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THE LONG-RANGE TRANSPORT OF AIR POLLUTION AND THE SIGNIFICANCE OF
NON-LINEARITY WITHIN OXIDATION-DEPOSITION PROCESSES

by

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May 1985

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Abstract

This paper presents results from two studies which are relevant to the consequences of emission reduction.

Several of the processes involved in oxidation and deposition of "acid rain" are strongly non-linear. However the stochastic nature of rainfall works to reduce the influence of the non-linearities. A model is described (Sec 3) which represents the important processes. Its results indicate that halving the emission would reduce deposition (at distances representative of transport from UK to Scandinavia) by at least 50%. A second model (Sec 4), with an improved description of mixing processes, confirms the result, which is shown (4.3) to be extremely robust to the values of parameters within the model. Orographic enhancement of rainfall is considered in Sec 5. It does not affect the overall conclusion that, as far as long-term depositions are concerned, non-linear processes are not a significant problem.

Annual UK SO₂ emissions changed by about 25% between 1977 and 1982. Daily deposition data at two EMEP sites in Southern Norway have been examined for those days when the air had come from the direction of the UK. The results (section 6) provide clear evidence of a relationship between observed deposition and reported emissions. Statistical tests support rather than contradict the hypothesis of a linear relationship.

The long-range transport of air pollution and the significance of
non-linearity within oxidation-deposition processes

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1. INTRODUCTION

The problem of the long-range transport of air pollutants has been studied with increasing intensity since the early 1970's following the implication that acid depositions from the atmosphere were having a disastrous affect on fish populations in freshwaters in southern Norway. The atmospheric processes were attacked first, primarily to establish whether or not pollutants could travel such long distances from the main industrial centres of mid-Europe and the UK to the sensitive receptors in Scandinavia and elsewhere. Later the equally challenging questions of what happens to the pollutants once deposited, and how the ecosystems are affected, were begun to be investigated. Even more recently the whole important question of photo-oxidant species damage to forests has been highlighted, and now attracts very considerable scientific effort.

It would be impossible in this short paper to cover all these topics. Consequently it will report on some advances on one small but very important aspect. Before introducing this, it is important to recognise that in very many aspects the freshwater fish issue and the tree-damage issue are two very different problems. Whilst both arise from the discharge to the atmosphere of waste gases and particulates, such as SO_2 , NO_x , particulate hydrocarbons etc, the former issue seems mainly to depend on the long-term depositions of acidity (mainly sulphate) whereas the latter seems to depend primarily on episodic (short-term) air-borne concentrations of ozone (a secondary pollutant formed by photochemical processes from the primary waste gases). Because of this difference it seems sensible to tackle and model the two issues in very different ways, if this is possible. Mathematical modelling has made and is making a very significant contribution to our understanding of both issues, but cannot of course be the whole answer and must go hand-in-hand with routine monitoring actual atmospheric concentrations, depositions and effects, as well as specifically-designed field experiments.

Modelling can be classified into four types as shown in Table 1. Each type has its own advantages, disadvantages and areas of application. They can be described as "statistical", "Lagrangian", "Eulerian" and "diagnostic". Statistical models rely on climatological statistics of trajectories and the atmosphere. They are essentially very simple, quick to run on a computer, versatile and appropriate only to the first issue. Lagrangian models use actual synoptic data, they ignore vertical wind shear, are fairly heavy on computer time and are mainly of value for the first issue. Three-dimensional Eulerian models on the other hand are much more complex and are being developed with detailed air-chemistry modules to treat the second issue. Being so complex their computer requirements are enormous and they cannot be run routinely and therefore their results may form a rather poor basis for political decisions on emission control. For this reason and for reasons of questionable input data, some scientists would question the wisdom of putting excessive effort into this area of work, and would rather recommend work of equal value in such questions as the residence-time distribution of polluted air within continental blocking-highs in summer which tend to produce high ozone levels. Such residence times will largely determine differences in ozone-level.

However such questions must be left aside in this paper. Instead we will concentrate on one important question within the first issue of fish-damage. This question relates to the consequences of emission reduction. Recognising that some of the processes (principally the rain-out process) involved in acid deposition are non-linear, to what extent are depositions in sensitive areas, like southern Norway and Scotland, reduced by reducing emissions. If the answer should be "very little", then it would be foolish to waste great quantities of money in reducing emissions with little benefit as a result. The question will be addressed firstly by modelling (Sections 2-5) and secondly by examining selected EMEP data (Section 6).

2. THE PROBLEM OF DETERMINING THE EFFECT OF NON-LINEAR PROCESSES

The word "rain" will be used in this paper to denote all forms of precipitation. Most rain occurring in significant quantities originates in cloud which feeds upon moist air drawn from the mixing layer (i.e. the atmospheric boundary layer). Sulphur dioxide carried by the air may become oxidised to sulphate provided sufficient quantities of oxidant are present, at a rate which appears to be normally very much faster than the typical rate of about 1% per hour in cloudless air. Some of the 'sulphur' (SO_2 and sulphate) may escape from the visible cloud through evaporation into the surrounding "free" troposphere above the mixing layer, and some may get taken into growing droplets and eventually fall out as rain. These physio-chemical processes may be strongly non-linear. To quote just a single example, in heavily polluted incoming air cloud droplets may become so acidified that they are unable to absorb relatively as much sulphur dioxide as when the incoming air is only slightly polluted. In general the overall non-linearity appears to operate in this same general sense, namely that the ratio of the concentration in the rain to the concentration in the inflowing air decreases as the latter increases. Thus should an air mass carrying a heavy sulphur burden enter a very extensive rain belt the "footprint" of sulphate deposition will depart radically from a simple exponential-decay expected on the basis of linearity:

$$D = D_0 e^{-x/l}$$

(where D is the deposition of sulphate per unit area, x is distance downwind from the point where the rain started, and l is some length-scale), and instead will start with depositions much smaller than D_0 , and the footprint will extend downwind to greater distances. Ultimately all the sulphur will be deposited so that the downwind-integrated deposition must be the same in the linear and non-linear cases. The deposition at a given point along the trajectory will depend on the degree of non-linearity, the original sulphur concentration, the rain intensity and x in such a way that no simple linear model could hope to predict. Consequently it has been argued that:

- (i) reducing emissions may not result in proportional reductions in depositions in those areas which are particularly at risk,
 - (ii) simple linear models are inadequate to describe the fate of sulphur emissions over a continental region,
 - (iii) complex air-chemistry models need to be developed which should include all relevant chemical reactions, involving many different species whose concentrations and spatial-temporal emissions should be determined as a matter of some urgency.
- Others argue that since most, if not all, ecological damage appears to result from accumulated depositions, integrated over many rain events, the effective relationship between concentrations and depositions is much more linear than feared from considerations of what might happen in a single rain event. They argue that the

diversion of effort into developing complex models has not been fully justified, and that anyway the processes involved demand so fine a spatial and temporal resolution that not only would computers be hard-pressed to cope but more importantly the input data (meteorological data, emission data and boundary-value data) would be totally inadequate no matter how much effort was expended. They further point to the apparent success of linear models, such as those of Eliassen and Saltbones (1983), Fisher (1978) and Smith (1981). These models produce annual deposition fields which agree favourably with the observed depositions currently measured at the European network of stations operated within the EMEP European Monitoring and Evaluation Programme (Eliassen and Saltbones, 1983). Such discrepancies as there are can usually be explained in terms of the role of extra-European background contributions, uncertain emission data, systematic biases in the monitored data introduced by certain analytical techniques, and the effect of surface layer stability on dry deposition processes which is inadequately allowed for in these rather simple models.

In the following sections of this paper an attempt is made to consider how effective the stochastic nature of meteorological events (and in particular of rainfall) is in minimising the long-term influence of the essential non-linearity of the wet-deposition process. Since the exact nature of the non-linearity is dependent on many factors, including the availability of oxidants and how quickly they can mix into industrial plumes, no attempt will be made to model this in any exact sense. Instead a purely arbitrary relationship between the wet deposition rate and the incident air concentration will be assumed. The relationship can be made as strongly non-linear as required by adjusting a single parameter ϵ . Although fictitious in form it is postulated that the deviations from linearity in the long-term consequent depositions will be fully representative of those to be expected from real-life relationships. In the same vein other gross simplifying assumptions will be made, on the premise that these will have negligible effect on the issue under investigation. These assumptions are:

- (i) the wind speed, wind direction and mixing depth will be held constant,
- (ii) dry synoptic regions and wet synoptic regions (where the probability of rain is relatively high) advect past the source areas and have time-scales which are statistically determined, both in an Eulerian sense at a fixed point, or in a Lagrangian sense following elements of polluted air within the mixing layer. The duration of such regions is assumed controlled by a Markov-type process along exactly the same lines as first postulated by Rodhe and Grandell (1972), and later by Smith (1981), to whom the reader is directed for fuller details.

Such a model should provide a basis for studying the consequences of non-linearity, except in one important respect. If orographic rain is particularly important in a particular location (e.g. the West Highlands of Scotland) then the Markovian assumption must be invalid there and the ensemble of depositions

over a long period of time will be biased to some degree towards the upwind end of the "deposition footprint", rather than be randomly disposed across it. Neglecting this exception (treated in Sec 5), the results of the model will illustrate the importance or otherwise of non-linearity by assuming different values of ϵ .

3. MODEL 1.

3.1 Mathematical Analysis

(i) Firstly we consider some simple properties concerned with the succession of wet and dry regions (or periods, if thought of in terms of time).

If p = the probability of leaving a dry region and entering a wet region in the next hour (relative to a parcel of polluted air within the mixing layer), then considering hourly steps in time T , the probability of change occurring between $T = 1$ and $T = 2$ is $(1 - p)p$ and between $T = r$ and $T = r + 1$ is $(1 - p)^r p$.

If p is fairly small the probability distribution approaches an exponential distribution pe^{-pt} . The mean time of change is thus $\int_0^\infty pt e^{-pt} dt = 1/p$. Since the mean square time is $\int_0^\infty pt^2 e^{-pt} dt = 2/p^2$, the standard deviation about the mean is also $1/p$.

The average duration of dry spells $= \frac{1}{p} = \frac{\sum nT}{\sum n} = \bar{T}$

where n is the number from a large sample that changed in the T th hour.

The average duration of a dry period "landed in" $= \frac{\sum (nT)T}{\sum nT} = \frac{T^2}{T} = \frac{2}{p}$ and the average duration to the end of the period from the time of "entry" which is not necessarily the beginning of the period, is $\frac{1}{2} \times \frac{2}{p} = \frac{1}{p}$.

(ii) Supposing the emissions from all sources are steady and continuous, then if x represents the distance downwind from some arbitrary origin, let $q_D(x)$ be the statistical average amount of sulphur dioxide at distance x associated with dry periods, and $q_W(x)$ the amount associated with wet periods. Of course $q_D(x)$ and $q_W(x)$ do not co-exist at any one time, but are average amounts after integrating across many dry and wet periods.

To accentuate the effect of non-linearity in the wet-removal processes we will deliberately neglect the rather slow oxidation of sulphur dioxide to sulphate in the gas phase. Consequently only two equations need to be considered, one each for $q_D(x)$ and $q_W(x)$, unlike in Smith (1981) where four equations were required, two being for sulphate.

Dry deposition of sulphur dioxide is included as well as the exchange of q_D and q_W on a statistical basis to represent the onset of different kinds of region. The two equations are:

$$\frac{dq_W}{dt} = s_D q_D(x) - s_W q_W(x) - \frac{v_d}{h} q_W(x) + \frac{s_D}{s_D + s_W} S(x) - \Lambda(q_W) \lambda q_W$$

$$\frac{dq_D}{dt} = -s_D q_D(x) + s_W q_W(x) - \frac{v_d}{h} q_D(x) + \frac{s_W}{s_D + s_W} S(x)$$

where $\frac{d}{dt}$ = the Lagrangian rate of change following the polluted air

v_d = the deposition velocity

h = the constant mixing depth

$s_D = p_{\text{dry}} = \frac{1}{T_D}$, $s_W = p_{\text{wet}} = \frac{1}{T_W}$ are the exchange probability scales

$S(x)$ = the source strength at position x

$\frac{s_W}{s_D + s_W}$ = the fraction of time the point x is within dry periods

$\frac{s_D}{s_D + s_W}$ = the fraction of time the point x is within wet periods

λ = the average rainfall rate in the wet regions in mm h^{-1}

$\Lambda(q_W)$ = the rain-out removal coefficient for q_W .

The equations will be solved along a line of gridsquares disposed along the direction of the constant wind. The size of the gridsquares is selected so that it takes a single timestep of 15 minutes to cross one square, and 16 such timesteps to cross one of the EMEP gridsquares ($150\text{km} \times 150\text{km}$). These requirements are consistent with a mean wind $u = 10.417 \text{ ms}^{-1}$ and a gridlength of $\frac{150}{16} = 9.4 \text{ km}$.

The choice of h is rather arbitrary but a value of 800 metres may be considered typical of European conditions associated with significant deposition. The deposition velocity v_d is taken to be 0.01 ms^{-1} in general accord with measured values. The values of $T_D = 40$ hours and $T_W = 8$ hours are taken from Smith (1981). s_D and s_W are therefore 0.025 h^{-1} and 0.125 h^{-1} respectively.

