LAWRENCE LIVERMORE LABORATORY
University of California/Livermore, California/94550

UCRL-52643

A MODEL OF LEAF PHOTOSYNTHESIS AND THE EFFECTS OF SIMPLE GASEOUS SULFUR COMPOUNDS (H₂S AND SO₂)

James R. Kercher

MS. date: August 10, 1978

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

CONTENTS

Abstract	1
Introduction	1
Description of the Model	2
Diffusion	2
Biochemical Processes of CO ₂ Assimilation at Steady State	4
Temperature Dependence of Respiration and Photosynthesis	7
Sulfur Metabolism	9
Estimation of Parameters for the Short-Term Model	11
Model of Long-Term Effects	13
Estimation of Parameters in Long-Term Models	16
Results and Analysis	17
Interpretation of Parameters	17
Analysis of Model	19
Conclusions	35
Acknowledgement	36
References	37

A MODEL OF LEAF PHOTOSYNTHESIS AND THE EFFECTS OF SIMPLE GASEOUS SULFUR COMPOUNDS (H_2S AND SO_2)

ABSTRACT

We present a theoretical development of a leaf model and the effects of simple sulfur compounds (H_2S and SO_2) on photosynthesis based upon biochemical mechanisms. The model is developed to interpret short-term fumigation experiments and to use with season-long fumigation experiments to assess the effects of these compounds on growth. The model is designed as a submodel in a growth-and-allocation model of the plant.

Included in this development are an analysis of the diffusion of CO_2 and sulfur compounds into the leaf, enzymatic interactions of sulfur in dark and light reactions of photosynthesis, temperature dependence of the kinetics and denaturation of enzymes, metabolism of sulfur compounds, and a hypothesis for the long-term effects of sulfur compounds. We can explain enhanced photosynthesis at low H_2S levels, depression of photosynthesis at high H_2S levels, threshold to effects of sulfur pollutants, and the nature of the temperature dependence of photosynthesis.

We have used parameters in the model for sugar beets from data in the literature and from experiments funded through LLL. We have analyzed the properties of the model and discuss data and experiments still required, sensitivities of the model to parameters and variables, implications to assessments, and the setting of standards for gaseous pollutants.

INTRODUCTION

Many energy technologies proposed for development would release H_2S or SO_2 into the atmosphere. We are particularly interested in the development of geothermal energy resources that is taking place in the Imperial Valley and The Geysers, California, and other places in the West. But the considerations discussed in this paper are applicable to the SO_2 released in the combustion of coal or fuel oil or the H_2S released in gasification or liquification of coal. In this paper, we present a model of the effects of SO_2 and H_2S on photosynthesis in the leaf. The model can be used as a submodel in models of vegetation growth subjected to pollutants. These models with the addition of accurate parameters and validation could be important to the assessment of ecological or economic impacts of pollution from energy development.

This model is intended for two purposes. One is the analysis of experiments on the photosynthetic response of leaves fumigated with sulfur compounds. These experiments are typically run in fractions of hours. The other purpose is a leaf submodel in a larger model of the growth of the entire plant to either assess longer term effects from energy technologies or analyze experimental growth data. These experiments span an entire growing season. Because the model covers two time spans, specific considerations are required in each case. In other words, we will construct a general model, which in the limit of very short periods, will approach one form and for longer periods will approach another analytical expression.

We have modeled leaf photosynthesis with several ideas in mind. In the short-term model, we wished to explain as many empirical observations as possible while limiting the model to reversible biochemical effects. Our short-term model therefore will not apply to data that involves the destruction of tissue. For example, SO_2 is implicated in the destruction of subcellular membranes that are the sites of many enzymatic reactions. Destruction of these tissues would, therefore, disrupt the reactions without direct inhibition by SO_2 . Such effects of membrane damage are not included. Instead, we examined only those reactions that are themselves enhanced or

inhibited. Effects resulting from membrane destruction would be important in the long-term model. Although they would not be modeled in detail, they must be accounted for with an empirical expression.

The model, therefore, is an attempt to explain effects by biochemical mechanisms, rather than phenomenologically, with the expectation that it will be more effective in predicting plant responses. Furthermore, the model must be consistent with accepted data and models of the effects of CO_2 , light, temperature, and diffusion resistances on photosynthesis.

Ziegler (1973, 1975) and Malhotra and Hocking (1976) reviewed the literature on the effects of SO_2 on plant metabolism and provide the following evidence.

- Very low doses of SO_2 enhance photosynthesis. In the light reactions of the photosynthesis, sulfite (SO_3^-) aids the shift of ferredoxin from the oxidized to the reduced form and enhances nicotinamide adenine diphosphate (NADP) reduction.

- Plants have a threshold to SO_2 damage. A certain amount of SO_2 can be taken up and metabolized by the plant without negative effects. Beyond that amount, deleterious effects appear and increase with increasing SO_2 .

- Plants take up SO_2 primarily through the stomates.
- Normal pathways in the plant metabolize SO_2 until these pathways are saturated.
- At active sites on ribulose 1,5-diphosphate (RuDP) carboxylase, a major link in the dark reactions of photosynthesis, SO_3^- competes with CO_2 .

- At high levels of SO_3^- , RuDP carboxylase is inhibited but for reasons other than competition with CO_2 .
- In plants with the C_4 pathway, SO_3^- interferes with phosphoenol pyruvate (PEP) carboxylase by an unknown (as of 1976) mechanism.

- Even at low concentrations, SO_2 damages the chlorophyllase enzyme system.

- At high concentrations, SO_2 converts chlorophyll into phaeophytin and Mg^{++} and further inhibits chlorophyllase activity.

- Some evidence exists that SO_2 binds irreversibly with the chloroplast iron in ferredoxin and cytochromes, causing a decrease in electron transport in the light reactions of photosynthesis.

- The damage to inner or outer chloroplast membranes and, thus, the inhibition of photosynthesis by SO_2 is suggested.

Shinn *et al.* (1976) reported nutritive effects of low and deleterious effects of high concentrations of a geothermal gas containing H_2S on photosynthesis in lettuce. In this report, we will use similar unpublished data from Shinn on sugar beets. Thompson and Kats (1978) reported a similar pattern of H_2S effects on the growth of lettuce, cotton, and sugar beets. We assume that H_2S is metabolized by the plant and incorporated into normal plant metabolism in an analogous manner to SO_2 metabolism. For mathematical modeling, we regard the effects of H_2S analogous to those of SO_2 .

DESCRIPTION OF THE MODEL

In CO_2 uptake and assimilation from air, two processes occur, either one of which can be limiting. Therefore, both must be considered in the modeling of photosynthesis. Chartier (1970), Stewart (1970), Hall (1971), and Sinclair (1972) explicitly used this information in their models. We will make extensive use of Sinclair's conceptualization. Initially, we will assume that all processes are at equilibrium.

DIFFUSION

The first process is the diffusion of CO_2 from ambient air at CO_2 concentration C_a (n mole cm^{-3}) into the leaf to the site of CO_2 assimilation, the chloroplast (Fig. 1). Here the concentration of CO_2 is C_c (n mole cm^{-3}). In the stomatal pore, the CO_2 concentration is C_i . Assuming diffusion governed by Fick's Law and steady state conditions, the diffusion of CO_2 from the ambient air to the stomatal pore is described by an electrical analog equation, e.g., as described by Hall (1971) and Sinclair (1972).

