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UPPER AND LOWER TOLERANCE LIMITS OF ATMOSPHERIC OZONE LEVEL AND EXTREME VALUE DISTRIBUTION

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SUMMARY. The role of atmospheric ozone to protect the living organism from the ultraviolet radiation is well known. It saves the earth from the ultraviolet radiation emitted by the sun. Some stable chlorine gases released by the human activities going above the earth eat up the ozone layer. Depletion of the ozone layer is a great threat to the human society. In this paper, we discuss the lethal effects of the ozone depletion and compute the upper and lower β content confidence limits for an extreme value distribution and show that this can be used to calculate the upper and lower tolerance limits to the level of atmospheric ozone layer. The technique is explained by a data set.

1. Introduction

The role of atmospheric ozone to protect the living organism from the ultraviolet radiation is well known. The *Ozone Layer* in the stratosphere protects the inhabitants of the earth from the ultraviolet (UV) radiation emitted by the sun. Without the ozone layer, the fatal levels of UV radiation would reach the earth's surface and could extinguish life on this green planet. Scientists have discovered that chemicals released by our industries are destroying the ozone column in the stratosphere. Human activities release some stable and insoluble gases called trace gases such as nitrous oxide, methane, carbon tetrachloride, and compounds that contain both chlorine and fluorine and which are known as chlorofluorocarbons (CFCs). They do not break up in the lower atmosphere (known as the troposphere), instead they slowly migrate to the stratosphere.

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There they react with other chemicals under the influence of ultraviolet radiation and release chlorine. Chlorine acts as a catalyst to destroy ozone in the stratosphere. A chlorine atom (Cl) reacts with ozone, (O_3) to form ClO and O_2 . The ClO later reacts with another O_3 to form two molecules of O_2, which releases the chlorine atom. Thus, two molecules of ozone are converted to three molecules of ordinary oxygen, and the chlorine is once again free to start the process. A single chlorine molecule can destroy thousands of ozone molecules. Some other catalytic gases are the oxides of nitrogen (NO_x) and hydrogen. Because the reaction does not affect the catalyst itself, which remains in the same state at the end of the reaction as at the beginning, even very small amounts of these elements can produce a lethal damage on the concentration of ozone in the atmosphere. (See Figure 1.)

$O_2 \xrightarrow[180-240nm]{uv} O+O$ $O_2 + O \rightarrow O_3$	1 ozone formation	$Cl + O_3 \rightarrow ClO + O_2$ $O + ClO \rightarrow Cl + O_2$ $\overline{O+O_3 \rightarrow 2O_2}$	3 catalytic destruction of ozone by chlorine and nitric oxide
$O_3 \xrightarrow[200-320nm]{uv} O_2 + O$	ozone breakdown 2	$NO + O_3 \rightarrow NO_2 + O_2$ $NO_2 + O \rightarrow NO + O_2$ $\overline{O+O_3 \rightarrow 2O_2}$	4

Figure 1. Formation (1) and breakdown (2) of ozone occur naturally in the stratosphere but the rate of ozone breakdown can be greatly accelerated by catalysts such as chlorine (3) and nitric oxide (4).

Table 1 summarizes some of the essential data on the trace gases that have most effects on ozone concentrations. The gases included in Table 1 are produced both naturally and as a result of industrial activity.

TABLE 1. TRACE GASES AFFECTING OZONE CONCENTRATIONS

gas	formula	average lifetime in atmosphere (years)	average global concentration (ppbv)	annual rate of increase (percent)
CFC 11	$CFCl_3$	75	0.23	5
CFC 12	CF_2Cl_2	110	0.4	5
CFC 113	$C_2F_3Cl_3$	90	0.02	7
Halon 1301	CF_3Br	110	very low	11
nitrous oxide	N_2O	150	304	0.25
carbon monoxide	CO	0.4	variable	0.2
carbon dioxide	CO_2	7	344.000	0.4
methene	CH_4	11	1.650	1

It is extremely hard to figure out the causes of the increasing concentrations of these trace gases. The chlorofluorocarbons are used as the propellants in aerosols, in refrigeration technology as solvents and foam producing agents and it is estimated that the combined effect on ozone destruction by CFC11 and CFC12 amount to about 25 percent. If the rate of the CFC production remains unchanged and the concentrations of other chemicals continue to rise at their present rates, total ozone levels will fall sharply in the stratosphere during the first half of the next century. If the world does not take enough precautions, this would happen and this beautiful green planet will be exposed to increased ultraviolet radiations. (See Tolba,1985).

In the next section we discuss what is called the 'Ultraviolet Radiation'. In Section 3, we describe the fatal effects of the ultraviolet radiation on human health, plants, and aquatic systems. In Section 4, we describe the 'Greenhouse Effect' and show that a consequence of that is the 'Sea Level Rise' which may destroy a part of Bangladesh and Egypt. In Section 5, we address the problem of model fitting. We propose a statistical model and estimate the parameters from the data set to find out upper and lower bound for ozone concentration. In the last section we discuss the world's policy towards the prevention of the ozone layer.

2. ULTRAVIOLET RADIATION

The sun emits radiation over a broad range of wavelengths, to which the human eye responds in the region from approximately 400 to 700 nanometers (nm). Wavelengths from 320 to 400 nm are known as UV-A; that from 280 to 320 nm are called UV-B, and from 200-280 nm are known as UV-C. (See Figure 2.)

