

Modelling the Effect of Precipitation on the Removal of Gaseous Pollutants Forming Secondary Species and Particulate Matters

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Abstract: In this paper, a nonlinear mathematical model is proposed to study the removal of gaseous pollutants undergoing chemical conversion to form secondary pollutants and particulate matters from the atmosphere of a city by precipitation. To model the problem, we assume that there exist seven interacting phases i.e. the raindrops phase, the primary gaseous pollutants phase, the secondary pollutants phase, the particulate matters phase and their corresponding absorbed phases in the raindrops. It is also assumed that the number density of raindrops, the concentration of pollutants and the concentration of same pollutants in the absorbed phases are governed by ordinary differential equations with nonlinear interaction terms. The model is analyzed using stability theory of differential equations and numerical simulation. When the primary pollutants and particulate matters are emitted instantaneously into the atmosphere, it is shown that these pollutants are removed completely from the atmosphere by precipitation. However, in the case of constant emission, the pollutants can still be washed out from the atmosphere under appropriate conditions with their equilibrium levels remaining at much smaller level after rain than their corresponding values before rain.

Keywords: Primary pollutants, secondary pollutants, particulate matters, equilibrium, stability analysis, numerical simulation.

1. INTRODUCTION

Most of the cities in developing countries suffer from air pollutants/toxicants released in the atmosphere which adversely affect the health and property of the inhabitants. These pollutants may be primary pollutants or secondary pollutants. The primary pollutants are emitted directly into the atmosphere from different sources such as industrial stacks, household discharges and vehicular exhausts etc. The secondary pollutants are formed in the atmosphere by means of chemical conversion of primary pollutants e.g. sulfur dioxide is converted to sulfur trioxide which combines with moisture and forms sulfuric acid. Particulate matters are also present in the atmosphere in the form of solid matter or liquid droplets come from dusts, smoke fly ash and condensing fugitive vapors. Air pollutants may be removed from the atmosphere either by dry or by wet deposition method. In dry deposition, the pollutants are removed by direct interaction with surfaces of buildings, plant leaves etc. and wet deposition is due to precipitation scavenging by rain, snow, fog etc. [2]. Precipitation scavenging, in which atmospheric gases/particulate matters are absorbed/trapped in raindrops falling on the ground, is one of the most important mechanism for removal of pollutants from the atmosphere. During low level precipitation, removal of gaseous pollutants and particulate air pollutants takes place by the absorption process in raindrops falling on the ground. The phenomenon of absorption of these pollutants by raindrops is the key step in removal of pollutants.

It has been shown in several experimental studies that the atmosphere of Indian cities becomes cleaner during and after monsoon season, [12, 14, 15, 18]. In particular, Sharma et. al. [18] measured the concentration of suspended particulate matters in Kanpur city, India and found considerable decrease in their concentrations

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during monsoon season. Pillai et. al. [14] have studied the wet deposition and dust fall in the city of Pune, India and emphasized the importance of wet removal. Similar experimental observations have also been made for industrial cities elsewhere in the world. For example, Davies [3] studied the removal of SO_2 by precipitation in an industrial area of Sheffield city in U.K. and found considerable decrease in its concentration after the rain.

Some modelling studies have been carried out to understand the scavenging of pollutants by precipitation, [1, 4-7, 9, 13, 16, 17, 19, 20, 22]. In particular, Hales [5] presented some fundamentals for the general analysis of precipitation scavenging emphasizing the importance of reversible phenomenon. Fisher [4] has studied the transport and removal of sulfur dioxide in a rain system using a simple model, which combines micro processes of absorption and chemical transformation of sulfur dioxide in cloud with the dynamics of air motion and obtained appropriate one-dimensional solution of the governing equations. Chang [1] has derived wet removal coefficient for nitric acid vapor in rain and snow systems and parameterized them in terms of precipitation rate under a number of approximations. Kumar [6] has given an Eulerian model to describe the simultaneous process of trace gas removal from the atmosphere and absorption of these gases in raindrops by considering the precipitation scavenging of these gases present below the clouds. Shukla et. al. [19] have calculated vertical concentration of gaseous pollutants emitted at ground level into stagnant fog layer containing uniform distribution of fog droplets by assuming reversible absorption of pollutants species. Shukla and Chauhan [20] presented a mathematical model to investigate the unsteady state dispersion of air pollutants from a time dependent point source forming secondary species by taking into account the dry and wet deposition on the ground. Pandis and Seinfeld [13] have studied the interactions between equilibration process and wet or dry deposition by proposing linear models. They considered three cases to obtain useful insight into the interaction and deposition process. The first case was related to a gas phase species, which can be reversibly transferred to aerosol phase. In the second case, the gas phase species in presence of droplets of liquid water (fog) was transferred reversibly to the aqueous phase. In the third case, two gases reacted to give a volatile aerosol phase. They have found interesting relationship in all the three cases and, in particular, found in the second phase i.e. in the fog episode, the deposition of gaseous species increased by as much as three times. Naresh [7] studied the effect of precipitation scavenging on the unsteady state dispersion of a reactive gaseous air pollutant emitted from a time dependent point source, assuming uniform distribution of raindrops in the atmosphere which absorb the pollutant and remove it by their fall on the ground.

It is pointed out here that the models related to precipitation scavenging due to rain, fog or snow studied above are linear in nature but in real situations during precipitation, the number density of the raindrops changes as the intensity of precipitation increases and as such the interactions between raindrops and gaseous pollutants as well as with particulate matters are nonlinear. In general, the removal of these pollutants due to precipitation is proportional to the concentrations of the absorbed pollutants as well as the number density of raindrops. A little attention has been paid to study the problem of removal of pollutants by precipitation using nonlinear models though it involves nonlinear interactions of various phases in the atmosphere [8, 10, 11, 21].

In view of the above, in this paper, a nonlinear mathematical model is proposed and analyzed to study the removal of gaseous pollutants forming secondary species and particulate matters by precipitation from the atmosphere by taking into account the interaction of raindrops phase with the pollutants phase. A numerical study of the model is also performed to see the influence of certain key parameters on the removal of pollutants.

2. THE MATHEMATICAL MODEL

In this section, we model the phenomenon of removal of primary gaseous pollutants, secondary pollutants and particulate matters by precipitation in the atmosphere of an industrial city. Consider that the atmosphere of a city where rain is taking place, consists of seven interacting phases as: the raindrops, the primary gaseous pollutants, the secondary pollutants, the particulate matters and their corresponding absorbed phases in the raindrops. It is noted that the main mechanism for removal of these pollutants from the atmosphere is due to falling of absorbed phases on the ground or by impaction caused by raindrops.