Fig. 1. Schematic diagram of diffusion of CO_2 into the plant. r_a = leaf boundary layer resistance, r_s = stomatal resistance, r_{cw} = cell wall resistance, r_p = cytoplasmic resistance, P_n = net photosynthesis, R = respiration, and P_g = gross photosynthesis.

$$P_n = \frac{C_a - C_i}{r_a + r_s}, \quad (1)$$

where

- r_a = resistance of the boundary layer of the leaf (s cm^{-1}),
- r_s = stomatal resistance to CO_2 diffusion (s cm^{-1}),
- P_n = net photosynthesis rate per unit area of leaf ($\text{n mole CO}_2 \text{ cm}^{-2} \text{ s}^{-1}$).

At the cell wall, CO_2 dissolves in water and diffuses across the cell wall; thus,

$$P_n = \frac{sC_i - C_p}{r_{cw}}, \quad (2)$$

where

$$\begin{aligned} r_{cw} &= \text{cell wall resistance (s cm}^{-1}\text{)}, \\ s &= \text{absorption coefficient of CO}_2 \text{ in water,} \\ C_p &= \text{concentration of CO}_2 \text{ inside the protoplasm (n mole cm}^{-3}\text{)}. \end{aligned}$$

Inside the cell, CO₂ is generated by the mitochondria (dark respiration), which is independent of light intensity. The CO₂ generated by photorespiration in the chloroplast is included in the term for gross photosynthesis P_g . Inside the cell, the total amount of CO₂, P_g , diffusing through the protoplasm to the chloroplast is equal to the CO₂ from respiration R and the CO₂ entering from the ambient air. Thus,

$$P_g = P_n + R, \quad (3)$$

and

$$P_g = \frac{C_p - C_c}{r_p}, \quad (4)$$

where

$$\begin{aligned} r_p &= \text{protoplasmic resistance (s cm}^{-1}\text{)}, \\ C_c &= \text{concentration of CO}_2 \text{ in the chloroplast (n mole cm}^{-3}\text{)}. \end{aligned}$$

Eliminating C_i and C_p from Eqs. (1) through (4), we find that

$$P_n = \frac{sC_a - r_p R - C_c}{r_{cw} + r_p + s(r_a + r_s)}. \quad (5)$$

We now consider the removal of C_c from Eq. (5).

BIOCHEMICAL PROCESSES OF CO₂ ASSIMILATION AT STEADY STATE

The second process in photosynthesis is the conversion of light energy to chemical energy. In Fig. 2 we consider the essential biochemical processes of photosynthesis with the concomitant conversion of CO₂ and H₂O to O₂ and CH₂O. In the construction of the model, we first consider the kinetics of the CO₂ fixation and the light absorption reactions. Stewart (1970) presented a similar model of photosynthesis with a less complex light reaction and without photorespiration. Hall (1971) and Hall and Björkman (1975) showed a very detailed photosynthesis model upon which ours is based. Sinclair (1972) modified Hall's model by excluding photorespiration. The dark or carboxylation reaction is on the left in Fig. 2, and the light or Hill reaction is on the right.

Photosynthesis proceeds by 1,5-ribulose diphosphate carboxylase (RuDPCase) at a concentration of E_1 , taking up CO₂ at a concentration of C_c , to form a complexed product at concentration E_2 . At a concentration of S_c , SO₃⁻ interacts competitively for the same sites and forms a complexed product with RuDPCase at a concentration E_3 . We assume a rapid equilibrium between these substrates and the RuDPCase such that

$$E_2 = k_1 C_c E_1, \quad (6a)$$

and

$$E_3 = k_5 S_c E_1. \quad (6b)$$

Fig. 2. Schematic diagram of photosynthesis. On the left is the dark reaction (carboxylation) and on the right is the light reaction (Hill reaction). Circles k_2 and k_4 on the right represent chloroplasts reducing ferredoxin in the presence of light. Ferredoxin reduces NADP to NADPH. RuDPCase = ribulose diphosphate carboxylase.

This assumption is often made in enzyme kinetics (Segel, 1975). Following Hall's model (1971), we assume that photorespiration proceeds by oxygen acting on RuDP via RuDPCase. Thus an O_2 -RuDPCase complex with a concentration E_4 is formed:

$$E_4 = k_9 O_{chl} E_1, \quad (6c)$$

where

$$O_{chl} = \text{oxygen concentration at the chloroplast.}$$

The total amount of RuDPCase is assumed to be constant for the time periods under consideration. Therefore,

$$E_1 + E_2 + E_3 + E_4 = E_o, \quad (7)$$

where

$$E_o = \text{total constant concentration of RuDPCase and complexes.}$$

We assume that the total photosynthesis rate is proportional to the product of the concentration of the CO_2 -RuDPCase complex and the concentration of RuDP, denoted as B .

$$P_t = k_{12} E_2 B. \quad (8)$$

This reaction produces 3-phosphoglyceric acid (PGA) at concentration A . The energy that runs the Calvin cycle is supplied by products of the Hill reaction, namely reduced nicotinamide adenine dinucleotide (NADPH), which interacts with PGA and ultimately regenerates RuDP. Thus, we use the approximation

$$B = k_3 A N_1 \quad (9)$$

to account for this part of the Calvin cycle. We assume that photorespiration R_L is proportional to the concentrations of RuDPCase- O_2 complex and RuDP. This is in accordance with work of Hall (1971).

$$R_L = k_{14} O_{chl} B \quad (10)$$

Gross photosynthesis is total photosynthesis less photorespiration:

$$P_g = P_t - R_L \quad (11)$$

In the light reactions, the energy that chlorophyll absorbs from light is ultimately used to reduce NADP at concentration N_2 to NADPH at concentration N_1 . According to the information given in the Introduction, two pathways exist for this: one in the presence of SO_3^- and the other in its absence. The concentration of NADP (N_2^*) in the presence of SO_3^- is assumed to be proportional to the product of the concentration of NADP in the absence of SO_3^- (N_2) and the concentration of SO_3^- (S_c). Thus,

$$N_2^* = k_6 N_2 S_c \quad (12)$$

We assume that for the time periods under consideration NADP and NADPH are conserved:

$$N_1 + N_2 + N_2^* = N_o \quad (13a)$$

and PGA and RuDP is conserved:

$$A + B = A_o \quad (13b)$$

where A_o and N_o are constants. The reduction of NADP to NADPH in light with intensity I is described by the constant k_2 in the absence of SO_3^- and k_4 in the presence of SO_3^- :

$$N_1 = k_2 I N_2 + k_4 I N_2^* \quad (14a)$$

where

$$k_4 > k_2 \quad (14b)$$

Combining Eqs. (6) through (14), we find:

$$P_g = \frac{(k_{12} k_1 C_c - k_{14} k_9 O_{chl}) E_o k_3 A_o N_o I (k_2 + k_4 k_6 S_c)}{(1 + k_1 C_c + k_5 S_c + k_9 O_{chl}) [1 + k_6 S_c + (1 + k_3 N_o) I (k_2 + k_4 k_6 S_c)]} \quad (15)$$