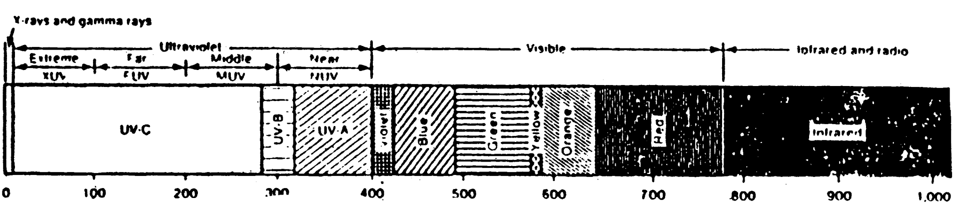

Figure 2

Attention has been focused, nowadays, mainly on the UV-B as the atmosphere absorbs virtually all UV-C. On the other hand, UV-B is partially taken in by ozone and future depletion of this layer would let the radiation reach the surface of the earth. It is estimated that a 10 percent reduction in ozone is likely to lead to an increase of around 20 percent in the incidence of ultraviolet radiation. The effects of ozone depletion on the society are widespread. Now let us examine the implications of such a depletion on human health, plants, aquatic organisms, materials, and air pollution.

3. Implications of depletion

3a. *Effects on human health.* The lethal effects on UV-B are well-known as it can cause the death of a cell or can damage the functions of the DNA and this may result in two forms of cancer in human beings : local skin cancer and the more serious skin cancer known as melanoma. Armstrong examines the role of UV-B exposure to melanoma patients and control subjects in Western Australia. Kollias and Baqer (1986) show that despite the presence of protective pigmentation 75 percent of cancers occur on 10 percent of the skin exposed to sunlight while examining skin cancer in Kuwait. The United States National Academy of Sciences estimates that each 1 percent depletion of ozone would increase the incidence of skin cancer by 2 percent. Scientists have surprisingly noticed that death rates from melanoma vary with latitude (see Figure 3).

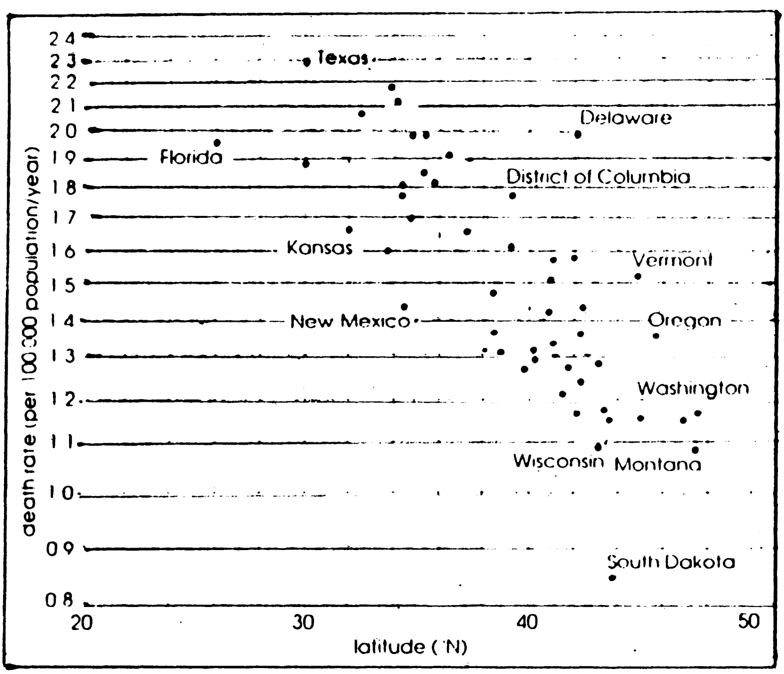

Figure 3. Shows how death rates from one form of skin cancer - melanoma - vary with latitude. Death rates among white people are much higher nearer the equator.

Worldwide extrapolation of such figures is difficult as white people are more susceptible to melanoma because of less pigmentation than black people.

Another severe effect of the increased levels of UV-B on the human body is to suppress the efficiency of the immune system. For this reason, ozone depletion would increase the skin infections, (see Scotto, 1986), blindness and ageing and wrinkling of the skin.

3b. *Effect on plants.* UV-B can damage plant hormones and chlorophyll, an important chemical for photosynthesis, and as a result, the rate of photosynthesis is lowered and the total mass production by the plant is reduced during a growing season. Teramura (1986) comes to a conclusion from this five year study of field tests on soybeans that a 25 percent depletion in ozone could result in a 20 to 25 percent reduction in soybean yield and adverse impacts on the quality of the yield. Sensitive species, such as cotton, peas, beans, melons, and cabbage grow more slowly at high levels of exposure of UV-B. (See Figure 4.)

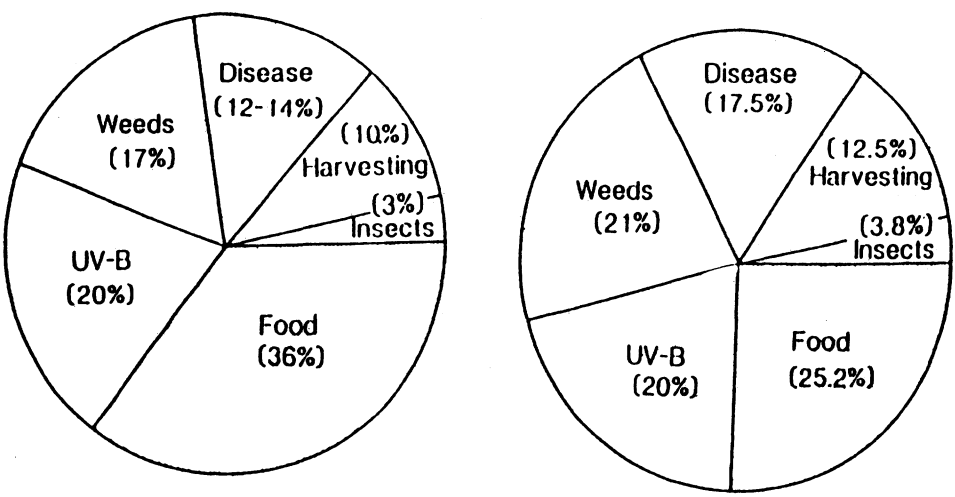

Figure 4. (left) Current sources of soybean crop losses in the United States in relation to anticipated losses due to a 25% ozone depletion (right) Anticipated yield losses due to a 25% ozone depletion assuming that UV produces a significant (25%) interaction with other sources of yield reduction