Here in the modeling process, our aim is to emphasize the cumulative removal of pollutants by rain rather than their chemical kinetics involved in the interaction process. Thus, the following assumptions are made:

- (i) The interaction of one phase with the other is governed by simple law of mass action.
- (ii) The pollutants are removed by precipitation as well as by natural factors. These natural factors may include the effects of gravity, interactions with plant leaves, buildings surfaces, etc.
- (iii) The removal rates of primary pollutants, secondary pollutants and particulate matters are assumed to be proportional to their respective cumulative concentrations.
- (iv) The rate of formation of raindrops is assumed to be constant, though it may be a function of time. The variation with time would not bring any qualitative change in the behavior.
- (v) The atmosphere of the city is assumed to be calm and hence the effects of convection and diffusion in the atmosphere are neglected.

Now we proceed to describe the model formulation. Let $C_r(t)$ be the number density of raindrops in the atmosphere, $C(t)$, $C_s(t)$ and $C_p(t)$ be the cumulative concentrations of primary, secondary and particulate air pollutants respectively, $C_a(t)$, $C_{sa}(t)$ and $C_{pa}(t)$ be the corresponding concentrations of primary, secondary and particulate air pollutants in the absorbed phases. It is assumed that $Q(t)$ and $Q_p(t)$ are the rates of emission of primary pollutants and particulate matters in the atmosphere. We assume that the primary pollutants are converted to secondary pollutants with a rate δC by means of chemical transformations. The growth rates of raindrops and pollutants may decrease naturally and these are assumed to be proportional to their respective cumulative concentrations. In the atmosphere, the primary pollutants, secondary pollutants and particulate matters are absorbed by raindrops in direct proportion to the cumulative concentrations of respective pollutants and the number density of raindrops (i.e. $\alpha C C_r$, $\alpha_s C_s C_r$ and $\alpha_p C_p C_r$). It is considered that the pollutants with concentrations C_a , C_{sa} and C_{pa} in absorbed phases may be removed by natural means with rates $k C_a$, $k_s C_{sa}$ and $k_p C_{pa}$ respectively. It is further assumed that the removal rates of absorbed primary pollutants, secondary pollutants and particulate matters, due to falling of these phases on the ground, are proportional to the number density of raindrops as well as their cumulative concentrations in the raindrops (i.e. $\nu C_r C_a$, $\nu_s C_r C_{sa}$ and $\nu_p C_r C_{pa}$ respectively). The raindrops depletion may also take place by interactions with the primary pollutants, secondary pollutants and particulate matters and this is assumed to be proportional to the raindrops density as well as the cumulative concentrations of these pollutants.

In view of the above assumptions and considerations, the dynamics of the system is assumed to be governed by the following nonlinear differential equations,

$$\frac{dC_r}{dt} = q(t) - r_0 C_r - r_1 C_r C - r_2 C_r C_s - r_3 C_r C_p, \quad (2.1)$$

$$\frac{dC}{dt} = Q(t) - (\delta_0 + \delta)C - \alpha C C_r, \quad (2.2)$$

$$\frac{dC_s}{dt} = \delta C - \delta_s C_s - \alpha_s C_s C_r, \quad (2.3)$$

$$\frac{dC_p}{dt} = Q_p(t) - \delta_p C_p - \alpha_p C_p C_r, \quad (2.4)$$

$$\frac{dC_a}{dt} = \alpha C C_r - k C_a - v_r C_r C_a, \quad (2.5)$$

$$\frac{dC_{sa}}{dt} = \alpha_s C_s C_r - k_s C_{sa} - v_s C_r C_{sa}, \quad (2.6)$$

$$\frac{dC_{pa}}{dt} = \alpha_p C_p C_r - k_p C_{pa} - v_p C_r C_{pa}. \quad (2.7)$$

$$C_r(0) \geq 0, C(0) \geq 0, C_s(0) \geq 0, C_p(0) \geq 0, C_a(0) \geq 0, C_{sa}(0) \geq 0, C_{pa}(0) \geq 0$$

where $q(t)$ is the rate of formation of raindrops assumed to be a constant (say q_0), r_0 is the natural depletion rate coefficient of raindrops, r_1 , r_2 and r_3 are the depletion rate coefficients of raindrops due to interaction with primary pollutants, secondary pollutants and particulate matters, the constant δ is the rate of change of primary pollutants to secondary pollutants due to chemical transformation. The constants δ_0 , δ_s , δ_p , k , k_s and k_p are the natural depletion rate coefficients of C , C_s , C_p , C_a , C_{sa} and C_{pa} respectively. The constants α , α_s and α_p are the absorption rate coefficients of C , C_s and C_p respectively in raindrops. The constants v , v_s and v_p are removal rate coefficients of absorbed phases C_a , C_{sa} and C_{pa} respectively due to falling raindrops on the ground.

It is remarked here from eq. (2.1) that if r_0 , r_1 , r_2 and r_3 are very large for a given concentration C , C_s and C_p due to atmospheric conditions, then dC_i/dt may become negative. In such a case no precipitation occurs and pollutants are not removed.

3. STABILITY ANALYSIS

Now we analyze the model (2.1) – (2.7) using stability theory of differential equations under the following two cases,

- (1) $q(t) = q_0$, $Q(t) = 0$, and $Q_p(t) = 0$
- (2) $q(t) = q_0$, $Q(t) = Q_0$, and $Q_p(t) = Q_p$

The first case corresponds to the situation when pollutants are emitted in the atmosphere by an instantaneous source, whereas the second case represents the emission of pollutants in the atmosphere with a constant rate.

3.1. Case 1. When $q(t) = q_0$, $Q(t) = 0$, and $Q_p(t) = 0$ (Instantaneous emission) – In this case the model has only one non-negative equilibrium $E_0 \left(\frac{q_0}{r_0}, 0, 0, 0, 0, 0, 0 \right)$ in $C_r - C - C_s - C_p - C_a - C_{sa} - C_{pa}$ space.

To study the local stability behavior of E_0 , we have computed the variational matrix for the model (2.1) - (2.7) corresponding to E_0 . It is found that all the eigen values of the variational matrix are negative proving that E_0 is locally asymptotically stable.

To study the global stability behaviour of E_0 , we propose the following theorem.

Theorem 1: If $C_r(0) > 0$, then E_0 is globally asymptotically stable with respect to the non-negative octant.