We will combine and redefine constants to simplify this expression. We will eliminate the dependence on O_{chl} , because in problems of interest to us, this is always constant. Letting

$$k'_1 = \frac{k_1}{1 + k_9 O_{chl}} \quad (16a)$$

$$k'_5 = \frac{k_5}{1 + k_9 O_{chl}} \quad (16b)$$

$$k'_2 = (1 + k_3 N_o) k_2 \quad (16c)$$

$$k_4' = \frac{k_4}{k_2}, \quad (16d)$$

$$k_3' = k_{12} E_o k_3 A_o N_o / (1 + k_3 N_o), \quad (16e)$$

$$k_9' = k_{14} k_9 O_{chl} / (k_{12} k_1), \quad (16f)$$

P_g becomes

$$P_g = \frac{k_1' k_2' k_3' (C_c - k_9') I (1 + k_4' k_6 S_c)}{(1 + k_1' C_c + k_5' S_c) [1 + k_6 S_c + k_2' I (1 + k_4' k_6 S_c)]}. \quad (17)$$

We have two expressions for photosynthesis, Eqs. (5) and (17). Both contain a nonobservable quantity C_c . Combining Eqs. (3), (5), and (17) and eliminating C_c , we obtain

$$P_n = \frac{-b - \sqrt{b^2 - 4ac}}{2a} - R, \quad (18)$$

where

$$\begin{aligned} a &= k_1' [1 + k_6 S_c + k_2' I (1 + k_4' k_6 S_c)] [r_{cw} + r_p + s (r_a + r_s)], \\ b &= -[1 + k_6 S_c + k_2' I (1 + k_4' k_6 S_c)] [s C_a k_1' + k_1' R (r_{cw} + s (r_a + r_s)) + 1 + k_5' S_c] \\ &\quad - k_1' k_2' k_3' I (1 + k_4' k_6 S_c) [r_{cw} + r_p + s (r_a + r_s)], \\ c &= k_1' k_2' k_3' I (1 + k_4' k_6 S_c) [s C_a + R (r_{cw} + s (r_a + r_s)) - k_9']. \end{aligned}$$

Because electron transfer, which reduces NADP to NADPH, occurs via ferredoxin and because ferredoxin reduction is enhanced by $SO_3^{=}$, one could include the extra step of ferredoxin reduction in a model of the light reactions. The results of that treatment are mathematically identical to those given above and, hence, could not be discriminated from the above treatment.

A more rigorous approach can be taken in the derivation of an expression for gross photosynthesis, Eq. (15). For example, in the enzyme kinetics of RuDPCase, E_1 could combine with RuDP first and then be inhibited by $SO_3^{=}$ or interact with CO_2 . Also, one should equate velocities of the various reactions of NADPH formation and the rate of PGA interacting with NADPH via phosphoglyceraldehyde dehydrogenase. Furthermore, Hall and Björkman (1975) have a detailed model for the contributions of carboxylation and light respiration of RuDP to PGA formation. Unfortunately, if a rigorous approach were followed, the solutions to the equations are far more complicated than Eq. (17), with even more parameters to be determined. With the data that were available for this study, we would not be able to discriminate between the result of the more rigorous approach and the result obtained here. Note that the equations used here do model all the processes in Fig. 2 and do explain all the data that were available. Note that r_s is often a function of pollutant level, and that this effect should be included in model calculations.

TEMPERATURE DEPENDENCE OF RESPIRATION AND PHOTOSYNTHESIS

Johnson *et al.* (1954) assumed that biological processes such as respiration can be considered as mediated at a critical stage by an enzyme-substrate complex. To form the activation complex, an activation energy must be overcome. Johnson *et al.* showed that the rate of such a process can be given by

$$\text{Respiration rate} = a E_n T \exp (-\Delta H / R_g T), \quad (19)$$

where

a = constant,
 E_n = enzyme concentration (n moles cm^{-3}),
 T = temperature ($^{\circ}\text{C}$),
 ΔH = Heat of the reaction (cal mole^{-1}),
 R_g = gas constant.

Suppose enzyme E can be denatured reversibly by heat, i.e., the molecule could be elevated to a higher energy level, e.g., a vibrational mode, in which it can no longer function as a catalyst. Let the concentration of enzymes in the ground state be E_n and those in the excited state be E_d .

Then

$$E_d/E_n = \exp. (\Delta S/R_g - \Delta H'/R_g T) \quad , \quad (20)$$

where

ΔS = entropy change for transitions $n \leftrightarrow d$,
 ΔH = heat change for transitions $n \leftrightarrow d$.

We assume that the total enzyme concentration is constant. Thus,

$$E_T = E_n + E_d \quad . \quad (21)$$

Using Eqs. (20) and (21) in Eq. (19), we can calculate the respiration rate as

$$R = R_x \frac{T}{T_x} \frac{\exp [-\Delta H/R_g (1/T - 1/T_x)] [1 + \exp (\Delta S'/R_g - \Delta H'/R_g T_x)]}{1 + \exp (\Delta S'/R_g - \Delta H'/R_g T)} \quad , \quad (22)$$

where

R_x = respiration at base temperature T_x ,
 T_x = base or reference temperature.

We follow this approach to derive a formula for the temperature dependence of photosynthesis. Because k'_3 is the only rate constant in Eq. (17), it behaves like

$$k'_3 = k''_3 (T/T_x) \exp ((-H_3/R_g)(1/T - 1/T_x)) \quad . \quad (23)$$

The equilibrium constants, k'_1 and k'_5 , specify the equilibrium between two competing substrates and the enzyme RuDPCase. We hypothesize that they should have a similar temperature dependence. This must be substantiated by further experimentation. For now, we assume

$$k'_1 = k''_1 \exp ((-H_1/R_g)(1/T - 1/T_x)) \quad , \quad (24a)$$

and

$$k'_5 = k''_5 \exp ((-H_1/R_g)(1/T - 1/T_x)) \quad . \quad (24b)$$

The parameter k'_9 is the ratio of two rate constants, hence the temperature dependence is given by

$$k'_9 = k''_9 \exp ((-H_9/R_g)(1/T - 1/T_x)) \quad . \quad (25)$$

We assume k'_2 , k'_4 , and k_6 are temperature independent. The parameters, k'_2 and k'_4 , are constants for reactions in which the activation energy is supplied by light not heat. Also, Sinclair (1972) in a similar model for corn found that k'_2 is independent of T . The parameter k_6 is not regarded as a true equilibrium constant in this model. Instead, it is a measure of the number of light reactions that take place in the presence of SO_3 . Thus, we make the simplest assumption for k_6 , namely, that it has no temperature dependence.

We assume that RuDPCase could be reversibly denatured if it were raised to a higher energy level with energy level ΔF_L above the ground state. We assume for now that all the complexes of RuDPCase have approximately the same energy for the excited state. Thus, the relationships,

$$E_1^d/E_1^n = \exp(-\Delta F_L/R_g T) \quad ,$$

$$E_2^d/E_2^n = \exp(-\Delta F_L/R_g T) \quad ,$$

$$E_3^d/E_3^n = \exp(-\Delta F_L/R_g T) \quad ,$$

$$E_4^d/E_4^n = \exp(-\Delta F_L/R_g T) \quad ,$$

lead to a factor of $1/(1 + \exp(-\Delta F_L/R_g T))$ in the expression for E_o in Eq. (15). Because E_o is absorbed into k'_3 (Eq. 16e), we rewrite Eq. (23) for k'_3 as

$$k'_3 = k''_3 (T/T_x) \exp((-H_3/R_g)(1/T - 1/T_x)) (1 + \exp(-\Delta F_L/R_g T_x)) / (1 + \exp(-\Delta F_L/R_g T)) \quad , \quad (26)$$

where

$$\Delta F_L = -T\Delta S_L + \Delta H_L \quad .$$

Eqs. (24) through (26) should be used in Eqs. (17) and (18). Now for each enzyme that moderates a reaction, a temperature-denaturation expression should be used. However, there will be a minimum denaturation energy $E_{\min}$, so that for temperatures greater than some $T_{\min}$, the photosynthetic rate will decrease. Thus, only one such denaturation expression will be necessary to explain the data.