3c. *Effect on aquatic organisms.* At the top of the aquatic food chain there live single-celled plants called algae - which are now facing a serious threat as UV-B penetrating through water is damaging their lives. Worrest (1986) points out that a reduction in their productivities is important as these plants directly and indirectly provide the food for almost all fish. Recent research shows that all anchory larvae can be killed up to a depth of 10 meters by 15 days exposure to UV-B some 20 percent higher than current levels. It may happen that there will be no change in net productivity but a reduction in diversity which may make more susceptible to changes in water temperatures, nutrient availability, diseases, or pollution. (See Figure 5.)

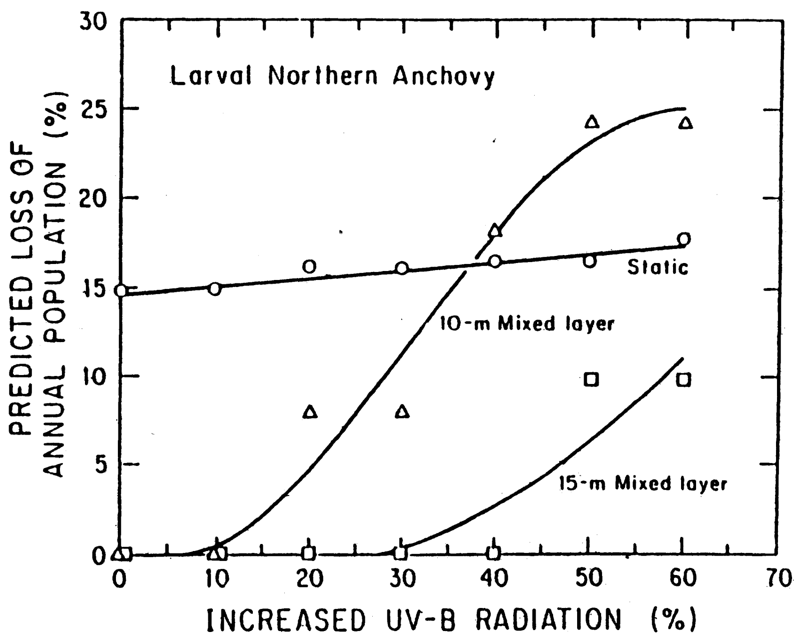

Figure 5. Effect of increased levels of solar UV-B radiation on the predicted loss of larval Northern Anchovy from annual populations, considering the dose/dose-rate threshold and the vertical mixing models (based on data of Hunter, Kaupp, and taylor 1981, 1982)

4. CLIMATE CHANGE

4a. *The greenhouse effect.* Water vapor, carbon dioxide and other gases in the atmosphere absorb some heat when the sunlight reflects from the earth's surface and goes to the space through the atmosphere. Because the atmosphere traps heat and warms the earth in a manner somewhat analogous to the glass panels of a greenhouse, this phenomenon is commonly known as the "greenhouse effect". Hansen *et al.* (1986) show that without the greenhouse effect the earth's temperature could be approximately 33°C colder than it is currently.

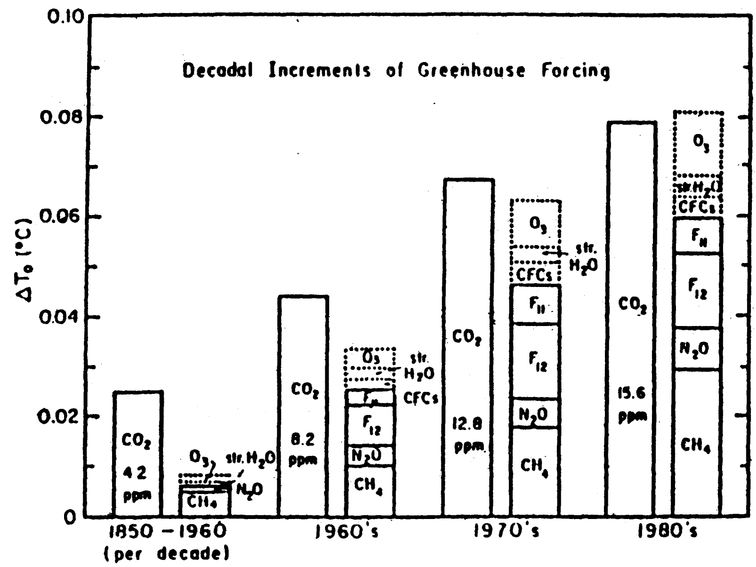

Figure 6. Decadal additions to global mean greenhouse forcing of the climate system. ΔT_0 is the computed temperature change at equilibrium for the estimated decadal increase in trace gas abundances, with no climate feedbacks included. Multiply ΔT_0 by the feedback factor f to get the most equilibrium surface temperature change including feedback effects. Most of the estimated trace gas increases are based on measurements. However, the O_3 and stratospheric H_2O trends (dotted bars) are based principally on $1 - D$ model calculations of Weubbles *et al.* (1983).