Proof: From eq. (2.1),

$$\frac{dC_r}{dt} \leq q_0 - r_0 C_r$$

From which we get $\limsup_{t \rightarrow \infty} C_r(t) \leq \frac{q_0}{r_0}$

Again from eqs. (2.2) and (2.5), we have,

$$\begin{aligned} \frac{dC}{dt} + \frac{dC_a}{dt} &= -(\delta_0 + \delta) C - k C_a - v C_r C_a \\ &\leq -(\delta_0 + \delta) C - k C_a \\ &\leq -\delta_e (C - C_a) \end{aligned}$$

where, $\delta_e = \min \{(\delta_0 + \delta), k\}$

Thus $C(t) + C_a(t) \leq \{C(0) + C_a(0)\} \exp(-\delta_e t)$

Hence the system is dissipative and, therefore, it follows that

$$\limsup_{t \rightarrow \infty} C(t) = \limsup_{t \rightarrow \infty} C_a(t) = 0$$

Similarly from eqs. (2.3) and (2.6), we get,

$$\limsup_{t \rightarrow \infty} C_s(t) = \limsup_{t \rightarrow \infty} C_{sa}(t) = 0$$

and from eqs. (2.4) and (2.7), we get,

$$\limsup_{t \rightarrow \infty} C_p(t) = \limsup_{t \rightarrow \infty} C_{pa}(t) = 0$$

Hence in the limit $C_r(t)$ tends to q_0/r_0 and since $C_r(0) > 0$, the theorem follows.

This theorem implies that in the case of instantaneous emission, the primary pollutants, secondary pollutants and particulate matters are removed completely from the atmosphere by rain and the time taken for removal will depend upon the rate of raindrops formation and removal rate coefficients.

3.2. Case 2. When $q(t) = q_0$, $Q(t) = Q_0$ and $Q_p(t) = Q_p$ (Constant emission) - In this case also the model has only one non-negative equilibrium namely $E^*(C_r^*, C_s^*, C_p^*, C_a^*, C_{sa}^*, C_{pa}^*)$, where $C_r^*, C_s^*, C_p^*, C_a^*, C_{sa}^*$ and C_{pa}^* are the positive solutions of the following system of algebraic equations,

$$C_r = \frac{q_0}{r_0 + r_1 f_1(C_r) + r_2 f_2(C_r) + r_3 f_3(C_r)} \quad (3.1)$$

$$C = \frac{Q_0}{(\delta_0 + \delta) + \alpha C_r} = f_1(C_r) \quad (3.2)$$

$$C_s = \frac{\delta f_1(C_r)}{\delta_s + \alpha_s C_r} = f_2(C_r) \quad (3.3)$$

$$C_p = \frac{Q_p}{\delta_p + \alpha_p C_r} = f_3(C_r) \quad (3.4)$$

$$C_a = \frac{\alpha C_r f_1(C_r)}{k + \nu C_r} \quad (3.5)$$

$$C_{sa} = \frac{\alpha_s C_r f_2(C_r)}{k_s + \nu_s C_r} \quad (3.6)$$

$$C_{pa} = \frac{\alpha_p C_r f_3(C_r)}{k_p + \nu_p C_r} \quad (3.7)$$

Now let,
$$F(C_r) = q_0 - r_0 C_r - r_1 C_r f_1(C_r) - r_2 C_r f_2(C_r) - r_3 C_r f_3(C_r) \quad (3.8)$$

We note from eq. (3.8) that $F(0) = q_0 > 0$ and $F\left(\frac{q_0}{r_0}\right) < 0$

It can be checked that $F'(C_r) < 0$, provided

$$r_0 + r_1 [f_1(C_r) + C_r f_1'(C_r)] + r_2 [f_2(C_r) + C_r f_2'(C_r)] + r_3 [f_3(C_r) + C_r f_3'(C_r)] > 0 \quad (3.9)$$

Thus there exists a unique positive root (say C_r^*) in $0 < C_r < \frac{q_0}{r_0}$ provided the condition (3.9) is satisfied. Using the value of C_r^* , we can find the values of $C^*, C_s^*, C_p^*, C_a^*, C_{sa}^*$ and C_{pa}^* from equations (3.2) - (3.7) respectively. Further, it can also be easily checked that $C^*, C_s^*, C_p^*, C_a^*, C_{sa}^*$ and C_{pa}^* decrease as q_0 increases.

In the following, we check the characteristics of various phases with respect to parameter q_0 .

3.2.1. Variation of C_r, C, C_s and C_p with q_0

(i) Variation of C_r with q_0

From eq. (3.1) we have

$$r_0 C_r + r_1 C_r f_1(C_r) + r_2 C_r f_2(C_r) + r_3 C_r f_3(C_r) = q_0$$

Differentiating both sides with respect to 'q₀', we get

$$\{r_0 + r_1[f_1(C_r) + C_r f_1'(C_r)] + r_2[f_2(C_r) + C_r f_2'(C_r)] + r_3[f_3(C_r) + C_r f_3'(C_r)]\} \frac{dC_r}{dq_0} = 1$$

Under the assumption (3.9), $\frac{dC_r}{dq_0} > 0$ for $C_r \geq 0$

Thus, C_r increases as q_0 increases.

(ii) Variation of C with q₀

From eq.(3.2) we get, $\frac{dC}{dC_r} < 0$

and since $\frac{dC_r}{dq_0} > 0$, it follows that $\frac{dC}{dq_0} < 0$

Therefore, C decreases with increase in q_0 .

(iii) Variation of C_s with q₀

From eq. (3.3), we get $\frac{dC_s}{dC_r} < 0$ and since $\frac{dC_r}{dq_0} > 0$ it follows that $\frac{dC_s}{dq_0} < 0$

Therefore, C_s decreases with increase in q_0 .

(iv) Variation of C_p with q₀

Similarly from eq. (3.4), we have $\frac{dC_p}{dC_r} < 0$ and since $\frac{dC_r}{dq_0} > 0$, therefore $\frac{dC_p}{dq_0} < 0$.

Thus, C_p decreases with increase in q_0 .

Hence, as the rate of precipitation q_0 increases, the cumulative concentrations of primary pollutants, secondary pollutants and particulate matters decrease and these may be removed completely for large q_0 . It is remarked here that,

- (1) If the coefficients α , α_s and α_p are so large that $\frac{dC}{dt} < 0$, $\frac{dC_s}{dt} < 0$, and $\frac{dC_p}{dt} < 0$, all the pollutants will be removed from the atmosphere of the city.
- (2) For large v , v_s and v_p , $\frac{dC_a}{dt} < 0$, $\frac{dC_{sa}}{dt} < 0$ and $\frac{dC_{pa}}{dt} < 0$ respectively and the formation of absorption phase is very transient and it may not exist.

To study the stability behavior of equilibrium E^* , we propose the following theorems.