SULFUR METABOLISM

In Eq. (18), the effects of sulfur compounds are expressed as S_c , the concentration in the chloroplast. The second and fourth points in the list of observations in the Introduction suggest that for predictive purposes we must establish some kind of relationship between the pollutant concentration in air S_a and the concentration S_c . We follow an approach similar to that for CO_2 metabolism. The sulfur compound must diffuse through the boundary layer and the stomate to enter the leaf. At the cell wall, the compound dissolves in the water and diffuses across the cell wall. From the cell wall, it diffuses through the cytoplasm to the chloroplast. Analogous to Eq. (5), this flux is given by

$$\text{Diffusive sulfur flux} = \frac{s_s S_a - S_c}{s_s (r'_a + r'_s) + r'_{cw} + r'_p} \quad , \quad (27)$$

where

s_s = absorption coefficient of the sulfur compound into water.

The resistances are the same as those described previously except that the primes indicate resistance to the sulfur compound instead of to CO_2 . We assume that both H_2S and SO_2 are metabolized in the cell to give the same

products, including SO_3^{2-} . We suspect that this assumption is better at low than at high concentrations. However, at high concentrations, damage is so extensive in such a wide variety of enzyme systems that the validity of this assumption is unimportant. The metabolism of the sulfite S_c proceeds by some enzymatic process in which the SO_3^{2-} is complexed by an enzyme with concentration D_1 to form an activation complex with concentration D_2 . We assume rapid equilibrium is established (Segel, 1975) such that

$$\text{D}_2 = \text{K}_1 \text{D}_1 \text{S}_c \quad (28)$$

and the total amount of enzyme plus complex is constant:

$$\text{D}_0 = \text{D}_1 + \text{D}_2 \quad (29)$$

Assuming that the rate of reaction is proportional to D_2 with coefficient K_2 , we combine this with Eqs. (28) and (29) to find

$$\text{Rate of enzymatic process} = \text{K}_2 \frac{\text{K}_1 \text{S}_c \text{D}_0}{1 + \text{K}_1 \text{S}_c} \quad (30)$$

Equating the rates in Eqs. (27) and (30), we find

$$\text{S}_c = \frac{\text{S}'_a}{2} - \frac{(1 + \text{K})}{2\text{K}_2} + \sqrt{\left(\frac{\text{S}'_a}{2} - \frac{1 + \text{K}}{2\text{K}_2}\right)^2 + \frac{\text{S}'_a}{\text{K}_2}} \quad (31)$$

where

$$\text{K}_2 = \text{K}'_2 \text{K}_1,$$

$$\text{K} = \text{K}_1 r \text{D}_0,$$

$$\text{S}'_a = s_s \text{S}_a,$$

$$r = s_s(r'_a + r'_s) + r'_{cw} + r'_p.$$

In Fig. 3 we show the plot of this expression, where the concentration in the chloroplast S_c is given as a function of the concentration in air S_a . At low values of S'_a , S_c behaves like

$$\text{S}_c \sim \frac{\text{S}'_a}{1 + \text{K}}, \quad \text{when } \frac{\text{S}'_a \text{K}_2}{1 + \text{K}} \ll 1, \quad (32)$$

i.e., S_c is linear in S_a with a slope of $\frac{1}{1 + \text{K}}$ for low values of S_a . At high values of S_a ,

$$\text{S}_c \sim \text{S}'_a - \frac{\text{K}}{\text{K}_2}, \quad \text{when } \frac{1 + \text{K}}{\text{S}'_a \text{K}_2} \ll 1. \quad (33)$$

That is to say, S_c as a function of S'_a asymptotically approaches a straight line with slope = 1 and an intercept at K/K_2 on the S'_a axis. There is an inflection at

$$\text{S}'_a = (\text{K} - 1) / \text{K}_2 \quad (34)$$

This inflection occurs where $\frac{d^2 \text{S}_c}{d\text{S}'_a{}^2}$ reaches its maximum, which is equal to

Fig. 3. The relationship of SO_3^- concentration at the chloroplast S_c to the concentration of sulfur compound in air, S'_a . A sharp inflection occurs at $S'_a = (K-1)/K_2$, the threshold for deleterious effects from SO_3^- .

$$\max \left(\frac{d^2 S_c}{dS_a^2} \right) = K_2 / (4\sqrt{K}) \quad (35)$$

To be consistent with the second and fourth pieces of evidence in the Introduction, K must be large. This will ensure a small slope at low values of S'_a . We set K_2 to fix the position of the inflection. If we work in the units in which the inflection is of the order of 1, then K_2 will be of the order of K . Thus, $\max (d^2 S_c / dS_a^2)$ at the inflection will be of the order $K^{1/2}$, which is large. The full width of the peak of $d^2 S_c / dS_a^2$ at half maximum is equal to $4\sqrt{(4^{1/3} - 1) K / K_2^2}$, which is of the order $1/\sqrt{K}$. This means that the inflection will be quite sharp, causing the curve to approach the linear asymptote of Eq. (33) rapidly. Thus, we have provided for the threshold effect described in the Introduction.

ESTIMATION OF PARAMETERS FOR THE SHORT-TERM MODEL

We have determined parameters for sugar beets because the model will be used to assess the possible effects of the development of geothermal energy resources in the Imperial Valley, California. Sugar beets are one of the five most important crops in the valley and have been studied extensively by others (Hall, 1970; Fick, 1971; Nevins, 1965). Kanemasu *et al.* (1969) found that the diffusion resistance of the leaf boundary layer to sensible heat was given by $r_{a \text{ Heat}} = 0.6\sqrt{D_L/U}$, where D_L is the leaf width in cm, and U is the windspeed in cm s^{-1} . Using $r_{a \text{ CO}_2} = 1.32 r_{a \text{ Heat}}$ (Stewart, 1970) and $D_L = 10$ cm, we find that

$$r_a = 2.5 / \sqrt{U} \quad (36)$$

Hall's (1970) work on photosynthesis found r_a equal to $0.37 \text{ (s cm}^{-1}\text{)}$ in his experiments, which is the value we used in our model described below. We followed Hall's (1970) estimation procedure for r_{cw} and used 0.17 s cm^{-1} . For the functional form of r_s , we used

$$r_s = \frac{a_1}{a_2 + I} + a_3 \quad (37)$$

We found a_1 , a_2 , and a_3 by fitting this expression to Hall's (1970) data. We found $a_1 = 84.7 \text{ nanoeinsteins cm}^{-3}$, $a_2 = 1.0 \text{ nanoeinsteins cm}^{-2} \text{ s}^{-1}$, and $a_3 = 0.55 \text{ s cm}^{-1}$. This fit is shown in Fig. 4a. We treated r_s as a function of S_a empirically. Data from Shinn *et al.* (1976) were used to generate a linear function of r_s vs S_a . From Hall (1971), the absorption coefficient of CO_2 in water s is given by $2.33 - 1.126 \log_{10} T \text{ (}^\circ\text{C)}$. We must next determine the parameters, k_1 , k_2 , k_3 , r_p , R , and k_0 , for the case $S_a = 0$. All the data on sugar beet photosynthesis were obtained when either light or CO_2 or both were limiting. The parameter k_3 is equivalent to P_g when both I and CO_2 are large, i.e., nonlimiting (Eq. 17). Thus, we cannot determine k_3 directly, but instead we must set its value arbitrarily. Sinclair (1972) suggests setting it to a high value compared to those of P_g for which either light or CO_2 or both are limiting. Brown's (1976) data on the response of field-grown beets to increased CO_2 support this approach. For sugar beets, we set k_3 at $180 \text{ n moles cm}^{-2} \text{ s}^{-1}$. After k_3 is chosen, then the remaining parameters, k_1 , k_2 , k_0 , r_p , and R , can be determined specifically by fitting Eq. (18) simultaneously to data of P_n as a function