The emission term will assume the source strength is uniform over any EMEP grid square and therefore will be at a single magnitude over 16 consecutive time-steps. If the emission of SO_2 over the EMEP square is $b \times 100$ thousand tonnes per year (where in an industrialised region b will typically lie between 1 and 5), the resulting increase in concentration within a single 15 minute timestep will be

$$\Delta q = \frac{b \times 100 \times 10^3 \times 10^{12}}{365 \times 24 \times 4 \times 150 \times 150 \times 10^6 \times 800} = 0.15856 b \text{ } \mu\text{g m}^{-3}$$

subdivided, as in the equations, between q_D and q_W .

Finally let us consider the wet deposition term $-\Lambda(q_W)\lambda q_W$. The average rainfall rate λ can be related to the total annual rainfall R (mm) by

$$\lambda = \frac{s_D + s_W}{s_D} \frac{R}{365 \times 24} \quad (\text{mm h}^{-1})$$

since rain only occurs in wet periods. The true nature of $\Lambda(q_W)$ is unknown, but should express the nett effect of all the complex non-linear chemical reactions and physical processes that affect the oxidation and uptake of 'sulphur' into the raindrops. If the sum effect at low q_W concentrations implies a virtually linear relationship between wet removal and SO_2 concentration, then Λ is a constant $= \Lambda_c$, which Fisher (1978) has estimated to be 0.34 mm^{-1} . At higher values of q_W the wet removal rate is expected to fall below $\Lambda_c \lambda q_W$ and we therefore assume, rather arbitrarily, that

$$\Lambda(q_W) = \frac{\Lambda_c}{1 + \epsilon q_W}$$

where ϵ is the non-linearity parameter.

In a 15-minute timestep the implied change in concentration is therefore:

$$q_W = 0.0408 \frac{q_W}{1 + \epsilon q_W}$$

If the equations are solved using a simple forward-difference scheme they become:

$$q_W(N+1) = 0.9575 q_W(N) + 0.00625 q_D(N) + 0.02644 b(N) - 0.0408 \frac{q_W(N)}{1 + \epsilon q_W(N)}$$

$$q_D(N+1) = 0.9825 q_D(N) + 0.03125 q_W(N) + 0.1325 b(N)$$

where $q(N)$ refers to the concentration at the N th timestep.

These simple linear marching equations are very simply solved when $b(N)$ and ϵ are specified. $b(N)$ is entirely within our own choosing in this simple test of non-linearity. Usually b will be given a non-zero value in only a few 150-km squares, and often in just one.

ϵ will be given values ranging from zero (the linear case) to 1 (extreme non-linearity). The effect of ϵ on the wet deposition is shown in Figure 1. If we imagine the real concentration is $30 \mu\text{g m}^{-3}$, say, and constant, the value of q_W is $\frac{S_D}{S_D + S_W} \times 30 = 5 \mu\text{g m}^{-3}$. The effect of ϵ is to reduce D , the annual wet deposition in $\text{g m}^{-2} \text{a}^{-1}$, from about 5.8 when $\epsilon = 0$, to 3.5 when $\epsilon = \frac{1}{8}$, to 2.5 when $\epsilon = \frac{1}{4}$, to 1.6 when $\epsilon = \frac{1}{2}$ and to 0.95 when $\epsilon = 1$.

3.2 Results

The results are portrayed in Figures 2 - 5. In Figure 2 a single EMEP 150km grid-square was assumed to emit SO_2 , the annual emission being 400 thousand tonnes. All other squares had zero emissions. The units of N are 150km in distance, or 4 hours in time of travel (i.e. 16 actual timesteps). The ordinate is the total deposition (wet plus dry) in $\text{g m}^{-2} \text{a}^{-1}$ under the assumptions made in our model. Curves are presented for four different values of ϵ ; $\epsilon = 0$ corresponds to the linear state while $\epsilon = 1$ is strongly non-linear. At small N the effect of non-linearity is to decrease the deposition whereas beyond about $N = 2.7$ the reverse is true. The amazing aspect of the Figure is the apparent insensitivity of the deposition to ϵ , except perhaps at very small N . This insensitivity cannot be explained away in terms of the precise form of $\Lambda(q_W)$, any reasonable form for Λ would produce very similar curves. The reason must lie in the smoothing-out effect caused by the stochastic nature of the wet and dry periods.

Figure 3 illustrates the effect of distributing a given emission over two 150km squares, rather than just one. The non-linearity is expressed by $\epsilon = 0.5$. Provided the sources for the two solutions are centred at the same point, the solutions are virtually identical outside the source squares. The same is true even if the emission is spread over a greater number of squares.

In the debate over what should be done to curb the effects of "acid rain", anxiety has been expressed that if industry goes to the enormous expense of reducing emissions, by $X\%$ say, then it may be found that depositions in sensitive

areas may not be reduced by $X\%$ but only by some fraction of $X\%$, and that the whole effort may appear very inefficient. Two points need to be made. Firstly many sensitive areas of N. W. Europe are subject to total depositions having a large "background" contribution, i.e. much of the deposited sulphate comes at low concentrations in rain coming preferentially off the Atlantic. It is possible, if not probable, that this sulphate would not be significantly affected by reductions in European emissions. In this sense an overall reduction in European emissions would not produce an equivalent reduction in depositions in these areas.

Secondly if one could 'tag' emissions from a given source and see where they are deposited, then the conclusion from this paper is that a reduction in these emissions would produce an almost proportional reduction in the related depositions. This is illustrated in Figures 4 and 5. Figure 4 shows the effect of halving emissions on depositions for $\epsilon = 0.5$ and a range of b , the source strength. Except within about 500km, the resulting depositions are actually less than 50%, not more. In other words, non-linearity actually enhances the benefits to be gained from reducing emissions, unless the sensitive area is very close to a major source area. The enhancement is fairly small but increases with the magnitude of the emissions. Figure 5 shows how the reduction in total deposition is split between wet deposition and dry deposition (for $\epsilon = 0.5$ and $b = 4$). Dry deposition shows an enhanced reduction at all values of N . The reason for this is easier to see in the reverse sense: doubling emissions would initially double air concentrations so that when rain occurred the non-linearity effect would tend to leave proportionally more sulphur unaffected and the subsequent dry deposition would be more than doubled.

The wet deposition is affected by non-linearity in a more complex way. Out to about 800km, a less than proportional reduction is experienced because of the non-linearity, but beyond that the resulting decrease in air concentration causes a greater than proportional reduction.

3.3 Conclusions

The method employed here demonstrates at least qualitatively how basic non-linearity in the uptake and oxidation processes involved in "acid rain" affect the long-term deposition fields. Although the model has used simplifying assumptions (e.g. constant wind speed and direction, constant mixing depth) the essential nature of the non-linearity has not been lost. The total deposition fields reflect the stochastic nature of rainfall, and the results strongly indicate that this "smooths out" the non-linear characteristics and produces a quasi-linear relationship between emissions and depositions. Relaxation of the simplifying assumptions would increase the smoothing and the approach to linearity.

4. MODEL 2.

4.1 Mathematical Analysis

Model 1 is perhaps deficient in one respect: when material is transferred from wet to dry regions (or dry to wet), it is assumed in one sense to be mixed in with the material already existing within the region so that only a single concentration q_D (or q_W) is considered. In an entirely linear model this does not matter but in a strongly non-linear model this could produce a systematic error. Model 2 attempts to overcome this deficiency.

The new model is based on exactly the same equations and the same representation of non-linearity. However the equations are solved in a different manner which enables a spectrum of concentrations associated with elements with differing past-history to be followed. The spectrum changes with time, or distance, of travel as the ensemble of possible histories grows. In this way the consequences of non-linearity can be simulated more realistically.

Consider Figure 6, which illustrates how the solution takes place. It is assumed that at the source the emitted SO_2 is mixed uniformly throughout the mixing layer and produces a concentration which depends on the magnitude of the emission and meteorological parameters such as wind speed and mixing depth. For illustrative purposes it will be assumed that this concentration is $25 \mu g m^{-3}$, typical of concentrations immediately downwind of the UK Midland source region. This concentration applies to both the fraction D which is emitted into dry regions and to the fraction $W = 1-D$ emitted into wet regions. These fractions are obviously related to S_D and S_W . They were taken to be 5/6ths and 1/6th respectively.

In a single time step various things happen to the SO_2 in each region. Dry deposition reduces the concentration in both regions; wet deposition further reduces the concentration in the wet regions. Exchanges take place between regions but these exchanges in themselves do not result in a change in concentration. Oxidation of SO_2 to sulphate must also occur but as in Model 1 this aspect is provisionally ignored in order to keep the investigation as simple as possible. Clearly it is no difficult step to expand the analysis to include oxidation.

Thus in Figure 6 we see these processes taking place within a time step. The vertical line of cells have associated fixed concentrations (dependent on the choice of the initial concentration). These concentrations are determined as follows: $C(I+1)$ is equal to the concentration an element would achieve at the end of a timestep as a result of the appropriate deposition processes having started the timestep with a concentration $C(I)$.

Note that $C(I + 1)$ is always less than $C(I)$, and that the drop in concentration is always greater in wet regions than in dry because of the additional affect of wet deposition. The arrows show how material and concentrations change during a single time-step. Because of the exchanges the number of concentration-boxes occupied by material grows with time: the spectra broaden and shift towards lower concentrations (greater I). In the exchanges concentrations in one region may not find an identical corresponding concentration on the other, so material has to be fed into the box with the closest correspondence, taking into account that during the exchange the deposition processes will continue to play their part.

It is appropriate at this point to note that in this model we are dealing much more with concentrations rather than total amounts of material associated with dry and wet regions as in the first model. Consequently the non-linear wet deposition term acts on each box and its associated concentration C : wet deposition $\propto \frac{C}{1 + \epsilon C}$, and appropriate values of ϵ now range from 0 to 0.1, see Figure 7. In the solution amounts of S-material associated with each box have to be determined as a function of time or distance of travel. The sum over the boxes of the products of amount times concentration yield the total amount of airborne material and hence, by time-differencing, the magnitude of the deposition.

4.2 Model 2 results

In solving the model rather long 30-minute time-steps were assumed and this causes some small scatter in the output data. However no significant bias is anticipated. Figure 8 gives the result for three different values of ϵ , the non-linearity parameter. The abscissa is the number of timesteps or the downwind distance in kilometres. The curves are very similar in shape to those in Figure 2 (remembering the different ordinates) and the implications regarding the importance of non-linear processes to long-term depositions are identical.

Figure 9 corresponds directly with Figure 4, showing the effect on depositions of halving emissions. Again a small enhanced "benefit" is seen beyond about 450 km.

4.3 Sensitivity Studies

Specific values of the various parameters that occur within the model have been chosen and held fixed in the model-results presented above. Some of our conclusions may be intimately tied to these values and before we can

generalise our understanding it is necessary to explore the consequences that arise when the parameters are given other values. The results are presented in Figures 10 to 15.

- (i) Firstly we explore the consequences of allowing the non-linearity parameter ϵ to vary over a much wider range than hitherto. Figure 10 shows the effect on the total deposition with time of travel N as ϵ varies from 0 to an extremely high value of 10. Note the deposition is plotted on a log-scale.

At small N , increasing ϵ decreases the rainout term and so the total deposition falls. Beyond about $N = 30$ (corresponding to about 500 km in a 10 ms^{-1} wind) the effect reverses and the depositions with the higher values of ϵ are slightly higher than those with lower ϵ . This is because as the air concentrations drop the influence of ϵ decreases and the higher depositions are associated with situations which have lost less material at small N . The full solutions (with $C_0 = 25 \text{ } \mu\text{gm}^{-3}$ and $12.5 \text{ } \mu\text{gm}^{-3}$) show that quasi-linearity in long-term depositions occur over the full range of ϵ (see later).

- (ii) A concentration of $25 \text{ } \mu\text{gm}^{-3}$ is generally typical of SO_2 concentrations immediately downwind of England. Bedded within this there may be "urban" plumes in which the concentration may be as high as $100 \text{ } \mu\text{gm}^{-3}$ (approximately = 35 ppb). Figure 11 shows that previous conclusions are hardly changed by choosing $C_0 = 100$. Depositions are increased virtually pro rata.
- (iii) In section (3.1) the rain-out removal coefficient Λ_0 (for small q) was given the value 0.34 mm^{-1} , following Fisher (1978). To test the sensitivity of the results to this value, Λ_0 was put equal to 0.34 L mm^{-1} and L was varied from 1 to 10 in the calculations. Figure 12 shows the consequences. Except at small N , where, as expected, a direct relationship between deposition and L exists, the effects are rather small. Increasing L , beyond about $N = 20$, causes a decrease in deposition because of the accumulated effect upstream on the total amount of material remaining in the air.
- (iv) Earlier calculations strongly pointed to an approximate linearity between long-term total depositions and C_0 (or the emissions). Figure 9 illustrates this. Note that two parameters characterise the curve, namely N_E , the value of N beyond which a slightly enhanced benefit is realised when emissions are halved, and D_∞ , the percentage

deposition experiences at large N when emissions are halved. The next three figures (13, 14 and 15) describe the sensitivity of N_E and D_∞ to ϵ , L , T_D and T_W .