Theorem 2: Let the following inequalities hold,

$$[r_1 C_r^* + \alpha C^*]^2 < \frac{2}{9} \frac{q_0}{C_r^*} (\delta_0 + \delta + \alpha C_r^*) \tag{3.10}$$

$$[r_2 C_r^* + k_2 \alpha_s C_s^*]^2 < \frac{2}{9} \frac{q_0}{C_r^*} k_2 (\delta_s + \alpha_s C_r^*) \tag{3.11}$$

$$[r_3 C_r^* + \alpha_p C_p^*]^2 < \frac{1}{3} \frac{q_0}{C_r^*} (\delta_p + \alpha_p C_r^*) \tag{3.12}$$

where $k_2 < \frac{4}{9\delta^2} (\delta_0 + \delta + \alpha C_r^*) (\delta_s + \alpha_s C_r^*)$

then E^* is locally asymptotically stable.

Proof: Consider the following positive definite function

$$V = \frac{1}{2} (C_{r1}^2 + k_1 C_1^2 + k_2 C_{s1}^2 + k_3 C_{p1}^2 + k_4 C_{a1}^2 + k_5 C_{sa1}^2 + k_6 C_{pa1}^2) \tag{3.13}$$

where C_{r1} , C_1 , C_{s1} , C_{p1} , C_{a1} , C_{sa1} and C_{pa1} are small perturbations about E^* , as follows

$$C_r = C_r^* + C_{r1}, \quad C = C^* + C_1, \quad C_s = C_s^* + C_{s1}, \quad C_p = C_p^* + C_{p1}, \quad C_a = C_a^* + C_{a1}$$

$$C_{sa} = C_{sa}^* + C_{sa1}, \quad C_{pa} = C_{pa}^* + C_{pa1}$$

Differentiating (3.13) with respect to 't' we get, in the linearized system corresponding to E^*

$$\begin{aligned} \dot{V} = & -\frac{q_0}{C_r^*} C_{r1}^2 - k_1 (\delta_0 + \delta + \alpha C_r^*) C_1^2 - k_2 (\delta_s + \alpha_s C_r^*) C_{s1}^2 - k_3 (\delta_p + \alpha_p C_r^*) C_{p1}^2 \\ & - k_4 (k + v C_r^*) C_{a1}^2 - k_5 (k_s + v_s C_r^*) C_{sa1}^2 - k_6 (k_p + v_p C_r^*) C_{pa1}^2 \\ & - [r_1 C_r^* + k_1 \alpha C^*] C_{r1} C_1 - [r_2 C_r^* + k_2 \alpha_s C_s^*] C_{r1} C_{s1} - [r_3 C_r^* + k_3 \alpha_p C_p^*] C_{r1} C_{p1} \\ & + k_4 (\alpha C^* - v C_a^*) C_{r1} C_{a1} + k_5 (\alpha_s C_s^* - v_s C_{sa}^*) C_{r1} C_{sa1} + k_6 (\alpha_p C_p^* - v_p C_{pa}^*) C_{r1} C_{pa1} \\ & + k_2 \delta C_1 C_{s1} + k_4 \alpha C_r^* C_1 C_{a1} + k_5 \alpha_s C_r^* C_{s1} C_{sa1} + k_6 \alpha_p C_r^* C_{p1} C_{pa1} \end{aligned}$$

\dot{V} will be negative definite under the following conditions,

$$[r_1 C_r^* + k_1 \alpha C^*]^2 < \frac{2}{9} \frac{q_0}{C_r^*} k_1 (\delta_0 + \delta + \alpha C_r^*) \tag{3.14}$$

$$[r_2 C_r^* + k_2 \alpha_s C_s^*]^2 < \frac{2}{9} \frac{q_0}{C_r^*} k_2 (\delta_s + \alpha_s C_r^*) \tag{3.15}$$

$$[r_3 C_r^* + k_3 \alpha_p C_p^*]^2 < \frac{1}{3} \frac{q_0}{C_r^*} k_3 (\delta_p + \alpha_p C_r^*) \quad (3.16)$$

$$k_4 (\alpha C^* - v C_a^*)^2 < \frac{q_0}{3 C_r^*} (k + v C_r^*) \quad (3.17)$$

$$k_5 (\alpha_s C_s^* - v_s C_{sa}^*)^2 < \frac{q_0}{3 C_r^*} (k_s + v_s C_r^*) \quad (3.18)$$

$$k_6 (\alpha_p C_p^* - v_p C_{pa}^*)^2 < \frac{q_0}{3 C_r^*} (k_p + v_p C_r^*) \quad (3.19)$$

$$k_2 \delta^2 < \frac{4k_1}{9} (\delta_0 + \delta + \alpha C_r^*) (\delta_s + \alpha_s C_r^*) \quad (3.20)$$

$$k_4 (\alpha C_r^*)^2 < \frac{2k_1}{3} (\delta_0 + \delta + \alpha C_r^*) (k + v C_r^*) \quad (3.21)$$

$$k_5 (\alpha_s C_r^*)^2 < \frac{2k_2}{3} (\delta_s + \alpha_s C_r^*) (k_s + v_s C_r^*) \quad (3.22)$$

$$k_6 (\alpha_p C_r^*)^2 < k_3 (\delta_p + \alpha_p C_r^*) (k_p + v_p C_r^*) \quad (3.23)$$

Now choosing, $k_1 = k_3 = 1, k_2 < \frac{4}{9\delta^2} (\delta_0 + \delta + \alpha C_r^*) (\delta_s + \alpha_s C_r^*)$ and

$$k_4 < \min \left\{ \frac{q_0 (k + v C_r^*)}{3 C_r^* (\alpha C^* - v C_a^*)^2}, \frac{2(\delta_0 + \delta + \alpha C_r^*) (k + v C_r^*)}{3(\alpha C_r^*)^2} \right\}$$

$$k_5 < \min \left\{ \frac{q_0 (k_s + v_s C_r^*)}{3 C_r^* (\alpha_s C_s^* - v_s C_{sa}^*)^2}, \frac{2k_2 (\delta_s + \alpha_s C_r^*) (k_s + v_s C_r^*)}{3(\alpha_s C_r^*)^2} \right\}$$

$$k_6 < \min \left\{ \frac{q_0 (k_p + v_p C_r^*)}{3 C_r^* (\alpha_p C_p^* - v_p C_{pa}^*)^2}, \frac{(\delta_p + \alpha_p C_r^*) (k_p + v_p C_r^*)}{(\alpha_p C_r^*)^2} \right\}$$

The eqs. (3.14) - (3.23) reduce to,

$$[r_1 C_r^* + \alpha C^*]^2 < \frac{2}{9} \frac{q_0}{C_r^*} (\delta_0 + \delta + \alpha C_r^*) \quad (3.24)$$

$$[r_2 C_r^* + k_2 \alpha_s C_s^*]^2 < \frac{2}{9} \frac{q_0}{C_r^*} k_2 (\delta_s + \alpha_s C_r^*) \quad (3.25)$$

$$[r_3 C_r^* + \alpha_p C_p^*]^2 < \frac{1}{3} \frac{q_0}{C_r^*} (\delta_p + \alpha_p C_r^*) \quad (3.26)$$

Under conditions (3.24) – (3.26), \dot{V} will be negative definite showing that V is a Liapunov's function and hence the theorem.