Fig. 4. Estimation of parameters for the short-term model of sugar beet growth. (a) Fit of stomatal resistance calculations to sugar beet leaf data at various intensities of incident light. (b) Fit of Eq. (18) to photosynthesis data (o) from sugar beets as a function of light intensity. (c) Photosynthesis as a function of external CO_2 concentration at fixed light ($130 \text{ nanoeinsteins cm}^{-2} \text{ s}^{-1}$). Data (o) from Hall (1970), Model fit (—).

of light and P_n as a function of external CO_2 . (See Figs. 4b and 4c). This was done using LSPFIT (Moore, 1976) and minimizing an estimated χ^2 . The results were $k_1'' = 0.913 \text{ cm}^3 \text{ n mole}^{-1}$, $k_2'' = 4.33 \times 10^{-4} \text{ nanoeinsteins}^{-1} \text{ cm}^2 \text{ s}$, $k_3'' = 1.10 \text{ n moles cm}^{-3}$, $r_p = 1.25 \text{ s cm}^{-1}$, and $R_x = 0.129 \text{ n mole cm}^{-2} \text{ s}^{-1}$. Note that all observable properties of photosynthesis, in the range of values of I and CO_2 for which either is limiting, are insensitive to the procedure of choosing k_3'' first and then determining the remaining parameters. This insensitivity results because any observable property that depends on k_3 also depends on one or more of the remaining parameters; these were chosen specifically to reproduce the photosynthetic response when either CO_2 or light are limiting.

Temperatures were fitted next using LSPFIT and minimizing the estimated χ^2 . Respiration as a function of temperature (Fick, 1971; Hofstra and Hesketh, 1969; Nevins and Loomis, 1970) was fit using Eq. (22). The result is shown in Fig. 5a; $\Delta H = 1.08 \times 10^4 \text{ cal mole}^{-1}$, $\Delta H' = 5.32 \times 10^4 \text{ cal mole}^{-1}$, and $\Delta S' = 164 \text{ cal mole}^{-1} \text{ K}^{-1}$. Similarly, we fit the data on photosynthesis rates with the results shown in Fig. 5b. This was done using Eqs. (22) through (26) in Eq. (18). The broad peak was obtained because of the multiplicity of heats involved. Eliminating or constraining any one of them produces a narrower peak. The data were obtained from Nevins and Loomis (1970), and the results were $\Delta H_1 = 4.01 \times 10^4 \text{ cal mole}^{-1}$, $\Delta H_3 = 15.3 \times 10^4 \text{ cal mole}^{-1}$, $\Delta H_9 = -1.77 \times 10^4 \text{ cal mole}^{-1}$, $\Delta S_L = 683 \text{ cal mole}^{-1} \text{ K}^{-1}$, and $H_L = 17.3 \times 10^4 \text{ cal mole}^{-1}$. ΔH_9 is negative because k_9 is the ratio of two rate constants with the numerator equal to the rate of RuDP oxidation and the denominator equal to carboxylation. The minus sign suggests that the activation energy of RuDP oxidation is lower than that of RuDP carboxylation.

The parameter K in Eq. (31) can be chosen arbitrarily if it is large. The parameter K_2 is chosen so that $(K-1)/K_2$ equals the observed threshold. Using data from Shinn (unpublished), we set $K = 100$ and $K_2 = 260 \text{ ppm}^{-1}$ with a threshold of 0.38 ppm. The parameters, k_4 and k_5'' , were also chosen to give an agreeable fit to Shinn's data on sugar beets. A description of the data and method is given by Shinn *et al.* (1976), who described experiments on lettuce. The sugar beet data and model fit are given in Fig. 6. The parameter k_4 was set at 5.0 and k_5'' at 60 ppm^{-1} . The estimation of k_6 is discussed below after the discussion of the long-term-effects model.

MODEL OF LONG-TERM EFFECTS

For experiments in which the leaf is subjected to a change in the external concentration of a gas for short periods in the order of a few hours, we can assume that the parameters discussed above are relatively constant. Thus, in short-term experiments, we assume that the plant can only adapt by changing stomatal resistance. However, in experiments in which the plant is subjected to increased levels of sulfur compounds or changes in CO_2 during an entire growing season, we cannot make the same assumptions. Adaptive or deleterious effects may appear under long-term fumigation that are not detectable under short-term conditions.

For example, we may assume that the enzyme E_o is generated at rate F (available nutrients) with a normal specific degeneration rate of d_1 . In the presence of elevated levels of SO_3 , we assume that the specific degeneration rate increases by $d_2 S_c$. Thus,

$$\frac{dE_o}{dt} = F (\text{available nutrients}) - (d_1 + d_2 S_c) A_o, \quad (38)$$

which can be solved by

$$E_o(t) = E_o(t_0) \exp[-(d_1 + d_2 S_c)(t - t_0)] + (F/(d_1 + d_2 S_c)) [1 - \exp(-(d_1 + d_2 S_c)(t - t_0))].$$

If we assume that the S_c is introduced at t_0 , then presumably before t_0 the leaf metabolism would be at steady state, and

$$E_o(t_0) = F/d_1. \quad (39)$$

For short times $[(d_1 + d_2 S_c)(t - t_0) \ll 1]$, $E_o(t)$ would continue to be nearly equal to F/d_1 . However, with time $E_o(t)$ would approach $F/(d_1 + d_2 S_c)$ asymptotically. Thus, a deleterious effect would appear in time. Another consideration should be noted about Eq. (38). The rate F is explicitly stated as a function of available nutrients.

Fig. 5. Model fit (—) to data on dark respiration (Fick, 1971) and data on photosynthesis rate (Nevins and Loomis, 1970) in sugar beets with changes in temperature. $\circ$ = data points. Respiration and photosynthesis at 25°C.

Fig. 6. Fits of photosynthesis and growth of PHOTO and BEETGROW2 (a) using LTSM1 and (b) using LTSM2. Data from Thompson and Kats (1978) and Shinn (unpublished). $\circ$ = experimental points, Δ $\square$ model; open symbols = growth, solid symbols $\square$ growth under CO_2 test; half solid = photosynthesis, (— · —) = model photosynthesis. Growth and photosynthesis at 0 ppm H_2S = 1.