Figure 13 shows the influence of ϵ . At very small ϵ , the non-linearities are negligible and halving the emissions halves the depositions so that $D_\infty = 50$. At very large ϵ , the wet deposition becomes very much smaller than the dry deposition (if L is held at 1). Since the dry deposition is linear, D_∞ must approach 50 again. Only at reasonable values of ϵ does a significant enhancement occur, corresponding to $D_\infty < 50$. The maximum effect appears to occur in the neighbourhood of $\epsilon = 0.4$. If L is increased as ϵ increases to maintain the importance of the wet deposition term then, as Figure 14 suggests, the value of D_∞ is still maintained very close to 50, implying a very close approximation to linearity.

Figure 14 also shows that as L increases the value of N beyond which enhancement occurs decreases. This is presumably because the large initial wet removal reduces concentrations to the level where the non-linearities are relatively unimportant and the deposition reflects the lower concentrations.

Figure 15 considers the influence of the timescales T_D and T_W , for dry and wet periods respectively, on the parameters D_∞ and N_E when $C_0 = 25 \mu\text{gm}^{-3}$, $L = 1$ and $\epsilon = 0.1$. The values used in the rest of the paper have been $T_D = 40$ hours and $T_W = 8$ hours, following Rodhe and Grandell (1972). These values are represented by the large dot in the centre of the figure. The contour lines for D_∞ and N_E show that these parameters are relatively insensitive to large changes in T_D and T_W .

In conclusion then, it appears that the model results are rather robust to fairly large changes in the input parameters (except of course the emission magnitude itself). This leads to a good degree of confidence in the conclusions regarding quasi-linearity between emissions and long-term deposition fields.

5. THE EFFECT OF OROGRAPHIC RAIN

Earlier we noted that areas of high orographic rainfall might be regions where these general conclusions breakdown. This can be tested by a very simple device. The coefficient of the non-linear wet deposition

term is proportional to the average rainfall rate. If this is doubled, say, this is equivalent to doubling the annual rainfall which is probably the main consequence of a range of mountains. ("Doubling" of course is just an arbitrary choice: the mountains may have a greater or a smaller effect than this). This doubling of the coefficient can be introduced into the solution for specific values of N (the time-step number) to simulate the interception of the plume with a fixed mountain range. Figure 16 illustrates the effect on the total average deposition field. Note that depositions are not doubled: dry depositions are not directly affected and wet depositions are most important on "dirty" air that has just exchanged from dry regions whereas much of the rain falls in relatively cleansed air that has been subject to rain for some time upwind. The depositions fall below no-hill values in the lee of the hills as expected, but overall the effects are not enormous. Figure 17 shows the effect of the mountain range on the reduction in depositions resulting from halving emissions within Model 2. The effect is very small being everywhere less than 0.5%. This supports the overall conclusion that as far as long-term depositions are concerned, non-linear processes are not a significant problem.

6. EVIDENCE FOR LINEARITY IN EMEP DATA

6.1 Data

Emissions of sulphur dioxide from all UK sources have changed significantly between 1977 and 1982. Table 2 gives the annual emissions in millions of tonnes.

During this time many of the EMEP monitoring stations have been in continuous operation making daily measurements of (inter alia) rainfall and the concentration of sulphate within the rain. Recently the Meteorological Synthesising Centre-West at the Meteorological Institute in Oslo have made available a detailed daily sector analysis for all the monitoring stations. The analysis is based on the following:

- (i) trajectories arriving at the station are calculated using the 850 mb wind field and are calculated over a 96 hour period ending at the site at 12, 18, 00 and 06 GMT. The day referred to is the day of arrival of the first of these four trajectories.
- (ii) the trajectories were used to allocate a transport direction every day at each station. The directions were represented by transport sectors defined as follows: each sector is 45° wide. Sector 1 is centred on north, sector 2 on north-east and so on, eight sectors in all.

Starting with the positions of the four daily trajectories every hour, all positions closer to the station than 150 km and farther away than 1500 km are discarded. If more than half of the remaining positions are to be found inside one sector then the day is allocated to that sector, otherwise it is allocated to a "mixed" sector, sector 9.

Figure 18 shows that two Norwegian stations of high repute, N1 and N8, are positioned in southern Norway very close to the coast and with very little local pollution. From these stations the main source areas of the UK lie almost entirely within Sector 6. Thus on days allocated to Sector 6 we may expect that most of the sulphate in rain originates either from the UK itself or from "background" sources upstream of the UK or from the North Sea.

Both stations have continuous records available at this time stretching from October 1977 to September 1982. The analysis that follows attempts to investigate the relationship, if any, between the changing UK emissions and the concentration of sulphate in rain on days allocated to Sector 6 at N1 and N8, stations that are close to the ecologically sensitive area of southern Norway.

Such an analysis is fraught by unrelated variations in concentration that arise from the following causes:

1. errors in analysis of the sulphate concentration.
2. contamination of the sample by dry deposition and by "foreign" material (insects, bird-droppings etc).
3. the spatially inhomogeneous source-distribution within the UK which will be differently "sampled" by the trajectory on different occasions.
4. day-to-day, or season-to-season, variations in emissions not accounted for.
5. Occasional input from other European sources when the criterion for sector allocation is only just met.
6. the influence of meteorological variability such as mixing depth, wind speed, upstream rainfall etc.

These sources of uncertainty are very much in evidence in the data and make the detection of a real relationship between source strength and concentration difficult and somewhat uncertain.

Even a quick inspection of the data reveals:

- (i) a satisfactory correlation between the concentrations measured at the two stations when rain was recorded on the same day, particularly when (ii) is allowed for, implying local sources are having little influence.
- (ii) There is a strong inverse relationship between concentration and rainfall amount, so that high concentrations are normally only experienced in very light rain. This relationship is confirmed in the statistics presented below.

6.2 The statistical analysis

(i) Analysis of variance test

Concentration data were first categorised according to year (or, equivalently, emission) and to rainfall amount. Five year-bands running from October to September have been used: 1977/78, 1978/79, 1979/80, 1980/81 and 1981/82. Rainfall was divided into seven bands corresponding to: < 1 mm, 1-3 mm, 3-5 mm, 5-10 mm, 10-20 mm, 20-40 mm, > 40 mm.

The standard variance test requires consideration of the following identity:

$$\sum_i \sum_j (C_{ij} - \bar{C})^2 \equiv \sum_i k (\bar{C}_i - \bar{C})^2 + \sum_j h (\bar{C}_j - \bar{C})^2 + \sum_i \sum_j (C_{ij} - \bar{C}_i - \bar{C}_j + \bar{C})^2$$

where C_{ij} is the one-day concentration within the i^{th} rainfall category and the j^{th} emission band, \bar{C} is the average concentration over all the data, \bar{C}_i is the average concentration within the i^{th} rainfall category (over all years), \bar{C}_j is the average concentration with the j^{th} emission-band (over all rainfalls). In our case $k = 5$, $h = 7$. The first term on the right-hand-side has $h-1 = 6$ degrees of freedom whilst the second term has $k-1 = 4$ degrees of freedom. The third term represents the random errors with which the other two terms may be compared to form the F-ratio in the standard F-test.

For the N1 and N8 data the variances and the F-values are shown in Table 3.

As expected the concentration shows a very strong dependence on rainfall amount, and it is very highly improbable a value of $F = 18.9$ could have occurred by chance if there were no such dependence.

More importantly Table 3 shows that there is a less than 5% probability that the F value of 3.0 associated with emissions could have occurred if there were no dependence of concentrations on UK emissions.

This test does not show, however, that this dependence is a linear one. A pointer in favour of it being linear is given by repeating the analysis having first normalised the concentrations C_{ij} by E_j , the emission for the j^{th} year. If linearity is "true", then the F value associated with emissions should now not be significant. Table 4 confirms this.

(ii) Correlation tests

In general great caution has to be displayed in interpreting correlation coefficients deduced from rather small samples, and our present situation is no exception. None of the correlations deduced below are highly statistical significant. Nevertheless they point in the same direction as the conclusions reached in (i) above, and are certainly not inconsistent with a hypothesis of a linear relationship between emissions and associated long-term depositions, or even with single-event concentrations, once the random effect and the rainfall effects have been allowed for.

Many tests involving correlations and related probabilities can be applied. None which have been tried have contradicted or opposed our hypothesis, but at the same time none have been 100% convincing either. The simplest of these tests is to sub-divide the occasions into rainfall bands as in (i) above and then to correlate the mean concentration within each band and in each "year" with the associated emission.

The results, displayed in Table 5, show some rather interesting aspects. Firstly it appears that 1979/80 is rather anomalous. Secondly the correlation is best in the 1-3 mm rainfall band and worst in the 20-40 mm

band (Note that the < 1 mm band and the > 40 mm band have been excluded for reasons of insufficient data). The reasons for this are not entirely clear. One hypothesis is that the low rainfall band may be associated with orographically induced rain, implying little or no rain-out having affected the SO_2 between the UK and the Norwegian coast just upwind of the stations. The amount of sulphur in the air waiting to be washed out will then be much more closely related to what entered the air over the UK. Conversely the heaviest rainfall band would often be associated with widespread rain when much of the UK emissions will have been removed by rain-out upstream and what comes out in the rain at N1 and N8 may originate either from small local emissions or more likely from free-tropospheric sulphur drawn into the cloud, the sulphur having originated from very distant sources.

The final row in Table 5 shows the correlations between E_j and (E_j/\bar{C}_j) . If concentrations are linearly proportional to emissions then these correlations should ideally be zero, or allowing for the small number of degrees of freedom, without significance. This is certainly true in the numbers given.

6.3 Conclusions

To repeat what has already been said, the statistical tests generally support rather than contradict the hypothesis of a linear relationship. The support is not totally convincing however, but it puts paid, at least, to the statement sometimes made that there is no evidence of a relationship between emissions and depositions. Such statements are generally based on an inadequate analysis of the basic data.

It is opportune to finish with a timely reminder from Fisher and Clark (1985) that to hope to understand the emission-deposition relationship properly "a background concentration of sulphate similar to that suggested by the OECD study needs to be incorporated". This is confirmed, I believe, by the correlation found in the 20-40 mm rainfall band above.

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TABLE 1

Models for studying transport of air pollution

Model Type	Averaging Time	Computer Requirements	Application	Net Requirements	Verification
EMPIRICAL (e.g. Fisher, Klug, Smith, Venkatram)	≥ 1 yr	Small	FRESHWATER ACIDIFICATION Long-term deposi- tion fields Source/Reception budgets	Climatological data low resolution	KLUG Study (inter-model & v. EMEP)
LAGRANGIAN (e.g. EMEP models)	Seasonal	Quite large but acceptable	"	Normal Synoptic data	v. EMEP daily data
3-D EULERIAN (e.g. PHOXA model)	Episodic	Enormous	HEALTH-DAMAGE Ozone Studies	virtually beyond current availability	Some inter-model comparisons in America
DIAGNOSTIC	Event-based	variable	Studying specific aspects of problem	Research	-

Table 2 : Estimates of UK SO₂ emissions

Year	1977	1978	1979	1980	1981	1982
Emission (Mt/y)	4.98	5.02	5.34	4.67	4.23	4.00

Table 3 : Variances and F-values for the N1 and N8 data

Source of Variation	Term on rhs	Variances	F	F required for 5% 1%		Significance
Rainfall	1	$\sum_i k(\bar{C}_i - \bar{C})^2 / (h-1) = 5.75$	$\frac{5.75}{0.305} = 18.9$	2.51	3.63	HIGH
Emissions	2	$\sum_j h(\bar{C}_j - \bar{C})^2 / (k-1) = 0.90$	$\frac{0.90}{0.305} = 3.0$	2.78	4.23	< 5%
"Random"	3	$\sum_i \sum_j (C_{ij} - \bar{C}_i - \bar{C}_j + \bar{C})^2 / (h-1)(k-1) = 0.305$	-			

Table 4 : F-test analysis for C_{ij}/E_j

Source of Variation	F	Required F 5% 1%		Significance
Rainfall	17.7	2.51	3.68	HIGH
Emissions	1.31	2.78	4.23	none

Table 5 : Table of mean concentrations and correlations in Sector 6 at Norwegian EMEP stations N1 and N8 from 1977 to 1982. The years have been ranked in order of emission magnitude.