To establish the nonlinear stability character of E^* , we need the bounds of dependent variables involved. For this we find the region of attraction in the following lemma, stated without proof.

Lemma 1: The set $\Omega = \{(C_r, C, C_s, C_p, C_a, C_{sa}, C_{pa}) : 0 \leq C_r \leq \frac{q_0}{r_0}, 0 \leq C + C_a \leq \frac{Q_0}{\delta_l}, 0 \leq C_s + C_{sa} \leq \frac{\delta}{\delta_l \delta_m}, 0 \leq C_p + C_{pa} \leq \frac{Q_p}{\delta_n}\}$ attracts all solutions initiating in the interior of non-negative octant, where $\delta_e = \min(\delta_0 + \delta, k), \delta_m = \min(\delta_s, k_s), \delta_n = \min(\delta_p, k_p)$.

Theorem 3: Let the following inequalities hold in Ω ,

$$\left(r_1 \frac{q_0}{r_0} + \alpha \frac{Q_0}{\delta_l} \right)^2 < \frac{2}{9} \frac{q_0}{C_r^*} (\delta_0 + \delta + \alpha C_r^*) \tag{3.27}$$

$$\left(r_2 \frac{q_0}{r_0} + m_2 \alpha_s \frac{\delta}{\delta_m \delta_l} \frac{Q_0}{\delta_l} \right)^2 < \frac{2}{9} \frac{q_0}{C_r^*} m_2 (\delta_s + \alpha_s C_r^*) \tag{3.28}$$

$$\left(r_3 \frac{q_0}{r_0} + \alpha_p \frac{Q_p}{\delta_n} \right)^2 < \frac{1}{3} \frac{q_0}{C_r^*} (\delta_p + \alpha_p C_r^*) \tag{3.29}$$

where $m_2 < \frac{4}{9\delta^2} (\delta_0 + \delta + \alpha C_r^*) (\delta_s + \alpha_s C_r^*)$

then E^* is nonlinearly asymptotically stable.

Proof: Consider the following positive definite function about E^* ,

$$U = \frac{1}{2} [(C_r - C_r^*)^2 + m_1 (C - C^*)^2 + m_2 (C_s - C_s^*)^2 + m_3 (C_p - C_p^*)^2 + m_4 (C_a - C_a^*)^2] + \frac{1}{2} [m_5 (C_{sa} - C_{sa}^*)^2 + m_6 (C_{pa} - C_{pa}^*)^2]$$

Differentiating with respect to 't' we get,

$$\begin{aligned} \dot{U} = & -m_4 v C_r (C_a - C_a^*)^2 - m_5 v_s C_r (C_{sa} - C_{sa}^*)^2 - m_6 v_p C_r (C_{pa} - C_{pa}^*)^2 \\ & - \frac{q_0}{C_r^*} (C_r - C_r^*)^2 - m_1 (\delta_0 + \delta + \alpha C_r^*) (C - C^*)^2 \\ & - m_2 (\delta_s + \alpha_s C_r^*) (C_s - C_s^*)^2 - m_3 (\delta_p + \alpha_p C_r^*) (C_p - C_p^*)^2 - m_4 k (C_a - C_a^*)^2 \end{aligned}$$

$$\begin{aligned}
 & -m_5 k_s (C_{sa} - C_{sa}^*)^2 - m_6 k_p (C_{pa} - C_{pa}^*)^2 \\
 & -[r_1 C_r + m_1 \alpha C_r](C_r - C_r^*)(C - C^*) - [r_2 C_r + m_2 \alpha_s C_s](C_r - C_r^*)(C_s - C_s^*) \\
 & -[r_3 C_r + m_3 \alpha_p C_p](C_r - C_r^*)(C_p - C_p^*) + m_4 (\alpha C_r^* - \nu C_a^*)(C_r - C_r^*)(C_a - C_a^*) \\
 & + m_5 (\alpha_s C_s^* - \nu_s C_{sa}^*)(C_r - C_r^*)(C_{sa} - C_{sa}^*) + m_6 (\alpha_p C_p^* - \nu_p C_{pa}^*)(C_r - C_r^*)(C_{pa} - C_{pa}^*) \\
 & + m_2 \delta (C - C^*)(C_s - C_s^*) + m_4 \alpha C_r (C - C^*)(C_a - C_a^*) \\
 & + m_5 \alpha_s C_r (C_s - C_s^*)(C_{sa} - C_{sa}^*) + m_6 \alpha_p C_r (C_p - C_p^*)(C_{pa} - C_{pa}^*)
 \end{aligned}$$

For \dot{U} to be negative definite, the following conditions must be satisfied

$$[r_1 C_r + m_1 \alpha C_r]^2 < \frac{2}{9} \frac{q_0}{C_r^*} m_1 (\delta_0 + \delta + \alpha C_r^*) \quad (3.30)$$

$$[r_2 C_r + m_2 \alpha_s C_s]^2 < \frac{2}{9} \frac{q_0}{C_r^*} m_2 (\delta_s + \alpha_s C_r^*) \quad (3.31)$$

$$[r_3 C_r + m_3 \alpha_p C_p]^2 < \frac{1}{3} \frac{q_0}{C_r^*} m_3 (\delta_p + \alpha_p C_r^*) \quad (3.32)$$

$$m_4 (\alpha C_r^* - \nu C_a^*)^2 < \frac{q_0}{3 C_r^*} k \quad (3.33)$$

$$m_5 (\alpha_s C_s^* - \nu_s C_{sa}^*)^2 < \frac{q_0}{3 C_r^*} k_s \quad (3.34)$$

$$m_6 (\alpha_p C_p^* - \nu_p C_{pa}^*)^2 < \frac{q_0}{3 C_r^*} k_p \quad (3.35)$$

$$m_2 \delta^2 < \frac{4 m_1}{9} (\delta_0 + \delta + \alpha C_r^*) (\delta_s + \alpha_s C_r^*) \quad (3.36)$$

$$m_4 (\alpha C_r^*)^2 < \frac{2 m_1}{3} (\delta_0 + \delta + \alpha C_r^*) k \quad (3.37)$$

$$m_5 (\alpha_s C_r^*)^2 < \frac{2 m_2}{3} (\delta_s + \alpha_s C_r^*) k_s \quad (3.38)$$

$$m_6 (\alpha_p C_r^*)^2 < m_3 (\delta_p + \alpha_p C_r^*) k_p \quad (3.39)$$

Now choosing, $m_1 = m_3 = 1, m_2 < \frac{4}{9 \delta^2} (\delta_0 + \delta + \alpha C_r^*) (\delta_s + \alpha_s C_r^*)$ and

$$m_4 < \min \left\{ \frac{q_0 k}{3C_r^* (\alpha C_a^* - \nu C_a^*)^2}, \frac{2(\delta_0 + \delta + \alpha C_r^*) k}{3 \left(\alpha \frac{q_0}{r_0} \right)^2} \right\}$$

$$m_5 < \min \left\{ \frac{q_0 k_s}{3C_r^* (\alpha_s C_s^* - \nu_s C_{sa}^*)^2}, \frac{2k_2 (\delta_s + \alpha C_r^*) k_s}{3 \left(\alpha_s \frac{q_0}{r_0} \right)^2} \right\}$$

$$m_6 < \min \left\{ \frac{q_0 k_p}{3C_r^* (\alpha_p C_p^* - \nu C_{pa}^*)^2}, \frac{(\delta_p + \alpha_p C_r^*) k_p}{\left(\alpha_p \frac{q_0}{r_0} \right)^2} \right\}$$