For example, if CO_2 were vital to the generation of E_o and sulfite were also essential, then a process for which the rate of generation was proportional to a power of C_c and a complexing substrate C_1 could easily be proposed:

$$F = f_1[C_1] C_c^n, \quad (40)$$

as well as a process for which the rate was proportional to S_c and a complexing substrate C_2' :

$$F = f_2[C_2] (1 + k_{11}S_c) \quad (41)$$

where the amount of substrates available is constant

$$C_o = [C_1] + [C_2] \quad (42)$$

Thus,

$$F = \frac{f_1 f_2 C_o C_c^n (1 + k_{11}S_c)}{f_2 (1 + k_{11}S_c) + f_1 C_c^n} \quad (43)$$

Thus, the long-term submodel (LTSM1) for the level of E_o is given by

$$E_o(S_c, C_c) = \frac{1 + k_{10}(C_c^o)^n}{(C_c^o)^n} \frac{C_c^n (1 + k_{11}S_c)}{1 + k_{11}S_c + k_{10}C_c^n} \frac{E_o^o}{1 + k_7 S_c} \quad (44)$$

where $k_{10} = f_1/f_2$, $k_7 = d_2/d_1$, and $f_1 C_c = [1 + k_{10}(C_c^o)^n/(C_c^o)^n]E_o^o d_1$. The constant C_c^o is the average CO_2 concentration in the chloroplast and C_a the normal ambient atmospheric concentration. Equation (44) demonstrates that as CO_2 increases, E_o increases. This equation shows that CO_2 can compensate for the deleterious effects of increased sulfite that arise from the $1/(1 + k_7 S_c)$ factor. Thompson and Kats (1978) showed in field experiments that CO_2 partially protects the plant from the injurious effects of H_2S (see Fig. 6).

A different analytic approach from that taken above is to assume that a fraction of the E_o in the presence of CO_2 is shielded from SO_3 . Thus, we might assume that there are, in effect, two types of E_o (E_o and E_o'), where the prime indicates that the E_o' is not acted upon by SO_3 . At equilibrium, we would assume, therefore, that E_o is generated at a rate F and destroyed at a rate $(d_1 + d_2 S_c)E_o$. Furthermore, E_o is converted to the form E_o' at a rate of $d_3 C_c E_o$. E_o' is generated at a rate $d_3 C_c E_o$ and lost at a rate $d_1 E_o'$. Thus,

$$F = (d_1 + d_2 S_c) E_o + d_3 C_c E_o \quad (45)$$

and

$$d_3 C_c E_o = d_1 E_o' \quad (46)$$

Solving these equations for the total amount of enzyme $E_o + E_o'$ available for photosynthesis, we find

$$E_o + E_o' = \frac{E_o'' (1 + k_8 C_c)}{(1 + k_7 S_c + k_8 C_c)} \quad (47)$$

where $E_o'' = F/d_1$, $k_8 = d_3/d_1$, and $k_7 = d_2/d_1$. To avoid solving a high order polynomial equation, we use an approximation for C_c . We assume that for fixed light at high intensities,

$$C_c \cong K_3 \frac{C_a}{r_s} \quad (48)$$

where K_3 is a constant. Equation (48) is equivalent to the assumption that the dominant diffusion resistance is stomatal. We divide C_a into two terms,

$$C_a = C_a^o + \Delta C_a \quad (49)$$

where the ambient level C_a^0 is assumed to be 13.27 n moles/cm³. Substituting Eqs. (47) through (49) gives

$$E_o + E'_o = \frac{E_o'' (1 + k'_8 \Delta C_a)}{(1 + k'_8 \Delta C_a + k'_7 S_c r_s)} \quad (50)$$

where $k'_8 = k_8 K_3 / (r_s + k_8 K_3 C_a^0)$ and $k'_7 = k_7 / (r_s + k_8 K_3 C_a^0)$. Under the assumption that most of the photosynthesis occurs at high light levels with adequate water, r_s can be regarded as approximately constant, and k'_8 and k'_7 can be considered as constants. Let us denote Eq. (47) or (50) as the second long-term submodel (LTSM2).

We can carry this approach even further to simplify Eq. (48) by using

$$C_c = K_3 C_a \quad (51)$$

where r_s is included in K_3 . We do this only for the case in which C_a is constant during a growing season. Then most CO₂ uptake will occur with r_s close to some modal value. When CO₂ fluctuates, or r_s fluctuates because of a dependence on leaf potential, or soil water potential fluctuates, then a closer approximation can be achieved by avoiding Eq. (51) and instead using C_c directly.

ESTIMATION OF PARAMETERS IN LONG-TERM MODELS

Thompson and Kats (1978) performed experiments on sugar beets grown in the field in fumigation chambers with external atmospheric H₂S maintained at various concentrations. We used this data to determine the parameters k_{10} , k_{11} , and n in the first long-term effects submodel (LTSM1) and the parameters, k_6 , k'_7 , and k'_8 , in LTSM2. In the former case, the determination of k_6 is based on the observation of Ziegler (1975) that the increase in photosynthesis due to SO₃ saturates at approximately half the value at which the deleterious effect begins. We used the photosynthesis submodels as photosynthate generators in a seasonal growth model modified for sugar beets with parameters specific for that crop (BEETGROW2) (Kercher, 1978). In the LTSM1 fit, k_{10} was adjusted to agree with the maximum increase attained in total plant growth, k_{11} to agree as closely as possible with the slope at H₂S = 0 of the curve for increased growth, and k_7 to fit the model results to data on the decrease in growth at higher H₂S levels; n was chosen to produce results agreeing with data on the combined effects of increased H₂S and increased CO₂ levels (see Fig. 6a). In Fig. 6a and b, the open triangles and circles are points from model calculations and experimental data, respectively. These data points are for measures of relative growth at various concentrations of H₂S compared to the absence of H₂S. They were all measured at ambient CO₂ concentrations. The solid triangles and circles are calculations and experiments made with 50 ppm CO₂ above ambient CO₂ concentrations. By growth we mean total growth of the sugar beet plant at harvest, including tops and roots. For the LTSM2 case, k_6 and k'_7 were adjusted to bring the results of the seasonal model into agreement with the data on sugar beet growth when plants were fumigated solely by H₂S. Then k'_8 was adjusted to produce results in the model that coincided with Thompson and Kats' (1978) data on effects of increased levels H₂S and CO₂. In the LTSM1 case, k_6 was 800 ppm⁻¹; k_7 , 9.0 ppm⁻¹; k_{10} , 8.39×10^{-4} n mole⁻² cm⁶; k_{11} , 4000 ppm⁻¹; and n , 2. The parameter n was not constrained to integer values, but an integer value to two significant digits was found best. In the LTSM2 case, (Fig. 6b) k_6 equaled 4000 ppm⁻¹; k'_7 , 2.5 cm s⁻¹ ppm⁻¹; and k'_8 , 0.76 cm³ n mole⁻¹. In using the procedure outlined above in both cases, we assumed implicitly that the constants, k_6 , k'_7 , k'_8 , r_p , etc., do not change in switching from a short-term to a long-term fumigation.

Also, to fit these results, a correction was made in the expression for K in Eq. (31). In the data on photosynthesis from Shinn (unpublished), the average r_s was 7.6 s cm⁻¹, whereas under optimal growing conditions, r_s is usually between 1.0 and 1.5 s cm⁻¹. Because K depends on r_s , we corrected for this value in calculations of the growth model. That is, the K used in the growth model was multiplied by $r_s / r_{s \text{ exp}}$, where $r_{s \text{ exp}}$ was set equal to the stomatal resistance found by Shinn.