The combustion of fossil fuels, deforestation, and industrial activities have been releasing enough greenhouse gases and as a result their concentration levels in the atmosphere are also going up. Ozone, like carbon dioxide and methane, is a greenhouse gas. When considering climate, all these gases have to be treated as a system, and their roles in changing the concentrations of other gases and thus further influencing climate have to be considered as a whole. Hansen *et al.* (1986) present the results that their climate models predict for an effective doubling of carbon dioxide. The atmospheric temperature would be warmer because of CO_2 and other gases released by human activities. (See Figure 7.)

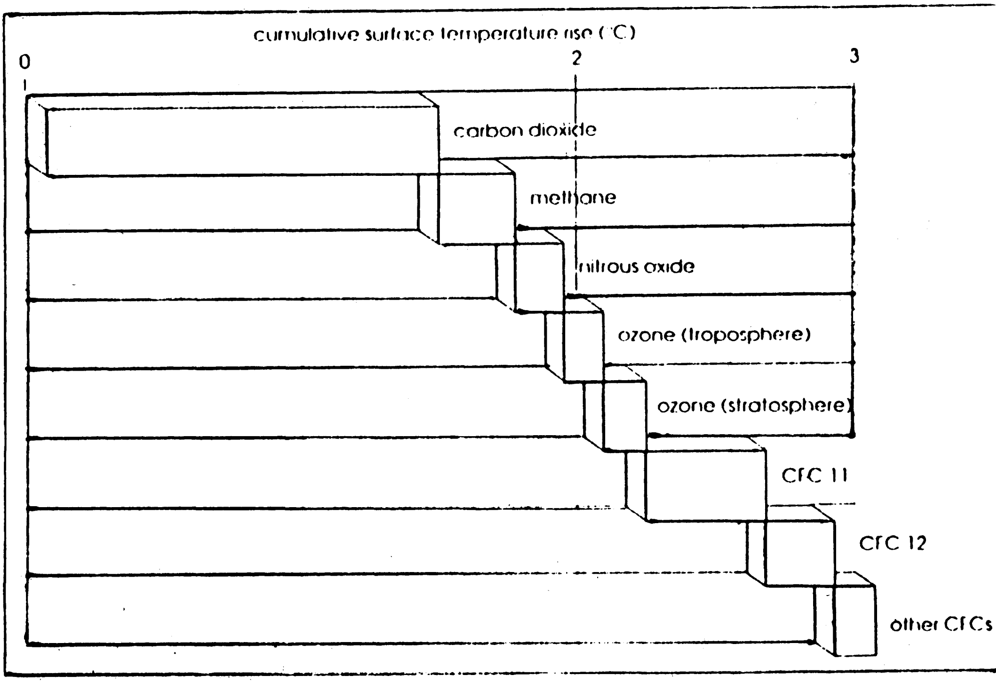

Figure 7. Predicted temperature rises caused by increasing concentrations of carbon dioxide and the other greenhouse gases by the year 2030. The predicted rise is about 3°C, of which only about one-half would be caused by carbon dioxide itself.

As the atmosphere gets heated up, its capacity to hold water vapor would increase. Because water vapor is also a greenhouse gas, this would contribute to a further warming. Ice and snow cover would retreat, causing sunlight that is now reflected by these bright surfaces to be absorbed instead, causing additional warming.

Most of the current models indicate that precipitation would increase overall by some 7 to 11 percent. However, increased rate of evaporation would result in drier soils, in the mid-latitudes at least and particularly in the northern mid-latitudes in early Spring. The lethal impact of this will be on germination of crops all over the world. (See Figure 8.)

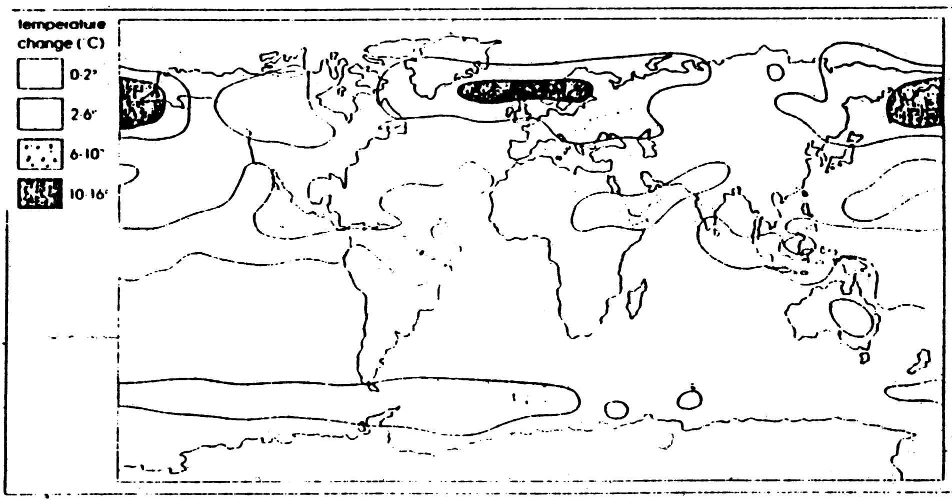

Figure 8. Temperature changes predicted by one atmospheric model caused by a doubling of carbon dioxide. In winter, temperatures might rise by as much as 6-10^{o}C in parts of northern Eurpoe.

4b. *Sea level rise.* Probably, the most fatal attack by the global warming will be a rise in the sea level. Scientists are predicting that the global warming would raise the sea levels by heating and thereby expanding ocean water, melting mountain galciers, and by causing polar glaciers in Greenland and Antarctica to melt and possibly slide into the oceans. The projected sea level rise would be about 30 centimeters by 2025 and this would in low-lying areas, destroy coastal marshes and swamps, erode shorelines, and increase the salinity of rivers, bays, and aquifers. Thomas (see Figure (9)) predicts that if global temperatures increase by 3^{o}C as predicted by many climate models, there is a good chance that the sea level would rise by approximately 1m by the year 2100.