The eqs. (3.30) - (3.39) reduce to,

$$\left(r_1 \frac{q_0}{r_0} + \alpha \frac{Q_0}{\delta_l} \right)^2 < \frac{2}{9} \frac{q_0}{C_r^*} (\delta_0 + \delta + \alpha C_r^*) \tag{3.40}$$

$$\left(r_2 \frac{q_0}{r_0} + m_2 \alpha_s \frac{\delta}{\delta_m \delta_l} \frac{Q_0}{\delta_l} \right)^2 < \frac{2}{9} \frac{q_0}{C_r^*} m_2 (\delta_s + \alpha_s C_r^*) \tag{3.41}$$

$$\left(r_3 \frac{q_0}{r_0} + \alpha_p \frac{Q_p}{\delta_n} \right)^2 < \frac{1}{3} \frac{q_0}{C_r^*} (\delta_p + \alpha_p C_r^*) \tag{3.42}$$

Under conditions (3.40) – (3.42), \dot{U} will be negative definite showing that U is a Liapunov’s function and hence the theorem.

The above two theorems imply that in the case of constant emission, the primary pollutants, secondary pollutants and particulate matters are again washed out by precipitation from the atmosphere under certain conditions and their remaining equilibrium amount in the atmosphere would mainly depend upon the rate of emission of primary pollutants and particulate matters, rate of change of primary pollutants to secondary pollutants, the rate of raindrops formation and the rate of falling raindrops on the ground. From the above theorems, we also note that if Q_0 and Q_p are small, then the possibility of satisfying the conditions (3.27) – (3.29) increases. This shows that if the rate of emission of pollutants into the environment is small, then the stability of the system is more plausible.

4. NUMERICAL SIMULATION

In this section, we present the results of numerical analysis of the model (2.1) - (2.7). For this we consider the following set of parameter values,

$$q_0 = 10.0, r_0 = 0.2, Q_0 = 15, Q_p = 10, r_1 = 0.002, r_2 = 0.001, r_3 = 0.0009, \delta_0 = 0.1,$$

$$\delta = 0.20, \delta_s = 0.30, \delta_p = 0.35, \alpha = 0.75, \alpha_s = 0.65, \alpha_p = 0.55, k = 0.65, k_s = 0.58$$

$$k_p = 0.72, v = 0.65, v_s = 0.60, v_p = 0.70$$

The equilibrium E^* is calculated as,

$$C_r^* = 49.72030706, C^* = 0.3985097828, C_s^* = 0.002443481172, C_p^* = 0.3617801990$$

$$C_a^* = 0.4507532035, C_{sa}^* = 0.002596620868, C_{pa}^* = 0.2786511407$$

Eigen values corresponding to E^* are obtained as follows,

$$-32.96819959, -30.41218424, -35.52421494, -0.2000018787, -27.69649512, -37.64100655, -32.61822028$$

Since all the eigen values corresponding to E^* are negative, therefore E^* is locally asymptotically stable.

The nonlinear stability behavior of E^* in $C_r - C$ and $C - C_a$ plane is shown in the Fig.1 and Fig.2 respectively. In Figs.(3-5), the variation of cumulative concentrations of primary pollutants (C), secondary pollutants (C_s) and particulate matters (C_p) with time ' t ' is shown at different levels of raindrops formation i.e. $q = 5, 10, 20$ respectively. From these figures, it can be seen that the cumulative concentrations of these pollutants decrease as the rate of raindrops formation increases. Figs. (6-8) depict the variation of cumulative concentrations of primary pollutants, secondary pollutants and particulate matters in absorbed phase with time ' t ' at different levels of raindrops formation respectively. From these figures, it can again be seen that the concentrations of