RESULTS AND ANALYSIS

INTERPRETATION OF PARAMETERS

The parameter k'_3 is the value that P_g approaches as both light intensity and CO_2 concentration in air become arbitrarily large, i.e., when neither are limiting.

The slope of the light curve at $I = 0$ is

$$\left. \frac{dP_n}{dI} \right|_{I=0} = k'_2 k'_3 \left[1 - \frac{k'_9}{s C_a + R (r_{cw} + s (r_s + r_a))} \right] \quad (52)$$

As C_a becomes large, $\left. \frac{dP_n}{dI} \right|_{I=0}$ approaches $k'_2 k'_3$, the quantum conversion efficiency. We can see that if

k'_3 is chosen as stated above, k'_2 is fit to produce the correct quantum conversion efficiency.

Denoting the point on the C_a axis where P_n is zero by Γ ,

$$\left. \frac{dP_n}{dC_a} \right|_{\Gamma} = \frac{k'_2 k'_3 I}{(1 + k'_2 I) (k'_9 + 1) + k'_2 k'_3 I (r_{cw} + r_p + s(r_s + r_a))}$$

As light intensity becomes large, $\frac{dP_n}{dC_a}$ approaches

$$\frac{k'_3}{(k'_9 + 1) + k'_3 (r_{cw} + r_p + s (r_s + r_a))}$$

which is approximately equal to

$$\left. \frac{dP_n}{dC_a} \right|_{\Gamma} \cong \frac{1}{r_{cw} + r_p + s (r_s + r_a)} \quad (53)$$

Thus, the slope at C_a where P_n is zero determines r_p (cytoplasm resistance) because r_{cw} , r_s , and r_a are determined by other considerations.

From Eq. (71) for nonlimiting light intensity, I becomes large, and

$$P_g \rightarrow \frac{k'_1 k'_3 (C_c - k'_9)}{1 + k'_1 C_c} \quad (54)$$

Therefore, $\left. \frac{dP_g}{dC_c} \right|_{C_c = k'_9} \cong \frac{k'_1 k'_3}{1 + k'_1 k'_9}$ at high light intensity. Thus, k_1 determines the slope of initial P_g as a

function of CO_2 concentration in the chloroplast at high light intensity. We will call this internal CO_2 -fixation efficiency. The value of C_c at which P_g reaches half its maximum value is given by $(1 + 2 k'_9)/k'_1$.

The parameter k_9 determines the value at which P_g intercepts the CO_2 axis. That is, P_g equals zero when C_c equals k_9/s or when $C_a = k_9/s - R(r_{cw} + s(r_a + r_s))/s$.

The magnitude of k_5 determines the rate at which SO_3^- inactivates the available carboxylation enzyme. At a fixed concentration C_c , E_1 falls to half its normal value when S_c equals $(1 + k_1 C_c)/k_5$. Thus, as k_5 increases, lower values of S_c are required to denature a fixed amount of E_1 .

The parameter k_6 determines the amount of NADP that is reduced to NADPH at the enhanced rate at a fixed concentration S_c . Thus, as k_6 approaches a large number,

$$N_1 \rightarrow \frac{N_0 k_2 k_4}{1 + k_2 k_4} \quad (55)$$

which means that all of the conversion of NADP to NADPH occurs at the rate $k_2 k_4$ (or k_4) rather than at the rate k_2 . The parameter k_4 is assumed to be greater than unity because it is the ratio of k_4 to k_2 , and the former is presumed to be greater than the latter.

The parameter k_{10} in LTSM1 determines the maximum value of E_o . When $S_c = 0$ and $C_a = C_a^o$, $E_o(S_c, C_a)$ equals E_o^o . Holding C_a at C_a^o and for values of S_c such that $S_c k_{11} \gg 1 + k_{10} C_a^o$ and $k_7 S_c \ll 1$, $E_o(S_c, C_a)$ approaches $E_o^o(1 + k_{10}(C_a^o)^n)$. This is the maximum value of $E_o(S_c, C_a)$. The parameter k_{10} is the ratio of the rate constant of E_o formation due to CO_2 uptake (f_1) with respect to the rate constant of E_o formation due to SO_3^- uptake (f_2). When S_c becomes large, the complexing agent C_2 is quickly converted to C_1 , and the balance between the two shifts so that $[C_1] \approx C_o$. Therefore, $F(S_c \rightarrow \infty) \approx f_1 C_o (C_c^o)^n$. On the other hand, when S_c equals 0, $F(S_c = 0) = f_1 f_2 [C_o (C_c^o)^n] / [f_2 + f_1 (C_c^o)^n]$. Taking the ratio of these two, $F(S_c \rightarrow \infty) / F(S_c = 0) = [f_2 + f_1 (C_c^o)^n] / f_2 = 1 + k_{10} (C_c^o)^n$.

For an interpretation of k_7 consider that as S_c continues to increase, $E_o(S_c, C_a)$ approaches $E_o^o(1 + k_{10}(C_a^o)^n) / (1 + k_7 S_c)$. At $S_c = 1/k_7$, $E_o(S_c, C_a)$ decreases to half its maximum value. The larger k_7 becomes, the faster $E_o(S_c, C_a)$ decreases. Therefore, k_7 determines the rate at which enzyme systems are destroyed in the long term. In fact, $k_7 S_c$ is the ratio of the rate at which SO_3^- irreversibly destroys enzyme systems or membranes on which the reactions occur to the rate at which such systems or sites normally require renewal or repair.

The product $S_c k_{11}$ is the ratio of the rate at which enzyme system renewal occurs in the presence of SO_3^- from atmospheric fumigation to the rate at which renewal occurs in the presence of SO_3^- from soil sources. Therefore, k_{11} determines the rate at which $E_o(S_c, C_a)$ initially increases as a function of S_c . When C_a equals C_a^o , $E_o(S_c, C_a)$ increases from E_o^o to a saturation value of $E_o^o(1 + k_{10}(C_a^o)^n)$. When S_c equals $(1 + k_{10}(C_a^o)^n) / k_{11}$, $E_o(S_c, C_a)$ is half saturated from the original value of E_o^o .

The parameter n is responsible for a large fertilization effect that can compensate for the inhibitory effect of SO_3^- . For example, when S_c becomes large as C_a increases from C_a^o to C_a , $E_o(S_c, C_a)$ changes from $E_o^o(1 + k_{10}(C_a^o)^n) / (1 + k_7 S_c)$ to $(C_a/C_a^o)^n E_o^o(1 + k_{10}(C_a^o)^n) / (1 + k_7 S_c)$, assuming that $k_{11} S_c \gg 1 + k_{10}(C_a^o)^n$. The parameter n in this kind of biochemical equation is called the order of the reaction in CO_2 . For actual chemical reactions, it is equal to the number of moles of CO_2 required to produce one mole of product. We did not constrain n to integer values. However, the best fit was found when n equals 2 to two significant figures.

The results of fitting LTSM1 to the data described above did not reveal any inconsistencies or difficulties.