Brouadus *et al.* (1986) examine two countries, Bangladesh and Egypt, in detail and draw the most scary picture. Bangladesh, which is already overcrowded, would lose 12 to 28 percent of its total area (see picture 9), which currently houses 9 to 27 percent of its population. There is a high chance that frequency of tropical storms will be doubled due to warm weather and floods could penetrate further inland.

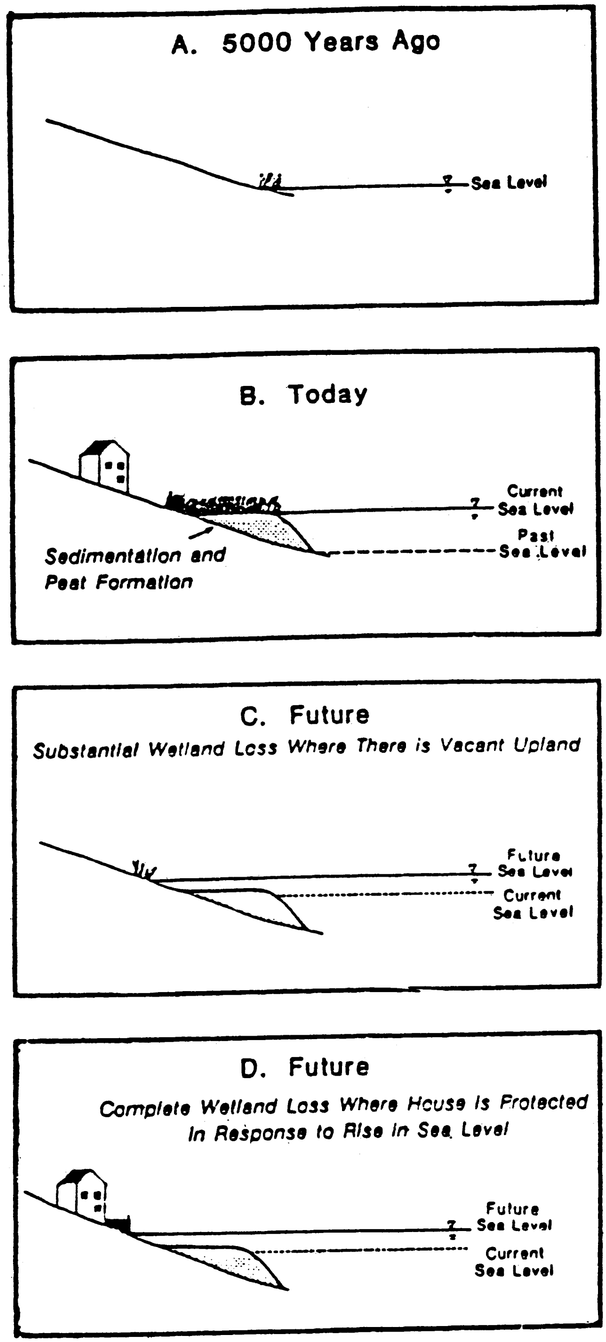

Figure 9. Evolution of Marsh as Sea Level Rises

5. Ozone models

In a particular place, the ozone concentration in the atmosphere depends on the altitude as well as on the hour of measurement. As for example, in the graph attached, the percentage deviation from midnight values of ozone concentration at an altitude of 40 km is seen to attain a global peak near 3 p.m. and then it gradually falls down.

As our aim is to safeguard the minimum level of ozone concentration, we would like to construct a lower bound using the given observations, such that at least β proportion of the future observations would be above that bound with a high probability γ. Such bounds are called lower β content tolerance limit. An upper tolerance limit can be defined similarly. As explained, β-content tolerance region S contains at least $100\beta\%$ of the population with a high probability γ. Wilks (1941) considered construction of such tolerance interval while sampling from a normal population with unknown mean and variance. The utilization of this type of added information leads to tolerance regions different from those provided by the distribution free cases. Wilks tolerance interval was of the form $(\overline{x} \pm ks)$ where $\overline{x}$ and s are the sample mean and sample standard deviation. Further works in different set up are available in Mee and Owen (1983), Bechman and Tietjen (1989), Bhaumik and Kulkarni (1991) among others.

It is well known that, under nominal assumptions, the standardised extremes of independent and identically distributed observations follow an extreme value distribution asymptotically and are one of the following three types.

$$
\begin{aligned}
\text{(I)}\ \ F(x) &= \exp(-(-x)^{\alpha}) && x < 0, \alpha > 0 \\
&= 1; && x \geq 0 \\[1em]
\text{(II)}\ \ F(x) &= 0, && x < 0, \alpha > 0 \\
&= \exp(-x^{-\alpha}), x \geq 0 && \\[1em]
\text{(III)}\ \ F(x) &= \exp(-e^{-x}), && -\infty < x < \infty.
\end{aligned}
$$

See e.g. Galambos (1978). The first type of distributions are negatively skew and the remaining types are positively skew.

A number of problems where the mathematical solutions depend on largest or smallest of measurements, lead to extreme value distribution. e.g. water level in a river, extreme temperature, extreme atmospheric pressure etc. Similarly, hourly/daily minimum level of ozone concentration may be assumed to follow an extreme value distribution after a suitable change of origin and scale. Also in many industrial contexts the job characteristic like ovality, eccentricity, etc. follow an extreme value distribution (see e.g. Dasgupta *et al.* (1981), Dasgupta (1993)). The results of the present paper are applicable in such situations as well.