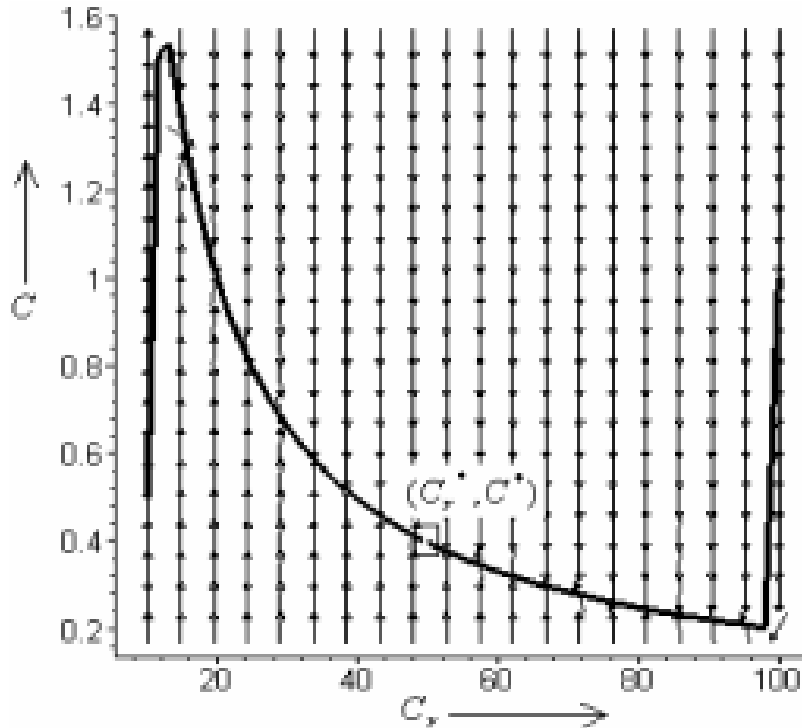


Figure 1: Nonlinear stability in $C_r - C$ plane

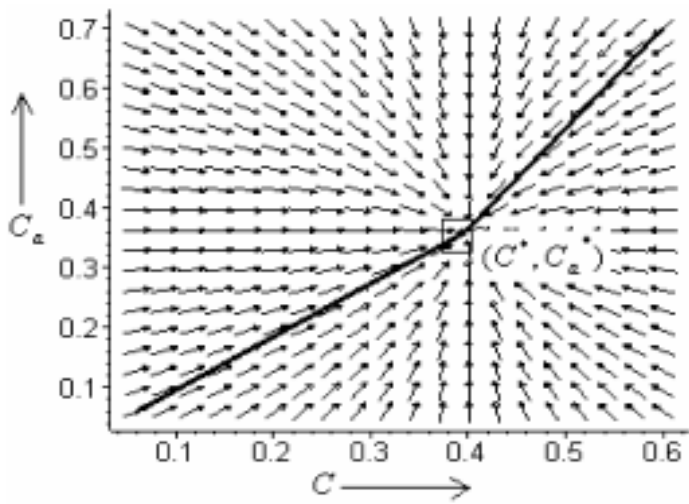


Figure 2: Nonlinear stability in $C - C_a$ plane

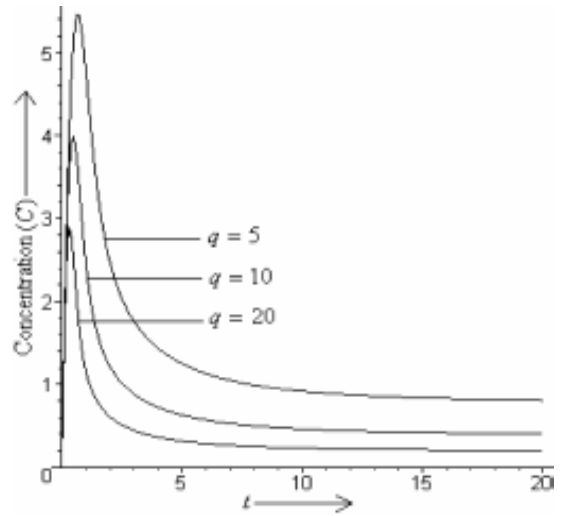


Figure 3: Variation of C with ' t ' for different values of q

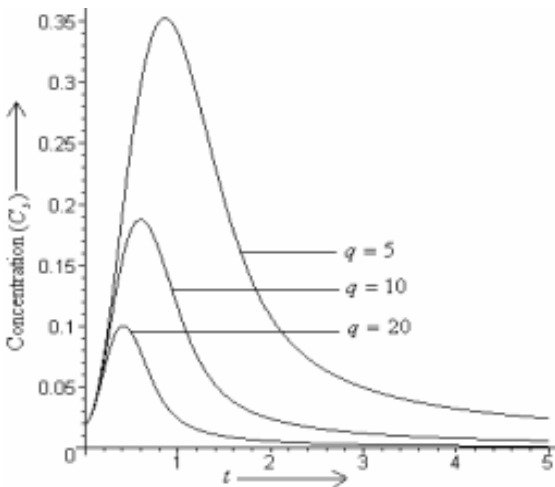


Figure 4: Variation of C_s with ' t ' for different values of q

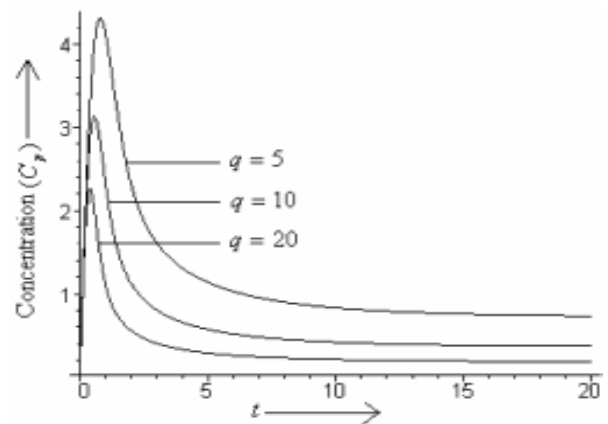


Figure 5: Variation of C_p with ' t ' for different values of q

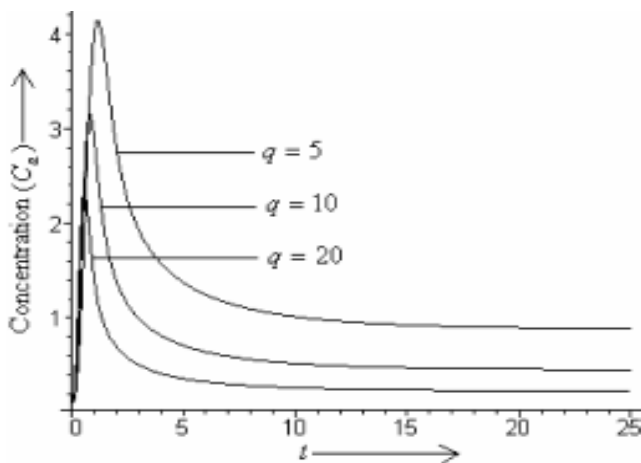


Figure 6: Variation of C_a with ' t ' for different values of q

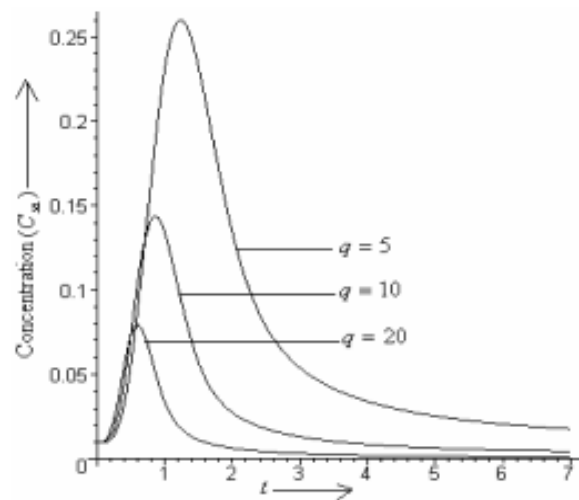


Figure 7: Variation of C_{sa} with ' t ' for different values of q

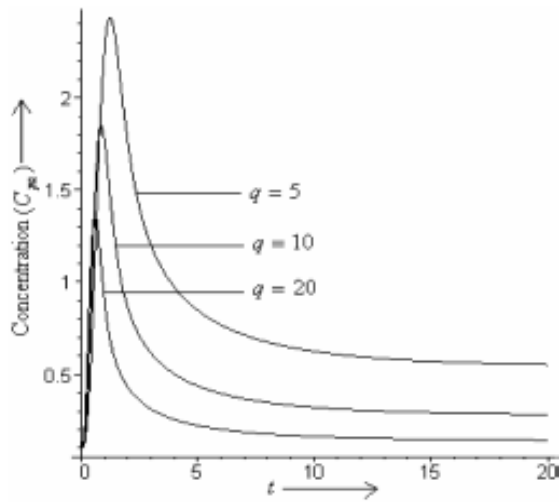


Figure 8: Variation of C_{pa} with 't' for different values of q

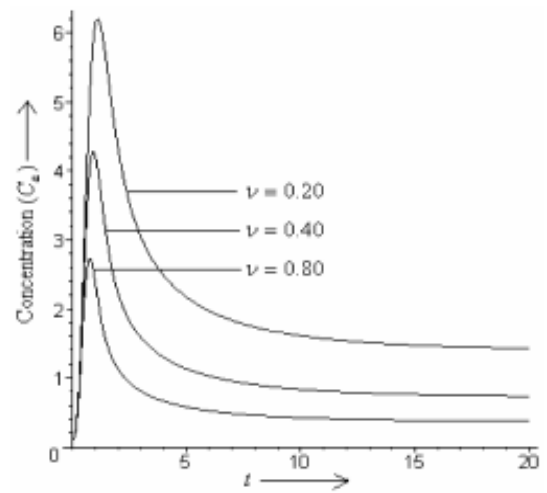


Figure 9: Variation of C_a with 't' for different value of ν

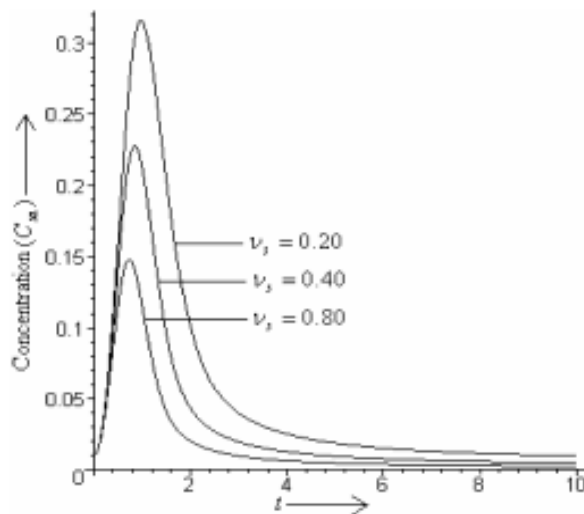


Figure 10: Variation of C_{sa} with 't' for different values of ν_s

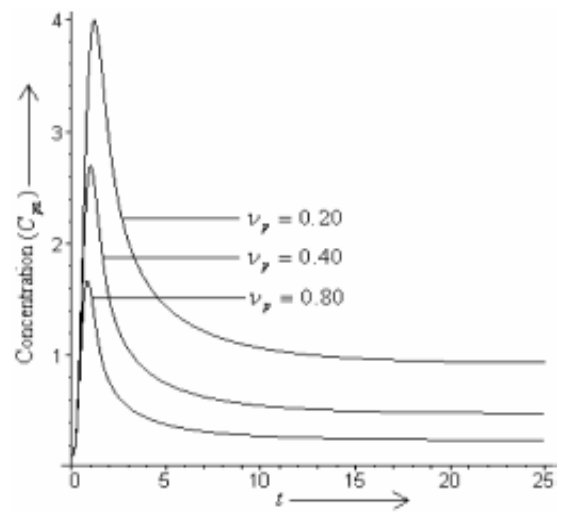


Figure 11: Variation of C_{pa} with 't' for different values of ν_p

Table 1
Variation of Equilibrium Values E^* with q

q	C_r^*	C^*	C_s^*	C_p^*	C_a^*	C_{sa}^*	C_{pa}^*
10	49.72030	0.398509	0.002443	0.361780	0.450753	0.002596	0.278651
20	99.71924	0.199628	0.000613	0.181354	0.228054	0.000657	0.141078
30	149.7188	0.133168	0.000272	0.121006	0.152636	0.000293	0.094445
40	199.7187	0.099907	0.000153	0.090793	0.114703	0.000165	0.070982
50	249.7186	0.079940	0.000098	0.072653	0.091871	0.000106	0.056856

Table 2
Variation of C_a^* with ν

ν	0.65	0.70	0.75	0.80	0.85
C_a^*	0.45075332	0.41914682	0.39168242	0.36759588	0.34630013

Table 3
Variation of C_{sa}^* with v_s

v_s	0.60	0.65	0.70	0.75	0.80
C_{sa}^*	0.00259662	0.00240040	0.00223175	0.00208525	0.00195679

Table 4
Variation of C_{pa}^* with v_p

v_p	0.65	0.70	0.75	0.80	0.85
C_{pa}^*	0.29963179	0.27865149	0.26041701	0.24442243	0.23027890

