_3 \quad = -(\text{Y1})\left[\left(\frac{\text{Y3}}{\text{Y4}}\right) + (\text{Y5})\right] \tag{16}$$

$$\text{A}_2\text{\_b}_3 \quad = -(\text{Y2})\left[\left(\frac{\text{Y6}}{\text{Y7}}\right) + (\text{Y8})\right] \tag{17}$$

$$\text{Y1} \quad = \frac{(a_1 a_3)}{(b_1 + b_3)} \tag{18}$$

$$\text{Y2} \quad = \frac{(a_2 a_3)}{(b_2 + b_3)} \tag{19}$$

$$\text{Y3} \quad = 1.0 - \exp[(b_1 + b_3)z] \tag{20}$$

$$\text{Y4} \quad = b_1 + b_3 \tag{21}$$

$$\text{Y5} \quad = z\exp[z(b_1 + b_3] \tag{22}$$

$$\text{Y6} \quad = 1.0 - \exp[z(b_2 + b_3)] \tag{23}$$

$$\text{Y7} \quad = b_2 + b_3 \tag{24}$$

$$\text{Y8} \quad = z\exp[z(b_2 + b_3)] \tag{25}$$

$$\text{Y9} \quad = a_1\exp(b_1 z) + a_2\exp(b_2 z) \tag{26}$$

$$\text{Y10} \quad = (a_1)\,(z)\,\exp(b_1 z) \tag{27}$$

$$\text{Y11} \quad = (a_2)\,(z)\,\exp(b_2 z) \tag{28}$$

$$\text{Y12} \quad = \frac{(a_3)}{(b_1 + b_3)} \tag{29}$$

$$Y13 = \frac{(a_3)}{(b_2 + b_3)} \tag{30}$$

$$Y14 = \frac{(a_1)}{(b_1 + b_3)} \tag{31}$$

$$Y15 = \frac{(a_2)}{(b_2 + b_3)} \tag{32}$$

$$Y16 = \left(\frac{1.0}{(Le)}\right) \tag{33}$$

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