Year	Emission E_j	\bar{C}_{1-3}	\bar{C}_{3-5}	\bar{C}_{5-10}	\bar{C}_{10-20}	\bar{C}_{20-40}	
81/82	4.04	1.82	1.30	1.34	0.74	0.96	
80/81	4.32	2.86	1.19	1.01	0.87	0.73	
79/80	4.90	3.57	2.76	1.92	1.41	0.88	
77/78	5.00	3.13	1.07	1.45	0.77	0.57	
78/79	5.31	3.79	1.97	1.72	1.37	0.93	
Correlations between:							Average
\bar{C}_j and E_j		0.915	0.440	0.680	0.670	-0.160	0.51
$E_j/\sqrt{C_j}$ and E_j		-0.753	-0.114	-0.306	-0.327	0.512	-0.20

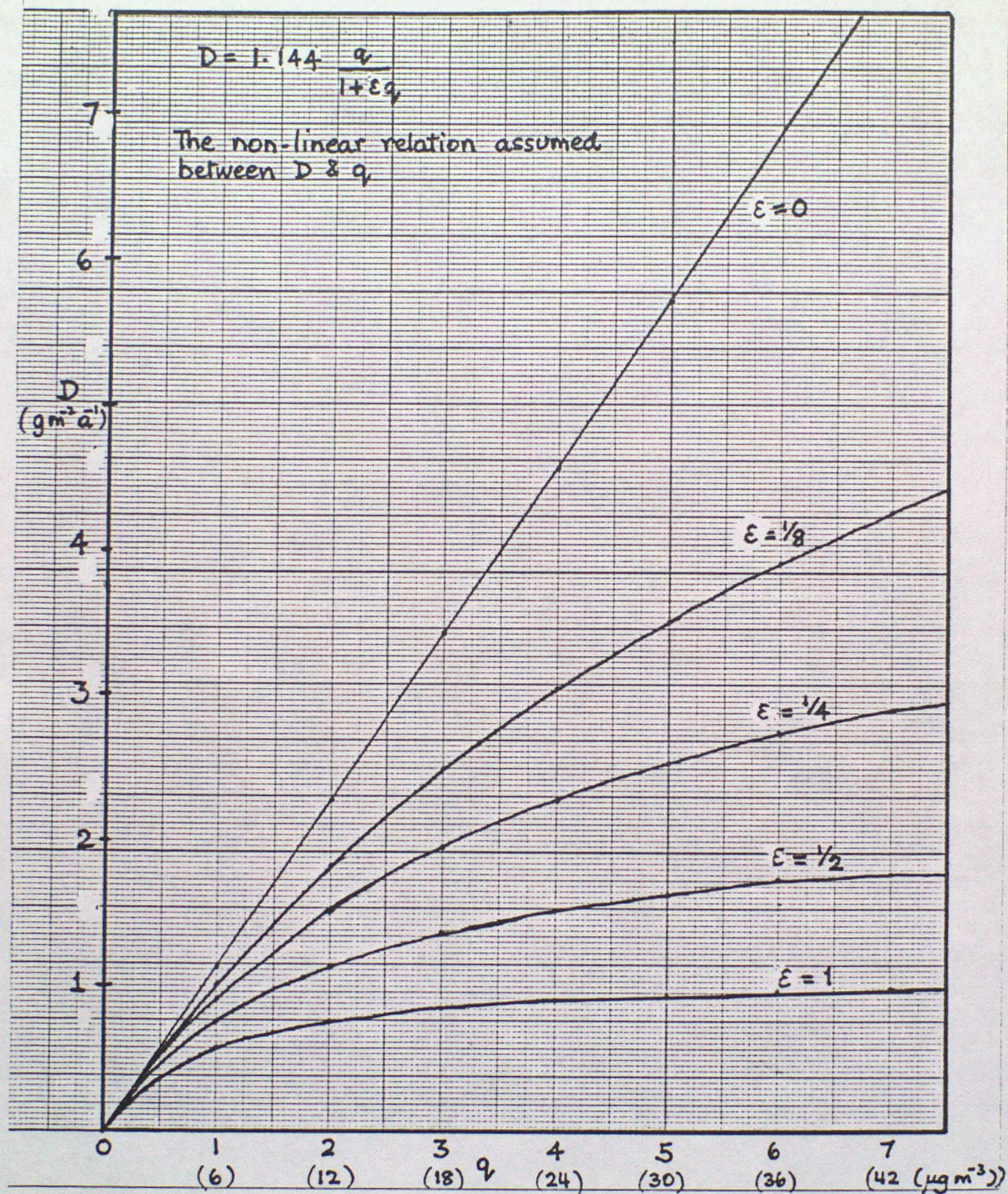


Figure 1.

The influence of the non-linearity parameter ϵ on the deposition rate in a single rain event. D is expressed as a function of q and ϵ .

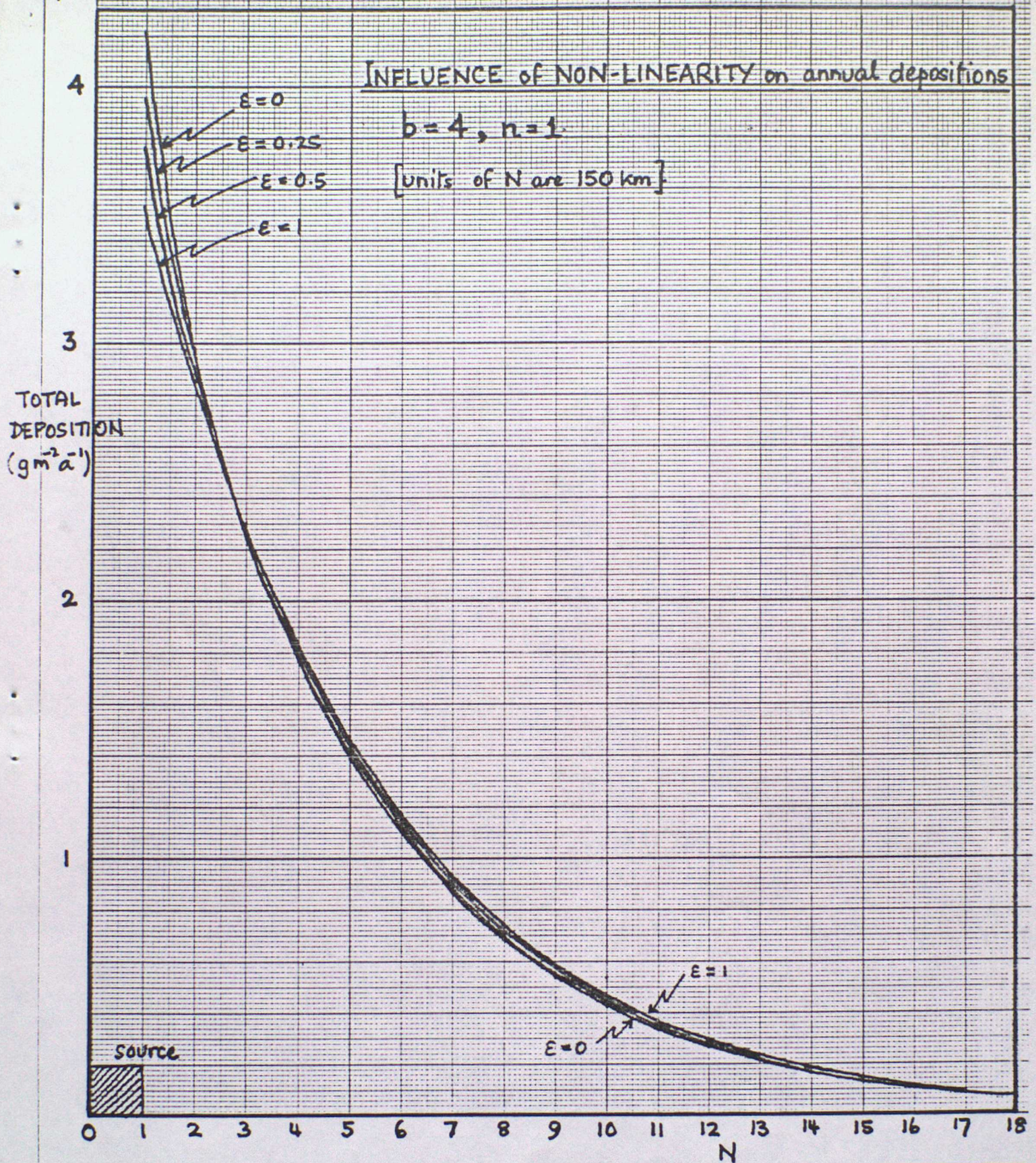


Figure 2. This figure illustrates the insensitivity of the long-term deposition field downwind from a source to the value of ϵ , the non-linearity parameter.

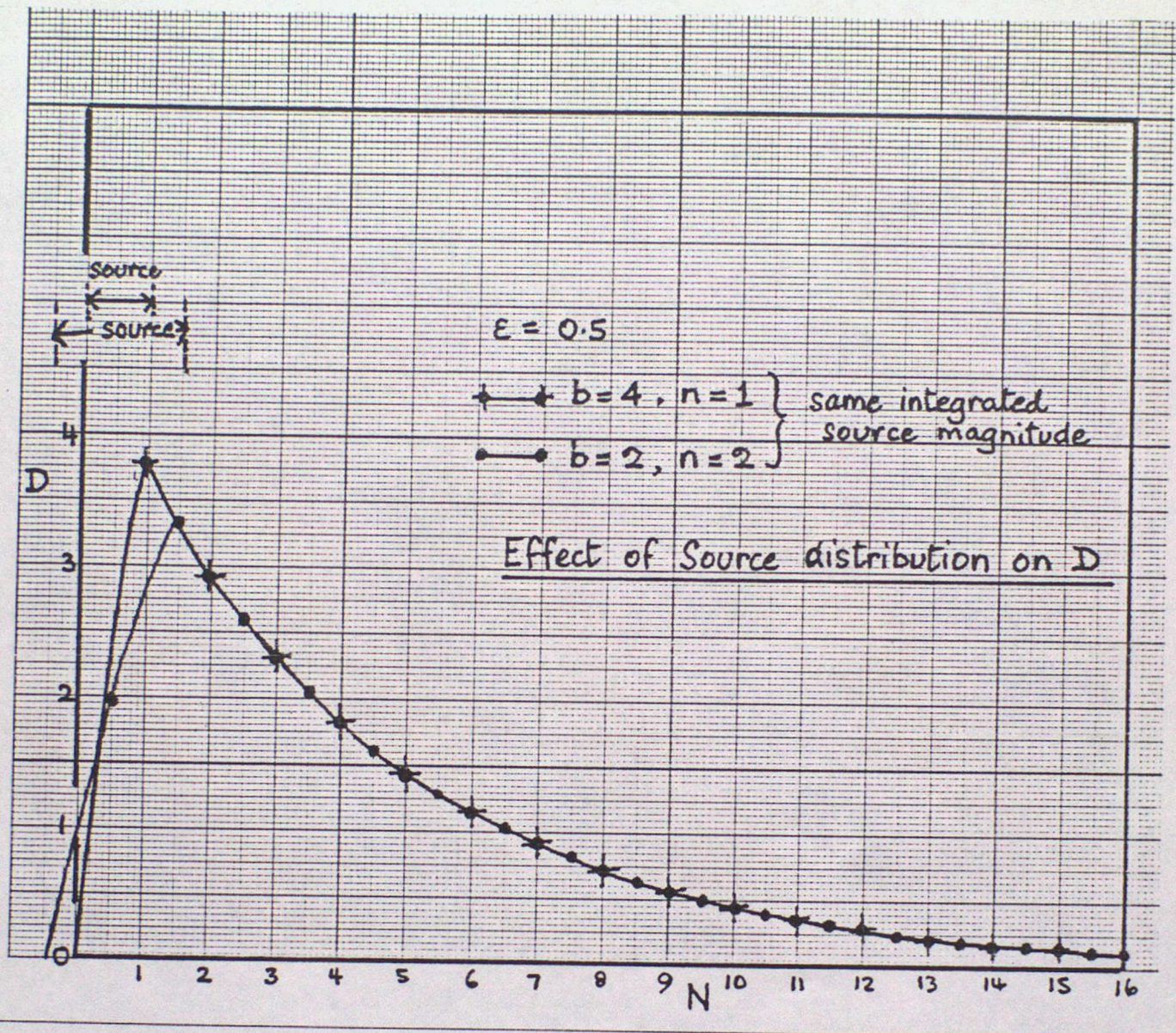


Figure 3. This Figure shows that outside the source region the depositions D are very insensitive to the way the emissions are distributed within the region.

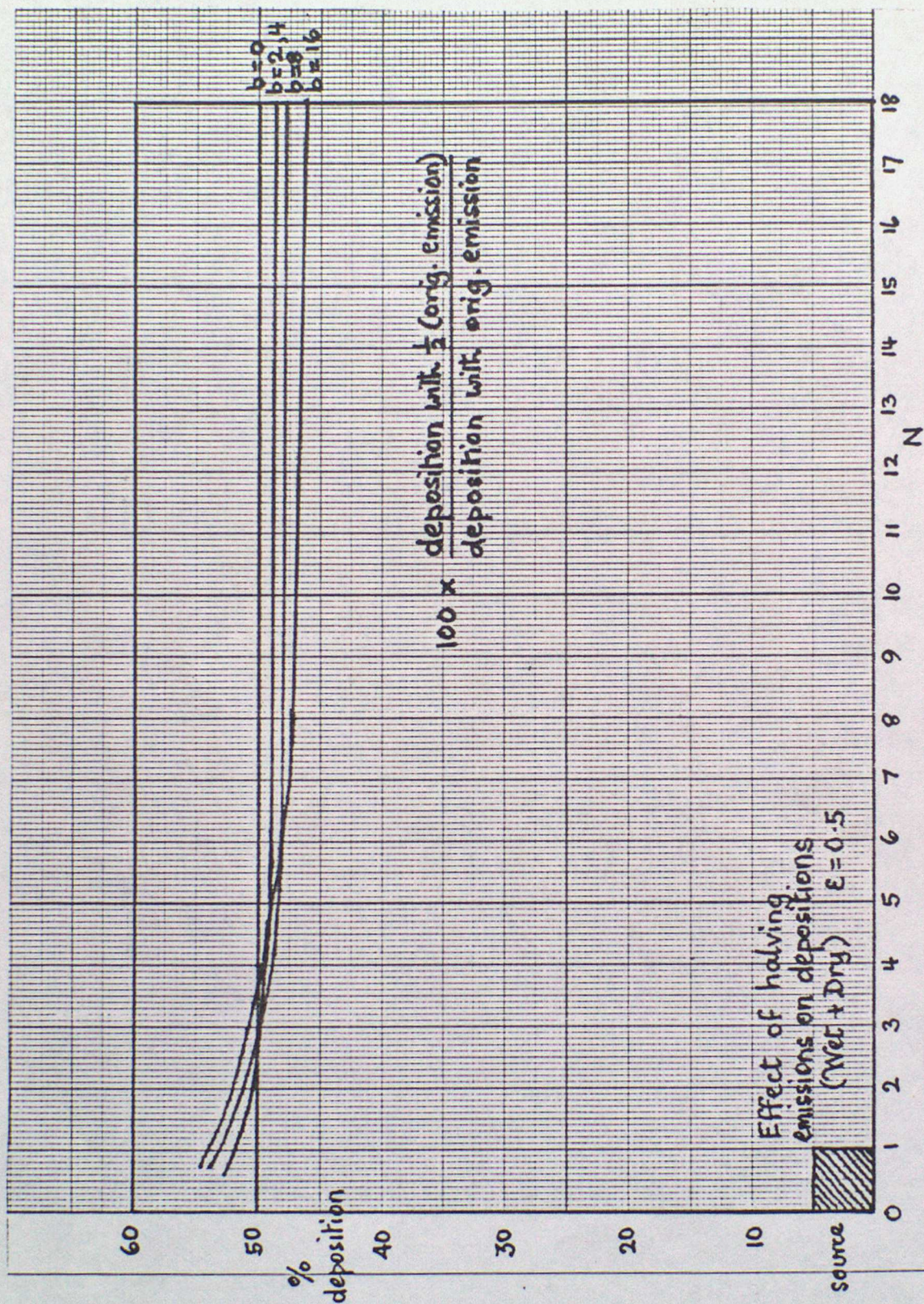


Figure 4. The effect of halving emissions produces almost 50% reduction in deposition. Beyond $N=4$ an enhanced reduction is achieved which increases with b , the source strength.