In this paper, we aim at constructing tolerance limits for an extreme value distribution and then use this to find lower/upper bound such that $100\beta\%$. Ozone concentration will be above/below that bound with a very high probability γ. The parameters of the extreme value distribution are estimated from data and any consistent estimator via method of moments or by equating empirical quantiles to population quantiles would suffice for the calculations presented.

In section 6 tolerance limits are constructed for extreme value distribution. In sec. 7 these limits are computed for a data set arising out of a model in Pyle (1985). In the last section some further discussions are provided.

6. Tolerance limits for extreme value distribution

First consider the distribution of type I

$$F(x) = \begin{cases} \exp(-(\frac{\mu - x}{\sigma})^{\alpha}), & x < \mu;\ \alpha, \sigma > 0 \\ 1, & x \geq \mu, \end{cases} \qquad \ldots (1)$$

This is negatively skewed distribution and the empirical distribution if negatively skew may suggest that this type of distribution may be used when the variable has an upper bound μ.

A reasonable lower tolerance limit for this distribution would be $x_{(1)}\delta(\mu, \alpha, \sigma)$ where δ is a positive function of μ, α and σ and $x_{(1)} = \min[x_1, \ldots, x_n]$ where x_i's are i.i.d with distribution F. Therefore we need

$$P_{x_{(1)}}[P_F\{Y \geq x_{(1)}\delta(\mu, \alpha, \sigma)\} \geq \beta] = \gamma \qquad \ldots (2)$$

where γ is a future observation from F and hence at least $100\beta\%$. of the future observations would be above $x_{(1)}\delta(\mu, \alpha, \sigma)$ with a high probability γ.

From (2) we get

$$P[1 - F(x_{(1)}\delta(\mu, \alpha, \sigma)) \geq \beta] = \gamma$$

i.e. $$P[x_{(1)}\delta(\mu, \alpha, \sigma) \leq F^{-1}(\overline{\beta})] = \gamma, \text{ where } \overline{\beta} = 1 - \beta \qquad \ldots (3)$$

Equivalently,

$$P[x_{(1)} > F^{-1}(\overline{\beta})/\delta(\mu, \alpha, \sigma)] = 1 - \gamma$$

i.e. $$G^n[F^{-1}(\overline{\beta})/\delta(\mu, \alpha, \sigma)] = 1 - \gamma, \text{ where } G = 1 - F$$

i.e. $$F[F^{-1}(\overline{\beta})/\delta(\mu, \alpha, \sigma)] = 1 - (1 - \gamma)^{1/n}$$

$$\delta(\mu, \alpha, \sigma) = F^{-1}(\overline{\beta})/F^{-1}(1 - (1 - \gamma)^{1/n}) \qquad \ldots (4)$$

Now solving for $F(x) = y$ one gets

$$F^{-1}(y) = x = \mu - \sigma(-log\ y)^{1/\alpha}.$$

Hence,

$$\delta(\mu, \alpha, \sigma) = \frac{\mu - \sigma(-log\overline{\beta})^{1/\alpha}}{\mu - \sigma[-log\{1 - (1 - \gamma)^{1/n}\}]^{1/\alpha}} \qquad \ldots(5)$$

In practice, μ, α and σ are to be estimated from data and one may take any consistent estimate. Observe that the function δ is cotinuous in its arguments. Now for any consistent estimates μ^*, α^* and σ^* writing $A = \{| \mu - \mu^* |> \varepsilon\}, B = \{| \alpha - \alpha^* |> \varepsilon\}$, $C = \{| \sigma - \sigma^* |> \varepsilon\}$, one gets $P(AUBUC) \leq P(A) + P(B) + P(C) = o(1)$ as $n \to \infty$, for any $\varepsilon > 0$.

Hence, as δ is continuous, considering the set $A \cup B \cup C$

$$P[| \delta(\mu, \alpha, \sigma) - \delta(\mu^*, \alpha^*, \sigma^*) |> \varepsilon'] = o(1) \text{ as } n \to \infty \qquad \ldots(6)$$

for any $\varepsilon' > 0$.

As for example one may consider consistent moment estimates for the parameters μ, α and σ. One may also consider estimates obtained by equating sample p-th quantile with p-th quantile of F.

The equations (1) - (5) along with (6) imply that

$$P[P\{Y \geq x_{(1)}\delta(\mu^*, \alpha^*, \sigma^*) \geq \beta] = \gamma + o(1)$$

Therefore $x_{(1)}\delta(\mu^*, \alpha^*, \sigma^*)$ where δ is given by (4) is an approximate lower tolerance limit for type I distributions. Hence we have

Theorem 1. *Let $x_1, \ldots, x_n$ be i.i.d with distribution $F(x)$ given by (1). Let $\mu^*, \alpha^*, \sigma^*$ be any consistent estimators of parameters μ, α, σ respectively. Then $x_{(1)}\delta(\mu^*, \alpha^*, \sigma^*)$ is an approximate β content lower tolerance limit for a future observation Y from F, where $x_{(1)} = min(x_1, \ldots, x_n)$ and δ is given by (4). That is*

$$P_{x_{(1)}}[P_F\{Y \geq x_{(1)}\delta(\mu^*, \alpha^*, \sigma^*)\} \geq \beta] = \gamma + o(1) \text{ as } n \to \infty.$$

Next consider the type III distributions which are positively skewed with infinite range viz.

$$F(x) = exp(-e^{-(\frac{x-\mu}{\sigma})}), -\infty < x < \infty,\ \sigma > 0, \mu\epsilon(-\infty, \infty) \qquad \ldots(7)$$

The same arguments remain valid and a relation like (4) holds. i.e. one has,

$$\delta(\mu, \sigma) = F^{-1}(\overline{\beta})/F^{-1}(1 - (1 - \gamma)^{1/n}) \qquad \ldots(8)$$

where $F^{-1}(y) = \mu - \sigma log(-log\ y)$.