these pollutants in absorbed phases also decrease as the rate of raindrops formation increases. In Figs.(9 – 11), the variation of concentrations of primary pollutants, secondary pollutants and particulate matters in respective absorbed phases (i.e. C_a , C_{sa} and C_{pa} respectively) with time ‘ t ’ is shown for different values of removal rate coefficients of absorbed phases i.e. v , v_s and v_p respectively. It is seen that the concentrations of these pollutants in their corresponding absorbed phases also decrease as the removal rate coefficients of absorbed phases increases. In the Table 1, the variation of equilibrium values E^* is shown for different values of raindrops formation q . From this, it is clear that as the rate of raindrops formation increases, the equilibrium concentrations of primary pollutants (C), secondary pollutants (C_s), particulate matters (C_p) and the concentrations of these pollutants in absorbed phases decrease whereas the number density of raindrops increases. In Tables 2, 3 and 4, the equilibrium concentrations of primary pollutants, secondary pollutants and particulate matters respectively in absorbed phases are shown to decrease with increase in removal parameter v , v_s and v_p respectively.

5. CONCLUSION

In this paper, a nonlinear mathematical model is proposed and analyzed to study the removal of primary gaseous pollutants, secondary pollutants and particulate matters from the atmosphere of a city by precipitation. It has been shown qualitatively and by numerical simulation that if the pollutants are emitted instantaneously, they are completely washed out from the atmosphere. The time of removal would depend on the rate of rain formation and the rate of falling raindrops on the ground. When the primary pollutants and particulate matters are emitted into the atmosphere at a constant rate, these pollutants can still be washed out from the atmosphere and the equilibrium level of remaining amount depends upon the rate of emission of pollutants, the rate of raindrops formation and the rate of falling absorbed phases on the ground. The equilibrium level of the concentration of these pollutants in the atmosphere is much smaller after rain than its corresponding value before rain. It is also shown numerically that the concentrations of these pollutants decrease with increase in the rate of raindrops formation. Further, it is also found that the concentrations of these pollutants in absorbed phases decrease with increase in respective removal rate coefficients.

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