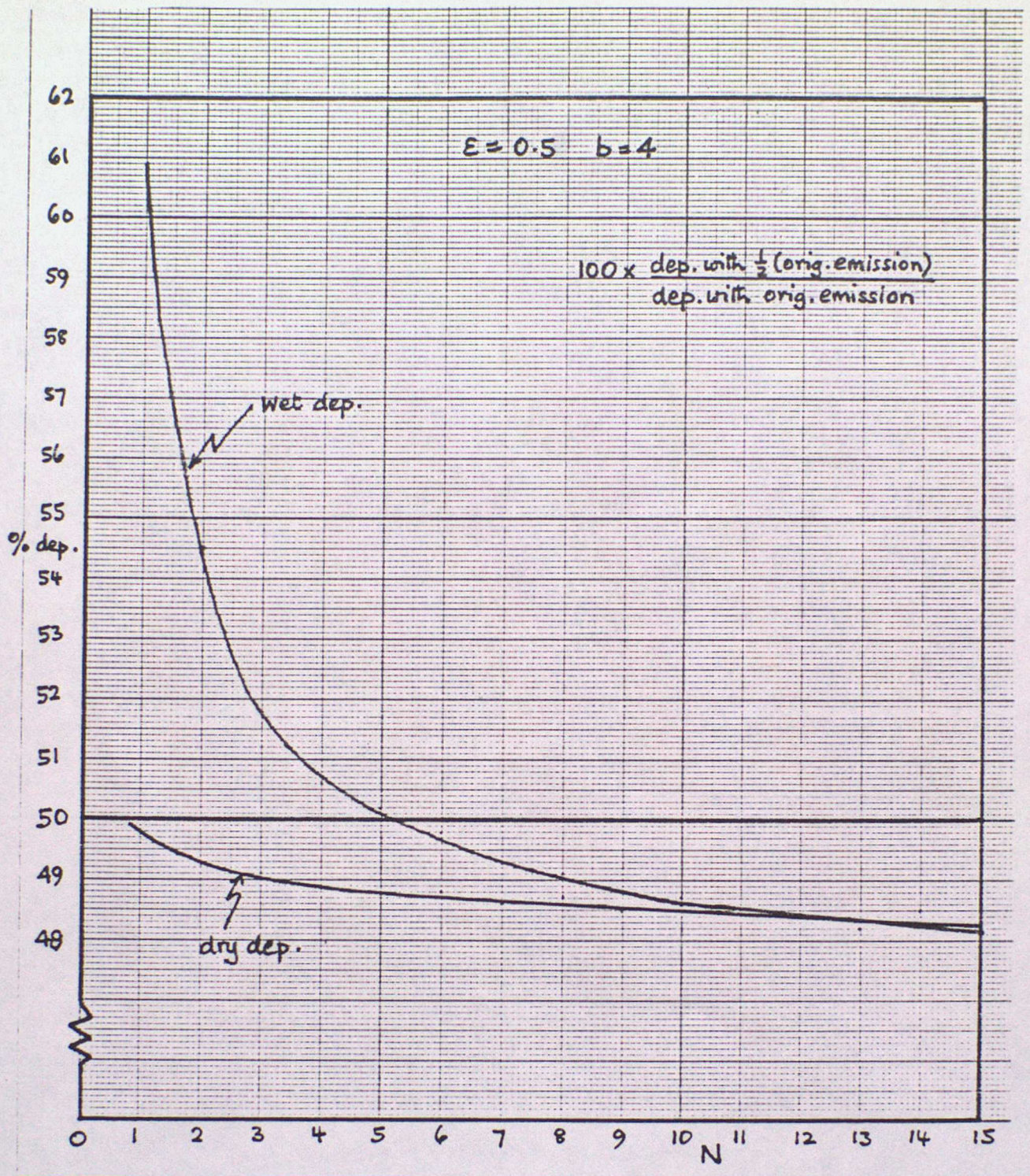
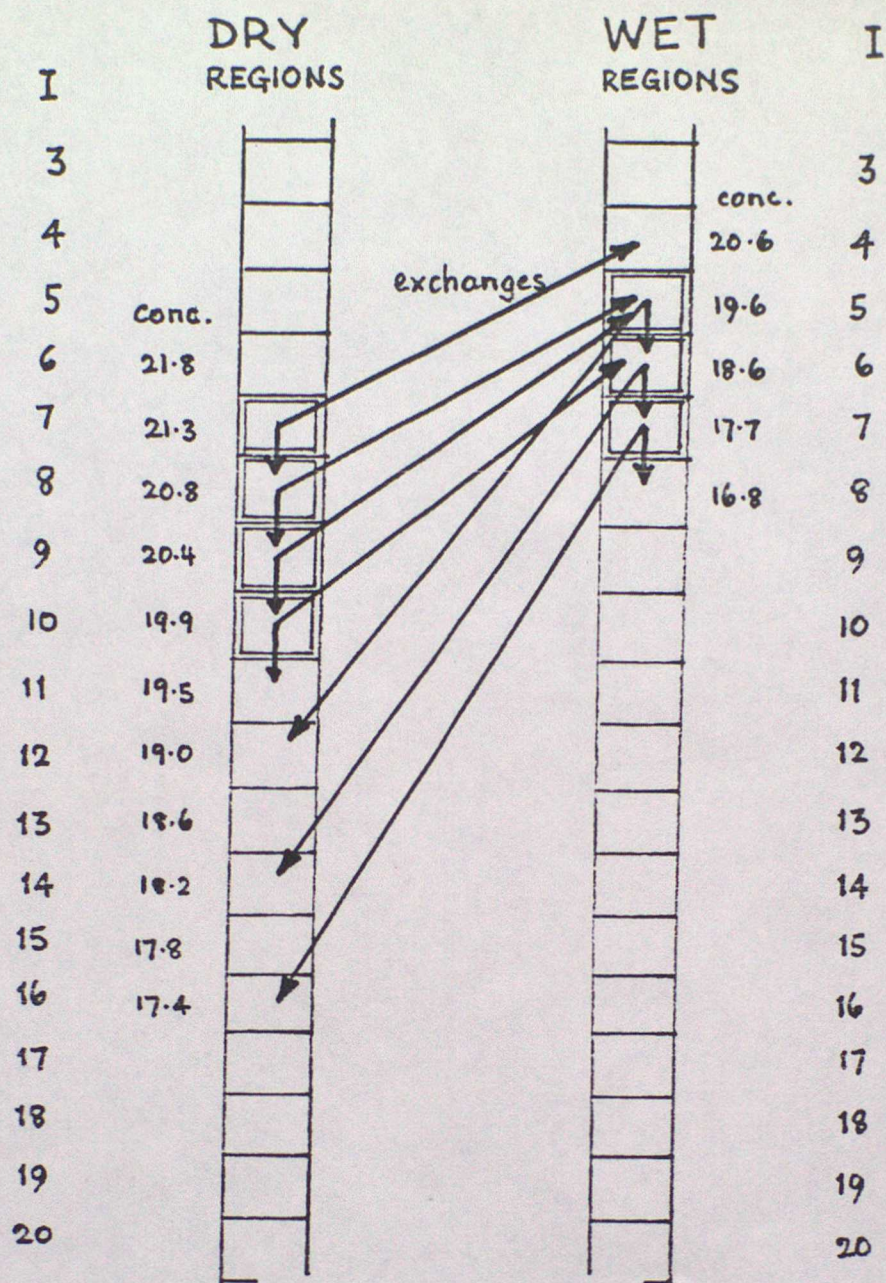


Figure 5. Non-linearity causes enhanced reduction in deposition when emissions are halved for dry deposition (all N) and for wet deposition ($N > 5.2$)

Spectra of
Concentrations
within the two
regions at a
given Time-step
(Schematic only)



The spectra are so chosen that within any one time-step the concentration in box I is reduced by dry and wet deposition to the concentration in box I+1. Material undergoing region-exchange enters at I', where the concentration is appropriate to the depositions experienced, and where

$I' > I+1$ if the move is from Wet to Dry

but $I' < I+1$ if the move is from Dry to Wet, as shown in the Figure.

Figure 6.

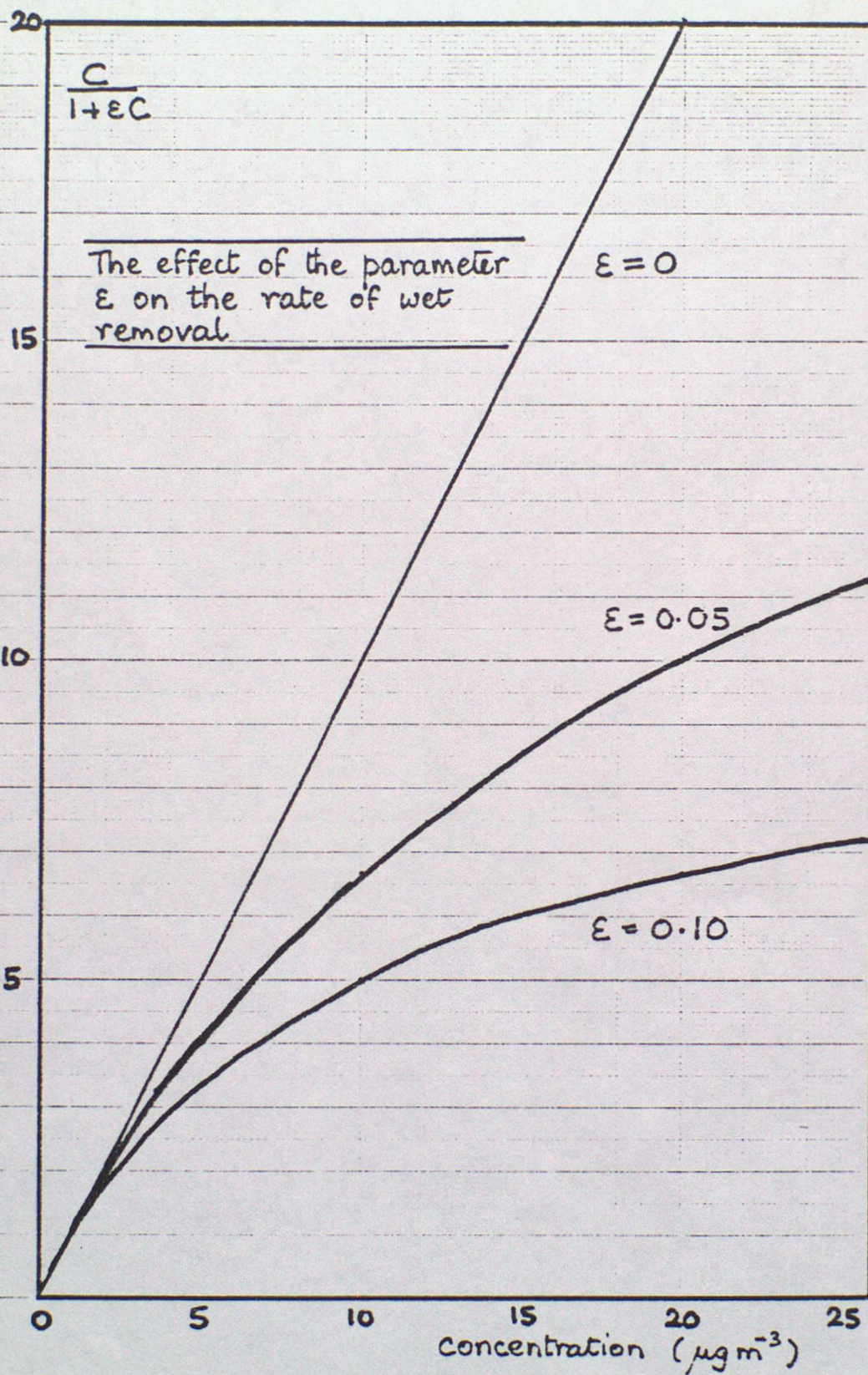


Figure 7.