Hence, in this case one may write,

$$\delta(\mu,\sigma) = \frac{\mu - \sigma log(-log\overline{\beta})}{\mu - \sigma log\{-log(1-(1-\gamma)^{1/n})\}} \qquad \ldots(9)$$

and $x_{(1)}\delta(\mu^*,\sigma^*)$ serves the purpose of an approximate lower tolerance limit, where μ^* and σ^* are consistent estimates of μ and σ. Hence we have

Theorem 2. *Let $x_1,\ldots,x_n$ be i.i.d as F given by (7). Let μ^* and σ^* be any consistent estimators of μ and σ respectively. Then $x_{(1)}\delta(\mu^*,\sigma^*)$ is an approximate β content lower tolerance limit for a future observation Y from F, where $x_{(1)} = min(x_1,\ldots,x_n)$ and δ is given by (9), i.e.*

$$P_{x_{(1)}}[P_F\{Y \geq x_{(1)}\delta(\mu^*,\sigma^*)\} \geq \beta] = \gamma + o(1) \quad as \quad n \to \infty.$$

For type II distributions there is a finite lower bound of the random variable. So construction of lower tolerance limit may not be required in such cases. One may also construct upper β content tolerance limits in a similar fashion and with similar interpretation. Situations arise when one requires an upper bound such that a large percentage of future observations have to lie below that bound with high probability, e.g. excessive concentration of ozone causes rise in global temperature known as 'green house effect'. Consider upper tolerance of the type $x_{(n)}\delta$ where $x_{(n)} = \max[x_1,\ldots,x_n]$ and $\delta > 0$. Then we need to have

$$P_{x_{(n)}}[P_F\{Y \leq x_{(n)}\delta\} \geq \beta] = \gamma \qquad \ldots(10)$$

where Y is a future observation from F and hence at least $100\beta\%$ of the future observations would be below $x_{(n)}\delta$ with a high probability γ.

Following the steps similar to (3) - (4), one gets

$$P_{x_{(n)}}[F(x_{(n)}\delta) \geq \beta] = \gamma \qquad \ldots(11)$$

or, $P_{x_{(n)}}[x_{(n)} < F^{-1}(\beta)/\delta] = 1-\gamma$. Hence,

$$\delta = \delta(\mu,\alpha,\sigma) = F^{-1}(\beta)/F^{-1}[(1-\gamma)^{1/n}]. \qquad \ldots(12)$$

Let F be a type III distribution as given in (7), then (12) takes the following form :

$$\delta(\mu,\sigma) = \frac{\mu - \sigma log(-log\beta)}{\mu - \sigma log(-\frac{1}{n}log(1-\gamma))} \qquad \ldots(13)$$

Estimating μ,σ from observed data by μ^* and σ^* respectively, one may use the approximate upper tolerance limit $x_{(n)}\delta(\mu^*,\sigma^*)$.

For a type II distribution of the form

$$F(x) = \begin{cases} 0, & x < \mu \\ exp(-(\frac{x-\mu}{\sigma})^{-\alpha}), & x \geq \mu,\ \alpha > 0, \sigma > 0 \end{cases} \qquad \ldots(14)$$

one has,

$$F^{-1}(y) = \mu + \sigma(-log\ y)^{-1/\alpha}.$$

Therefore (12) takes the form,

$$\delta = \frac{\mu + \sigma(-log\beta)^{-1/\alpha}}{\mu + \sigma[-\frac{1}{n}log(1-\gamma)]^{-1/\alpha}}. \qquad \dots(15)$$

Once again, $x_{(n)}\delta(\mu^*, \alpha^*, \sigma^*)$ may be considered as approximate upper tolerance limit, where μ^*, α^* and σ^* are sample estimates of μ, α and σ respectively. Summarizing the above we have

Theorem 3. *Let $x_1, \dots, x_n$ be i.i.d with distribution $F(x)$ given by (14). Let $\mu^*, \alpha^*, \sigma^*$ be any consistent estimators of the parameters μ, α, σ respectively. Then $x_{(n)}\delta(\mu^*, \alpha^*, \sigma^*)$ is an approximate β content upper tolerance limit for a future observation Y from F, where $x_{(n)} = max(x_1, \dots, x_n)$ and δ is given by (15). That is*

$$P_{x_{(n)}}[P_F\{Y \le x_{(n)}\delta(\mu^*, \alpha^*, \sigma^*)\} \ge \beta] = \gamma + o(1) \ as \ n \to \infty$$

Similarly, for $x_1, \dots, x_n$ i.i.d with F given by (7), an approximate β content upper tolerance limit is given by $x_{(n)}\delta(\mu^*, \sigma^*)$ where δ is given by (13).

7. The data and fitting an extreme value distribution

In the graph, the midnight observations are considered as origin. The minimum of 4 observations per hour (at an interval of 15 minutes in terms of percentage deviation) are recorded below for two different altitude corresponding to high fluctuation of observations viz. 40 km and 48 km. The graphs relates to a theoretical model of Pyle (1985), recorded in Dobson scale.