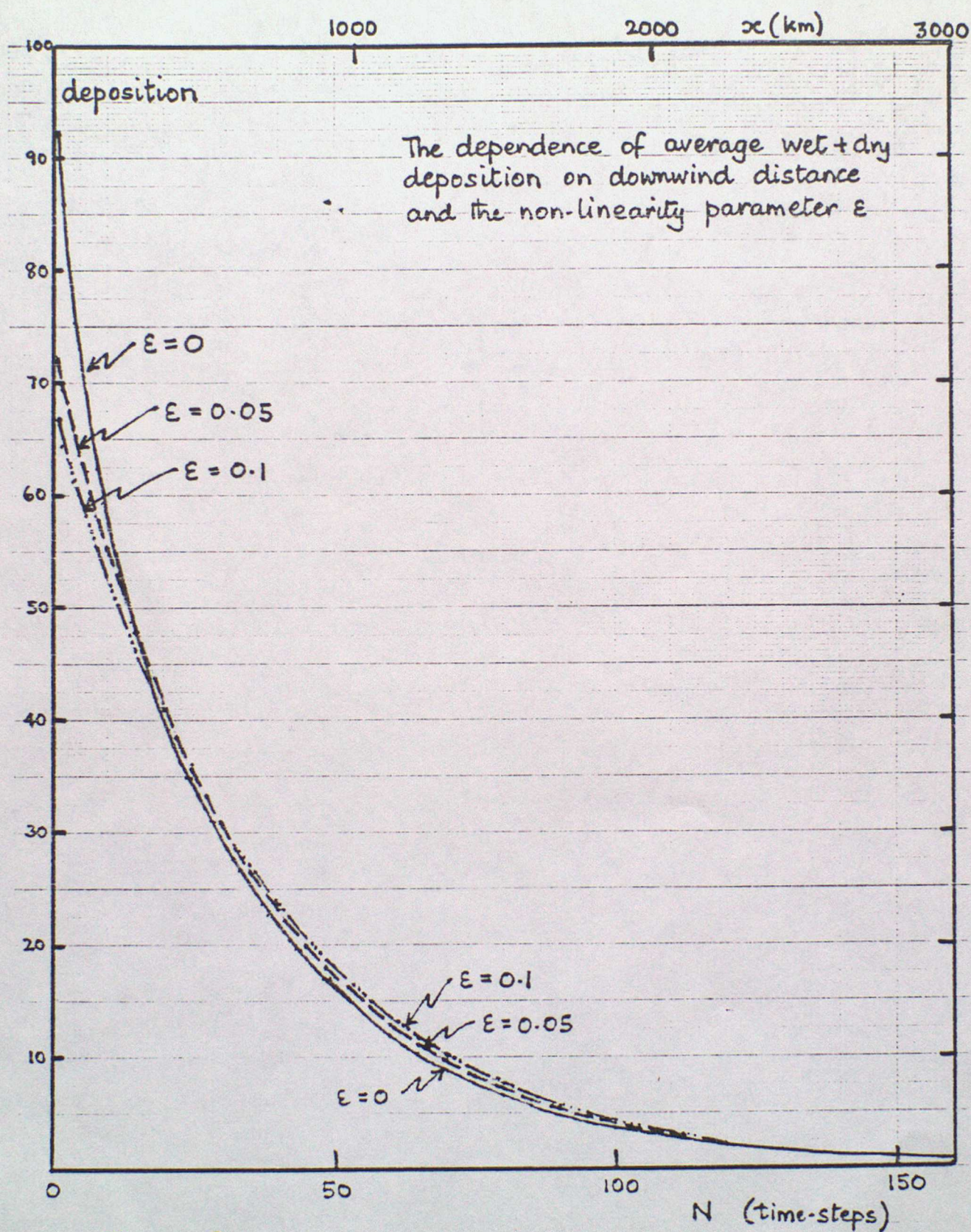


Figure 8.

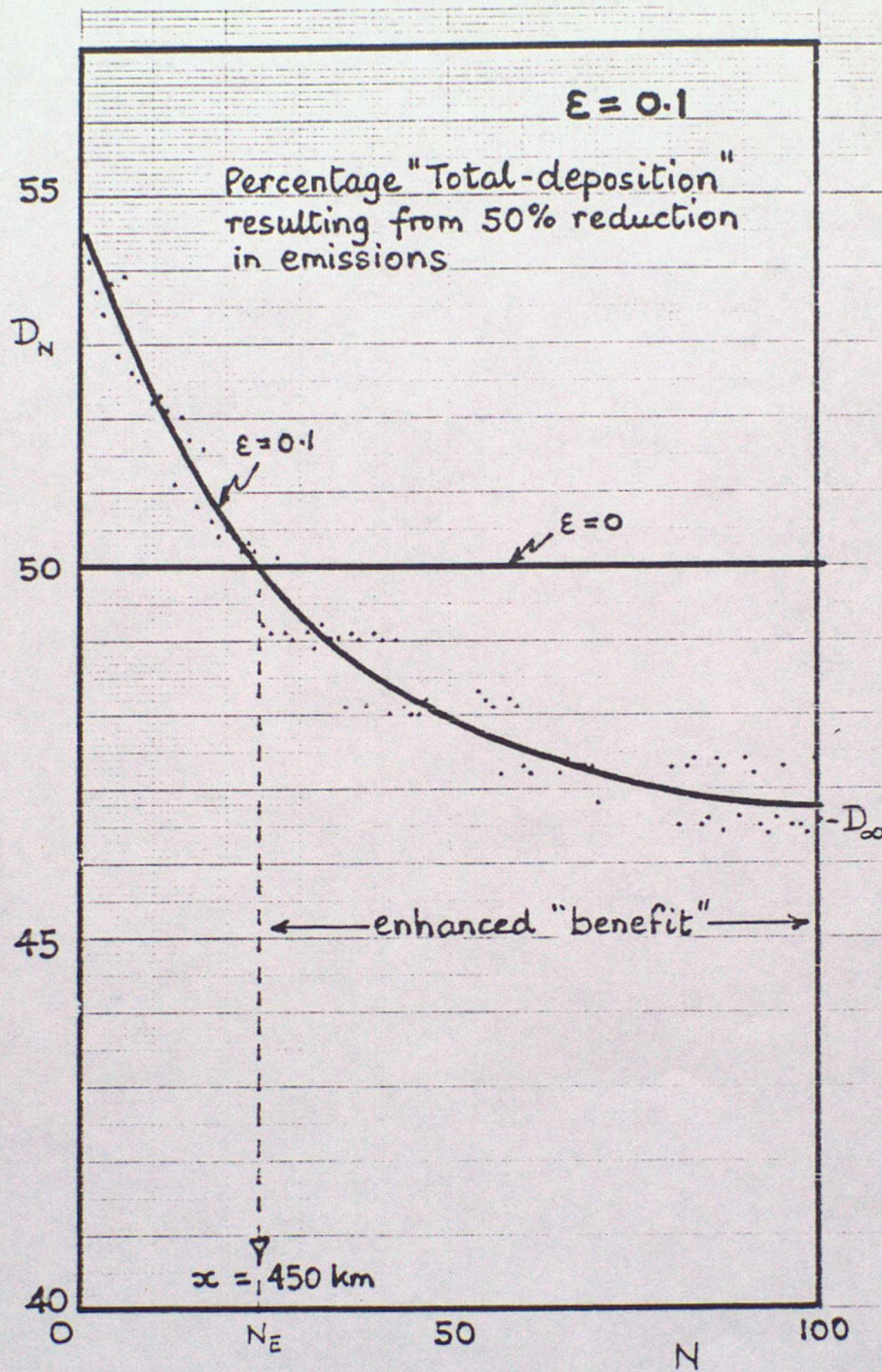
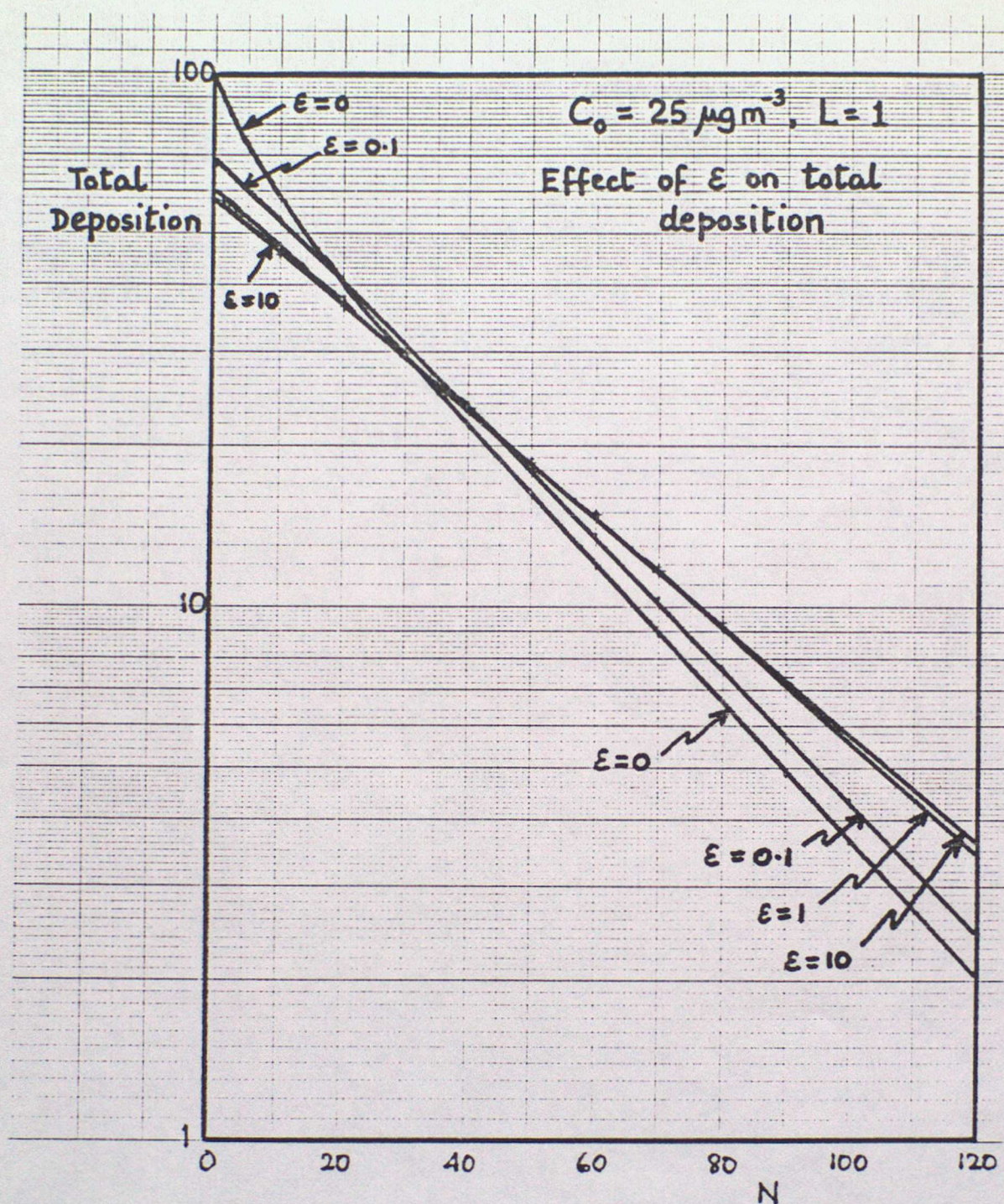


Figure 9



- Figure 10. Shows the insensitivity of the total deposition (wet + dry) with N (the number of half-hour timesteps) to changing the non-linearity parameter ϵ . Note how the changes become negligible above $\epsilon = 1$.

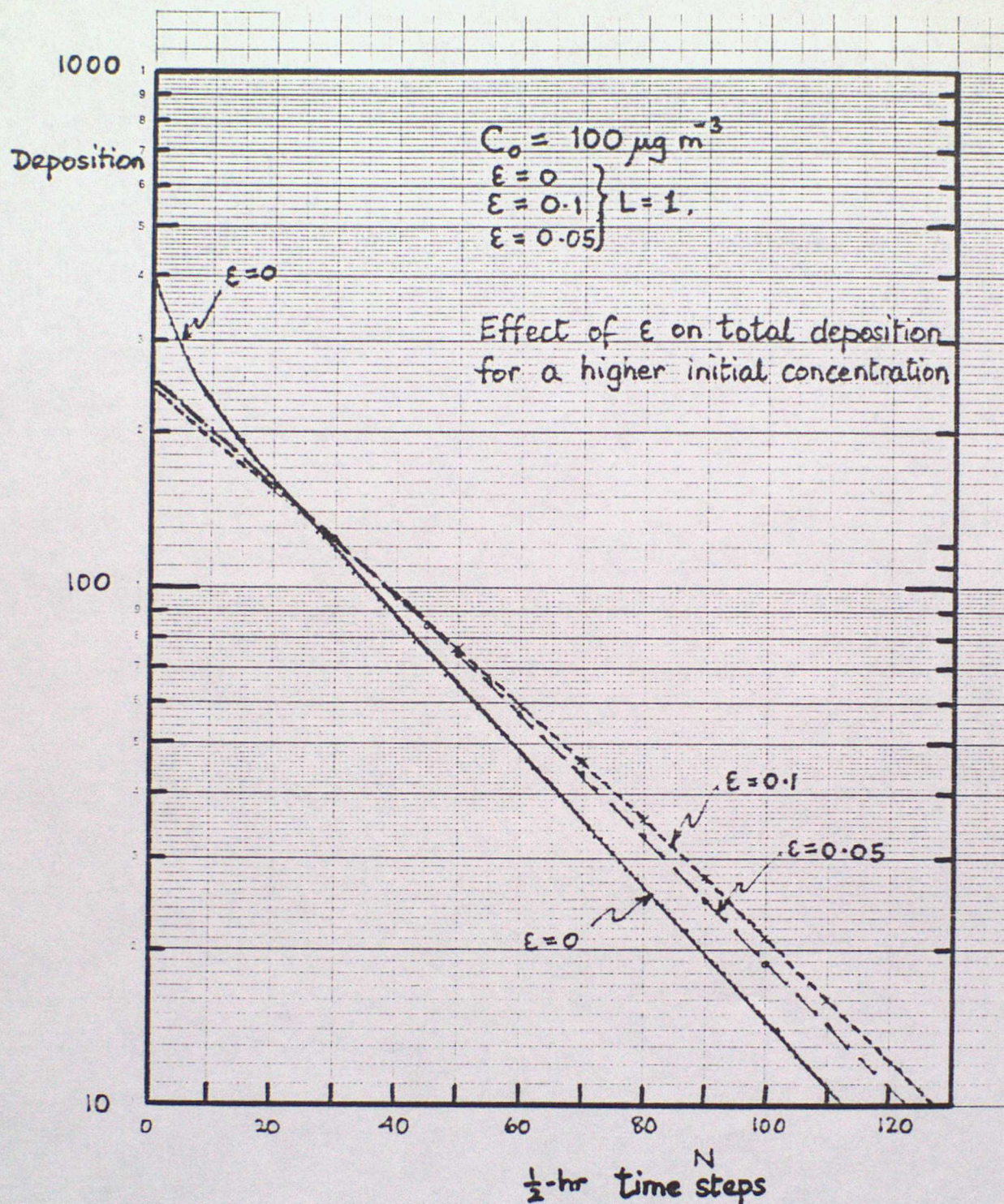


Figure 11. Increasing the initial concentration C_0 does very little to the conclusions, regarding the influence of non-linearities, drawn elsewhere in this paper.

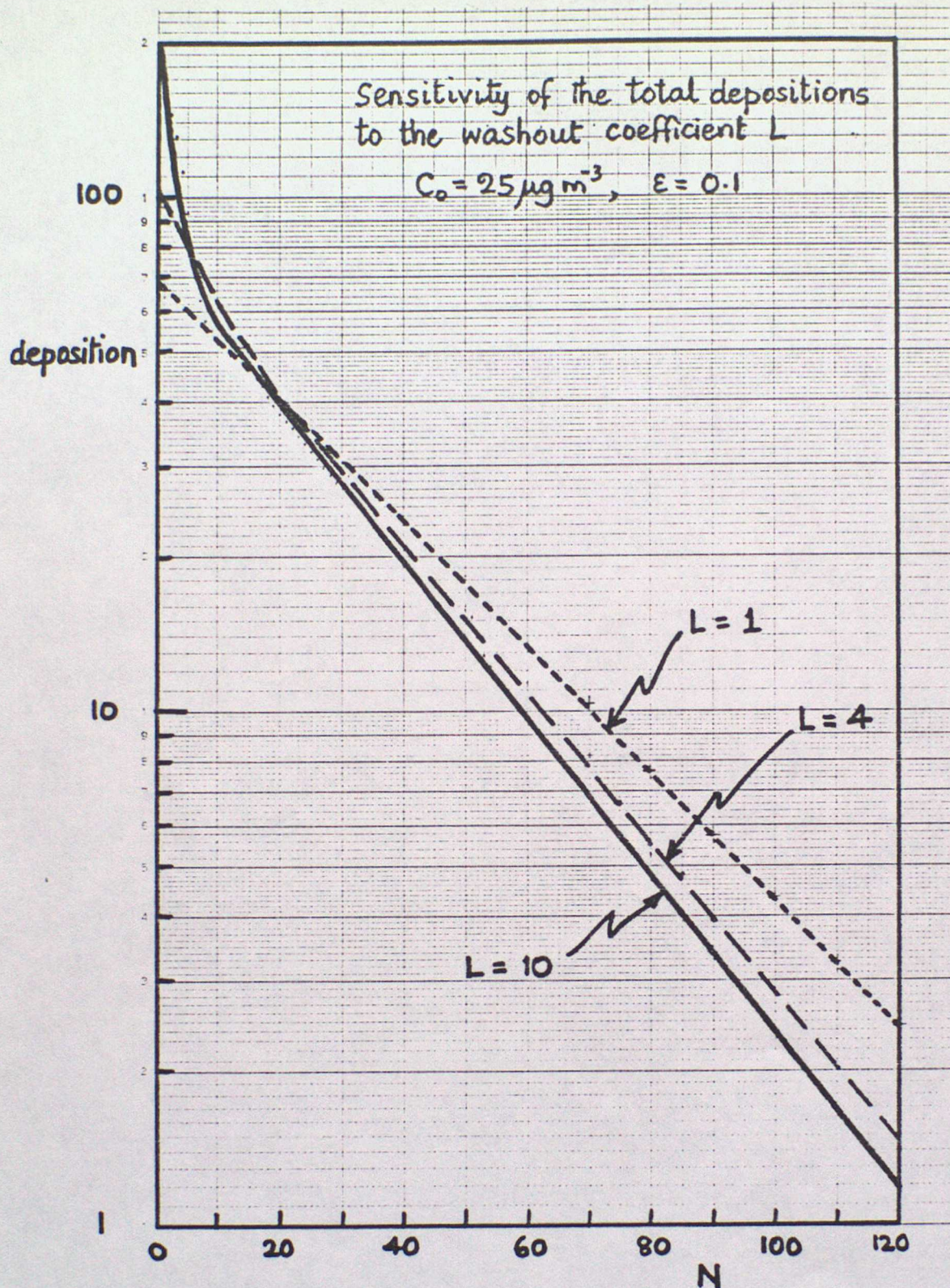


Figure 12. The rain-out term has been given a constant coefficient derived from a value given by Fisher (1978). In this Figure we see the consequences of multiplying this constant by a "washout coefficient" L . The effects are seen to be rather small except at small N .

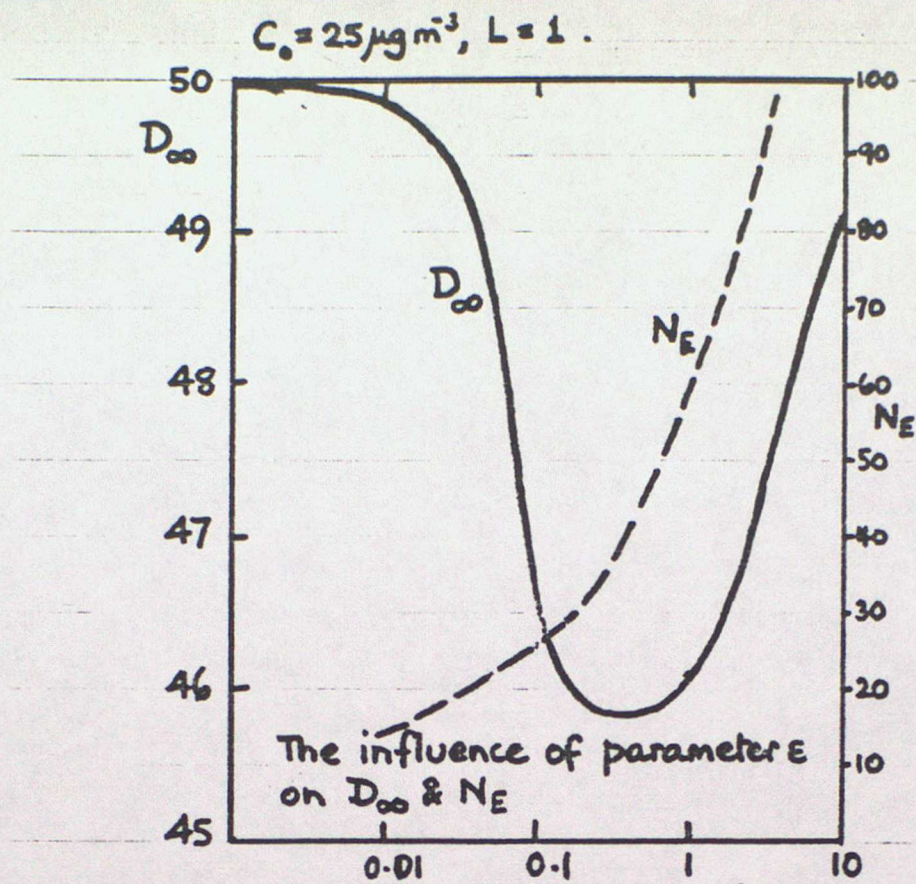


Figure 13

Halving the initial concentration C_0 reduces the resulting deposition to D_N % of its original value ($D_\infty = \lim_{N \rightarrow \infty} D_N$)

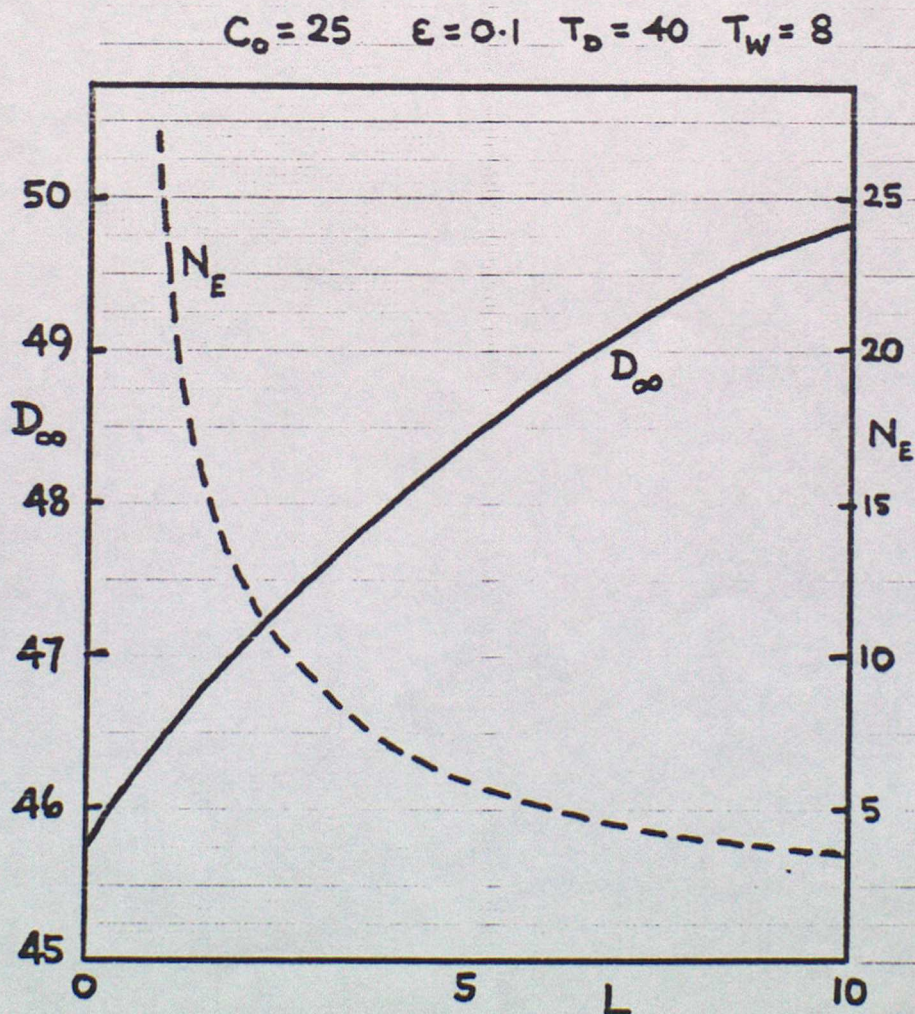


Figure 14. This figure shows the influence of the "washout coeff." L on D_∞ and N_E (the value of timestep N beyond which enhancement occurs).