Hour Altitude (km)	0	1	2	3	4	5	6	7	8	9	10	11	12
40	0	.1	.2	.15	.2	.25	.3	-1	-1.14	-.71	.21	1.43	2.64
48	0	.1	.15	.15	.2	.25	.3	-.21	.86	-.57	-2.71	-4.14	-5.21

Hour Altitude (km)	13	14	15	16	17	18	19	20	21	22	23
40	3.43	4.14	4.43	4.14	1	0	-.25	-.2	-.15	-.1	-.05
48	-5.86	-6	-5.71	-4.14	-1.43	-.14	-.25	-.2	-.15	-.1	-.05

Data corresponding to altitude of 40 km is positively skew. So we fit a type III distribution. The random variable is not bounded for this type of distribution.

Equating the median and first quartile of the sample with that of population F, we obtain the estimates of μ and σ. That is,

$exp(e^{-(\frac{x-\mu}{\sigma})}) = 1/4$ and $1/2$ at $x = -.1625$ and $x = .125$ respectively.

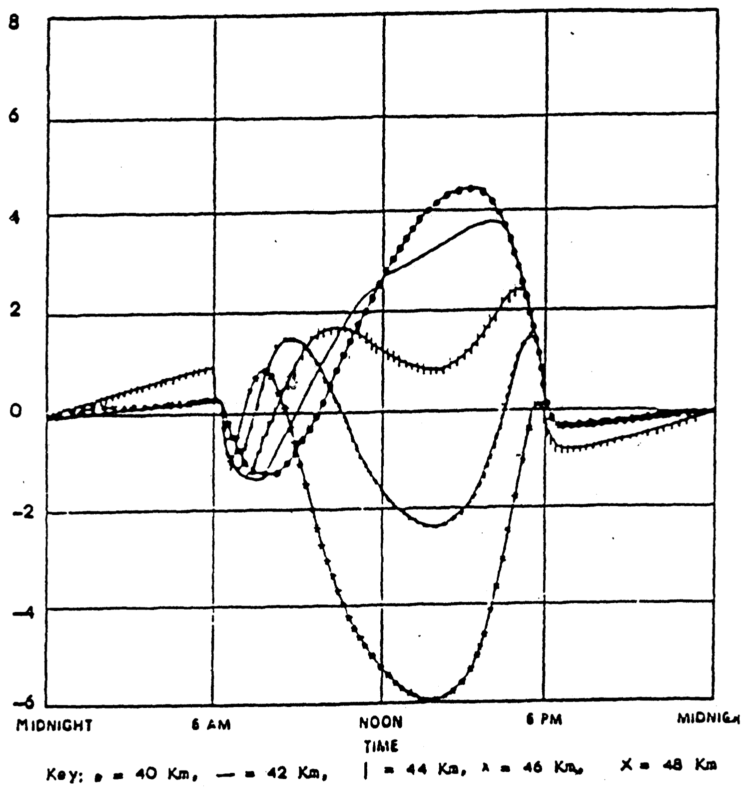

Fig. A. Percentage deviation from midnight values of ozone cocentrations for a diurnal cycle.
Source : Pallister and Tuck (1983), ref. Pyle (1985).

This gives,

$$\mu^* = -2.5158 \text{ and } \sigma^* = 7.2055.$$

Now consider $\gamma = .95$ and $\beta = .9$, then the lower tolerance limit from (9) is

$$x_{(1)}\delta(\mu^*, \sigma^*) = (-1.14) \times 1.0648 = -1.214.$$

The interpretation of the above is that 90% of the future centered observations at an altitude of 40 km are likely to be above -1.214 with a high probability near to .95. Similarly, from (13) an upper tolerance limit with same β and γ in this case is $x_{(n)}\delta(\mu^*, \sigma^*)$, where δ is given in (13). This equals (4.43) $\times$ 1.0979 = 4.864.

Next consider the data corresponding to the altitude 48 km. The data suggest a negatively skewed distribution and we fit a type I distribution. The upper bound μ of the distribution is estimated by the maximum of the observations

$x_{(n)}$ and α and σ are estimated by the equating sample median and first quartile to the corresponding population values.

Hence $\mu^* = x_{(n)} = .86$ and $exp(-(\frac{\mu^*-x}{\sigma})^\alpha) = 1/2$ and $1/4$ at $x =$ -.205 and x = -4.14 respectively.

Hence, with $\gamma = .95$ and $\beta = .9$, the lower tolerance limit is

$$x_{(1)}\delta(\mu^*, \alpha^*, \sigma^*) = (-6) \times 1.1864 = -7.118$$

Therefore 90% of the future centered observations at an altitude of 48 km are likely to be above -7.118 with a high probability nearabout .95.

8. Discussion

For protection of living beings from ultraviolet radiation the ozone layer plays an important role. Due to industrial release of some gases and some others which are produced naturally like chlorofluorocarbons and oxides of nitrogen, the concentration of ozone layer is sharply diminished. The minimum concentration of ozone should be above some level so that damage due to radiation is within limit.

In this paper, assuming an extreme value distribution we compute the lower tolerance limit for ozone concentration. That is, we compute a bound such that $100\beta\%$ of future observations on ozone concentration will be above that level with a high probability γ. For a given set of data these bounds are specifically computed with $\beta = .9$ and $\gamma = .95$.

On the other hand, too much ozone concentration may cause global rise of temperature also known as green house effect. Therefore, we also compute upper tolerance limit based on an extreme value model. That is, we compute an upper bound such that $100\beta\%$ of future observations on ozone concentration will be below that level with a high probability γ. These bounds are also computed for a set of data.

There are three types of extreme value distributions. The appropriate type is found by skewness of the observed data and the population parameters are also estimated from the data.

The technique remains valid whenever an extreme value distribution seems to be an appropriate model. For example some industrial characteristics like ovality, eccentricity follow extreme value distributions. Tolerance limits may be computed similarly for such characteristics, see for example (Dasgupta *et al.* (1981), Dasgupta (1993)).

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