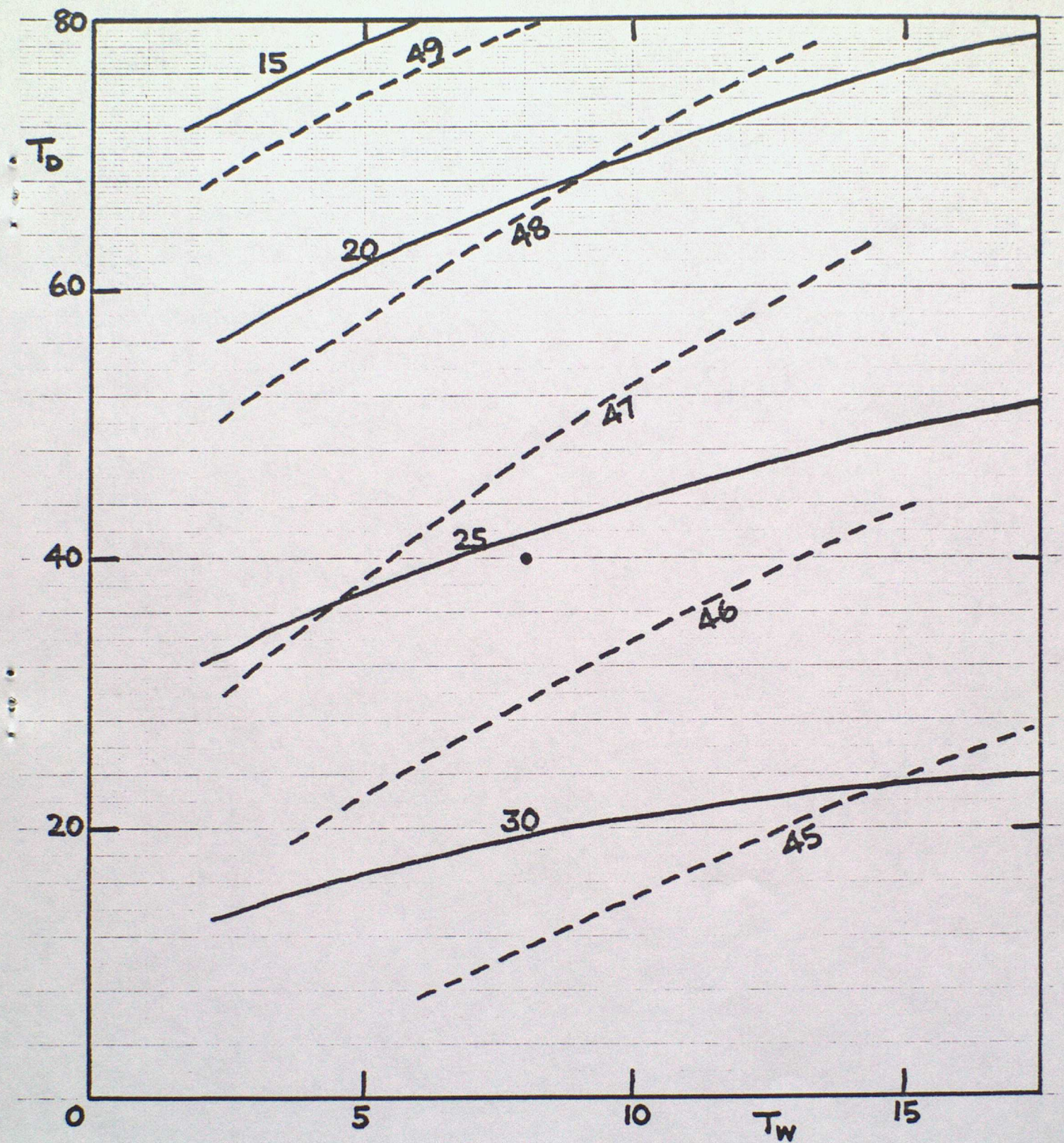


Figure 15.

————— Contours of N_E

----- Contours of D_∞

$$C_0 = 25 \mu\text{g m}^{-3}, L = 1, \varepsilon = 0.1$$

The influence of the timescale T_D and T_W , for dry and wet periods respectively, on the parameters D_∞ and N_E .

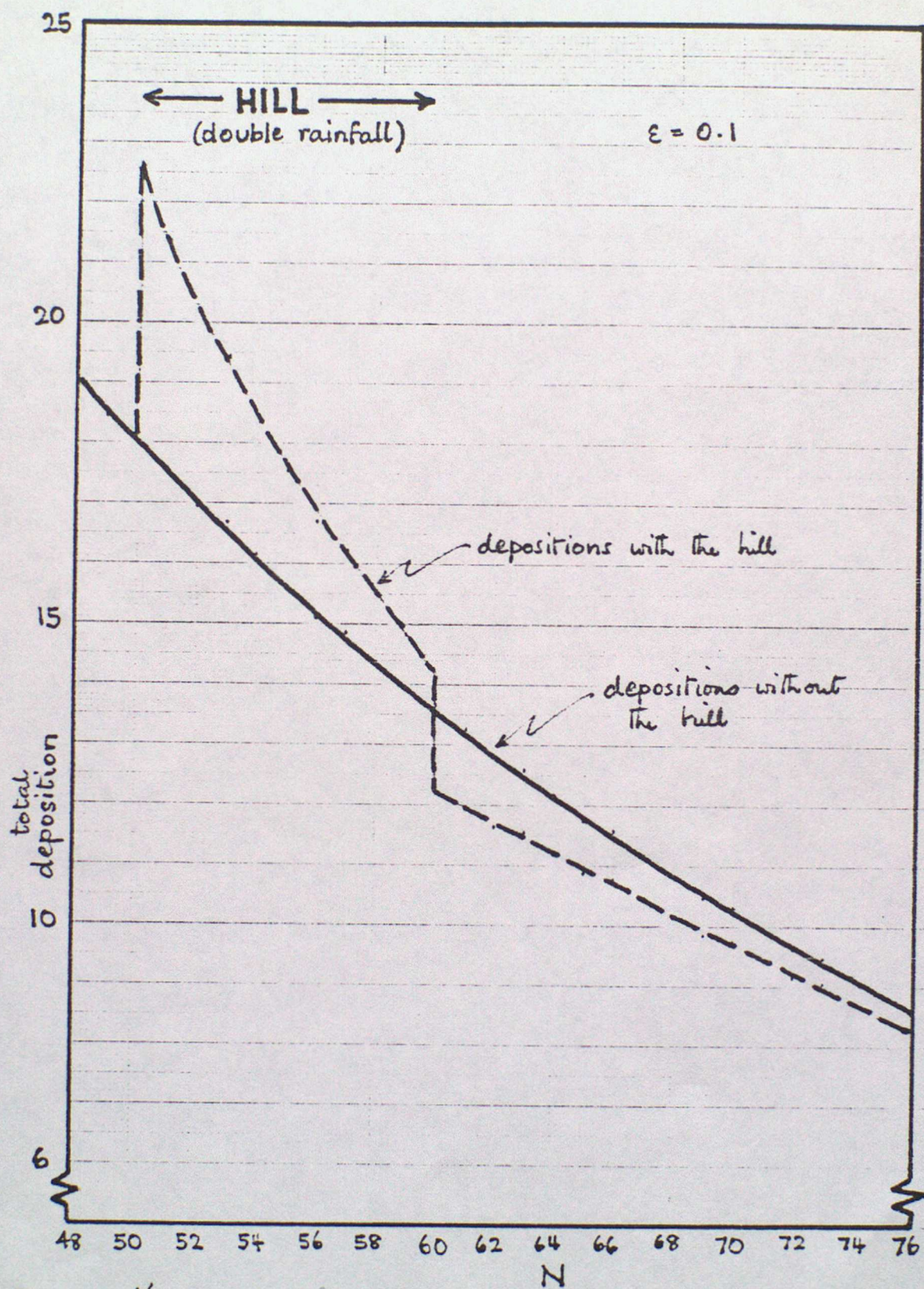


Figure 16

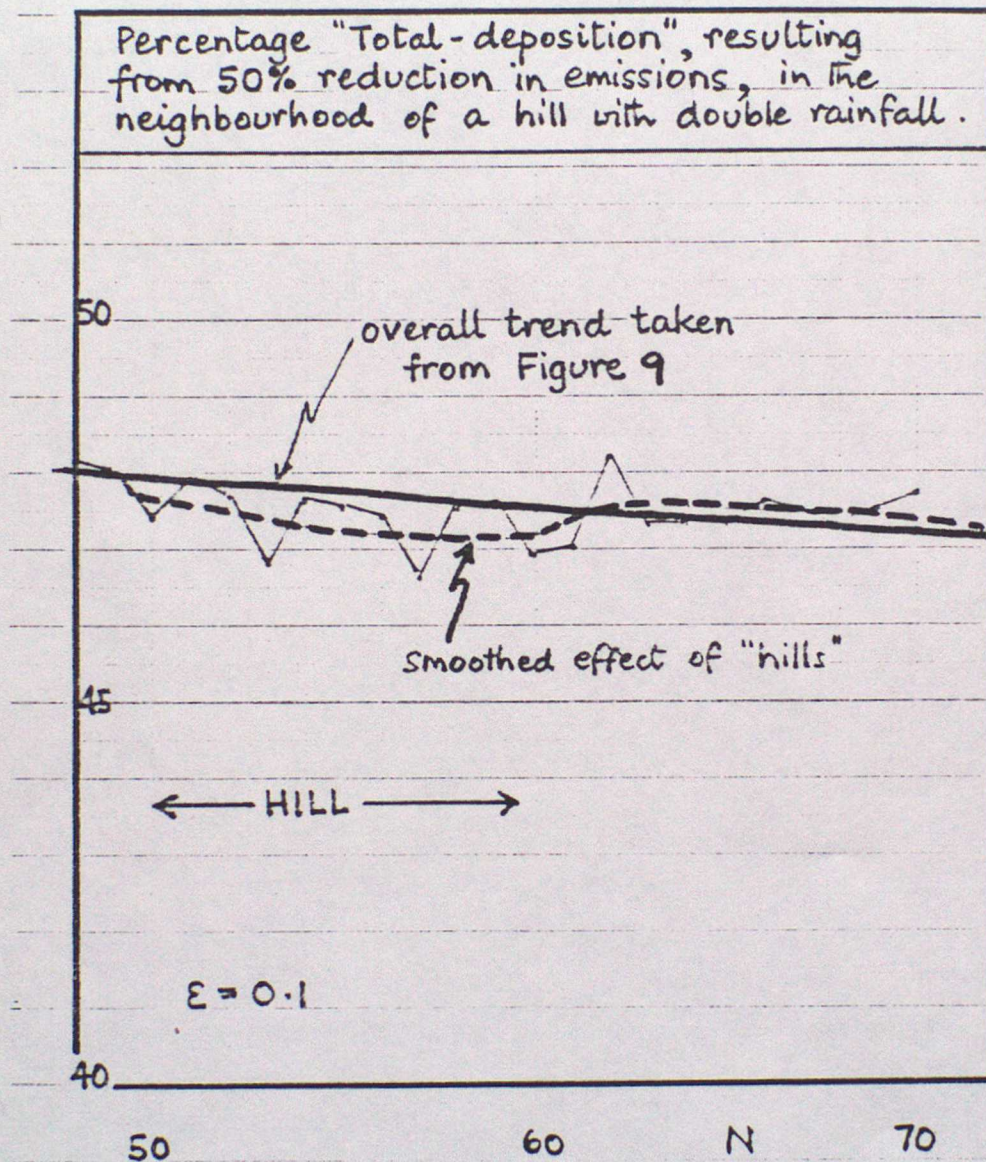


Figure 17.

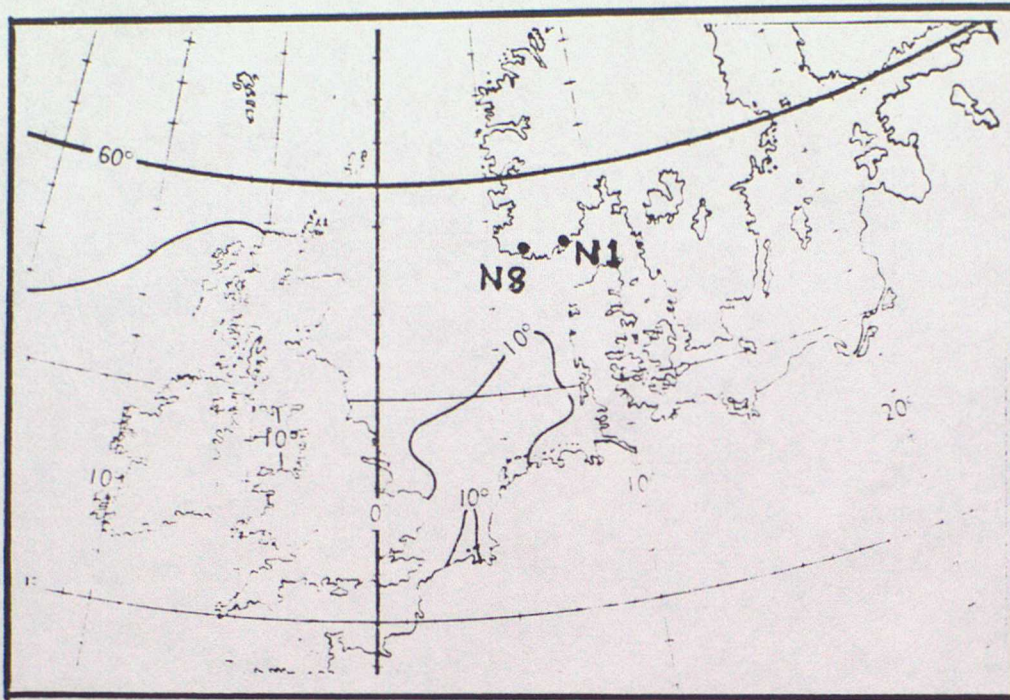


Figure 18. Location of the Two Norwegian EMEP monitoring stations, N1 and N8, used in the statistical analysis.