Let us now consider the LTSM2 case. The basic model is Eq. (47), although some simplifying assumptions led to Eq. (50), which is much easier to fit. Both k_6 and k_7 have the same meaning in this case as described above for LTSM1. The expression $k_8 C_c$ is the ratio of the rate at which the enzymes or reaction sites are removed from possible irreversible denaturation by SO_3^- to the rate at which these protected sites or enzymes require normal renewal. When C_c equals C_o , and if S_c increases from 0 to S_c , E_o falls from E_o^o to $E_o^o(1 + k_8 C_o) / (1 + k_7 S_c + k_8 C_o)$. For the concentration to increase halfway to its original value, $E_o^o(1 + k_8 C_o + k_7 S_c/2) / (1 + k_8 C_o + k_7 S_c)$, the concentration C_c must increase to $2C_o + (1 + k_7 S_c) / k_8$. The parameter k_8 in Eq. (50) was found to be $0.76 \text{ cm}^3 \text{ n mole}^{-1}$. Assuming a value for r_s of 1.5 s cm^{-1} and C_a^o of $13.3 \text{ n mole cm}^{-3}$, $k_8 K_3$ is $-0.13 \text{ n mole}^{-1} \text{ s cm}^2$. This is clearly inconsistent because k_8 and K_3 should both be positive. Furthermore, at most reasonable values of S_c and r_s , there is a pole in Eq. (50) at

approximately $\Delta C_a \approx -30$ ppm or $C_a \approx 295$ ppm. That is, Eq. (50) can be cast in the form $a/(\Delta C_a + 30 \text{ ppm})$, which diverges or becomes infinite at $\Delta C_a = -30$ ppm. Mathematical expressions of this type $a/(x + b)$ are termed poles, and the pole occurs at $-b$. The problem does not seem to be in the assumption in Eq. (48). The problem is in forcing Eq. (47) to fit the data. It thus seems that to have a biologically and physically consistent model, one must include CO_2 - and SO_3^- -fertilization effects in the construction of the photosynthesis enzymes or reaction sites themselves. To evoke a mechanism that solely protects the apparatus from the damaging effects of SO_3^- does not seem to provide an adequate description. We recognize that many assumptions are involved in these calculations that ideally should be tested experimentally. Specifically, the attributes of the model to be discussed below, the assumptions involved in using constant parameters throughout an entire growing season, and those involved in the growth itself should be tested. A very important experiment would be to repeat the growth experiment and determine the characteristics of the photosynthesis response in the different treatments.

ANALYSIS OF MODEL

The model is a single-valued function defined in a large multidimensional space. To examine the properties of the model over some of this space, we varied the input parameters such as the physical variables, C_a , I , and r_s , and the model parameters k_1 and k_2 , and then displayed the model output (photosynthesis) in several different ways. Displaying model output from these different perspectives should give a more comprehensive view of the relationship among the variables and a greater understanding of model dependence on input parameters.

In the first set of cases to be discussed here, we set all model parameters equal to their values determined by the fitting procedures described above and each physical variable equal to a value typical for daytime conditions in a temperate climate. We then pick two variables, V_1 and V_2 . Holding V_2 at a value of interest, we let V_1 vary continuously over a fixed range and plot P_n . Then we pick another value of interest for V_2 and repeat the variation of V_1 while plotting P_n . We continue this procedure for all the discrete values of V_2 of interest. This procedure will generate a family of curves with V_2 fixed in each curve; the variation in V_1 will be along the x axis and P_n along the y axis. In Fig. 7, we show eight such families of curves. In each of these, S_a was fixed at 0.0 ppm; neither V_1 nor V_2 were taken to be S_a . Figure 7 displays model behavior in the case of no pollution. The results in Fig. 7 should be consistent with previous studies of leaf photosynthesis. In Fig. 7a, we let I vary between 0 and 140 nanoeinsteins $\text{cm}^{-2} \text{ s}^{-1}$, while holding C_a at the discrete values, 200, 250, 300, 350, and 400 ppm CO_2 . Near $I = 0$, the slopes of all these curves are equal. Thus, the quantum efficiency is independent of CO_2 concentration. However, at high light intensity, P_n is closer to saturation at low CO_2 levels than at high CO_2 levels. That is, both the slope and maximum value of P_n at high light intensities depends on C_a , so that the greater the value of C_a , the greater are the slope and maximum value of P_n . Figures 7b and c suggest that at fixed T and I , P_n can be expressed as $(aC_a - b)/(r_s + c)$, where a , b , and c are functions of T , I , etc. This expression can only be assumed valid for $200 < C_a < 500$ ppm and $0.9 r_s < 7 \text{ s cm}^{-1}$. When $T = 25^\circ\text{C}$ and $I = 130$ nanoeinsteins $\text{cm}^{-2} \text{ s}^{-1}$, a is approximately 1.0, $b = 1.3 \text{ n mole cm}^{-3}$, and $c = 3.0 \text{ s cm}^{-1}$. In other words, when I is fixed at a high level and T is constant, P_n is proportional to C_a and behaves like an inverse hyperbolic function of r_s .

Figure 7d demonstrates an interesting property of the model. At high values of T , P_n is relatively insensitive to changes in C_a ; whereas at low to moderate values in temperature, P_n is very sensitive to changes in C_a . The interpretation of this is that as temperature increases, the ratio of inactivated to functional E_1 increases. Thus, the carboxylation process changes from one that is CO_2 limited to one that is enzyme limited. Thus, changes in CO_2 level have a diminished effect on photosynthesis rates. Figure 7e demonstrates that at low light intensities P_n is light limited and insensitive to the changes in CO_2 brought about by changes in r_s . Figure 7e also shows that at high stomatal resistance, a rapid transition occurs from a zone in which light is the major limiting factor to the zone in which light is almost not limiting. In the latter region, we suppose that CO_2 must be limiting. At low stomatal resistance, the transition between these two zones is very gradual. In Fig. 7f we see that changes in light intensity alter the slope and maximum value in the curves of P_n vs CO_2 concentration. Note that at high light intensity, these changes are insensitive to variations in light intensity. Also note that the concentration at which saturation

Fig. 7. Short-term predictions of photosynthesis as a function of variable V1 with V2 fixed at several values. (a) V1 = I , V2 = CO_2 ; (b) CO_2 , r_s ; (c) r_s , CO_2 ; (d) T , CO_2 ; (e) I , r_s ; (f) CO_2 , I ; (g) r_s , I ; (h) T , I .

occurs varies with light intensity. At low light levels P_n approaches saturation, whereas at high light intensities saturation does not occur in the CO_2 range shown. We see in Fig. 7g that changes in light over the natural variation in r_s that might be expected during the day alter the curvature of the inverse hyperbolic curve that describes P_n as a function of r_s . At high light and stomatal resistance, P_n is insensitive to light changes; but at low light levels, it is sensitive to light intensity at high and low stomatal resistance. At very high light levels, P_n is insensitive at all r_s shown. The sensitivity to mid-range light intensities changes as stomatal resistance increases. Compare Figs. 7c and g. Note that for CO_2 (Fig. 7c), the sensitivity to changes in CO_2 remains very constant over the entire region of CO_2 and r_s . Compare Figs 7d and h. The difference between the effects of CO_2 and light photosynthesis as a function of temperature are striking. Photosynthesis is sensitive to variations in light intensity over the entire temperature range shown. The region of highest sensitivity is at moderate temperatures and low light intensities. In this region, photosynthesis is primarily light limited; at higher temperatures, enzyme limitation becomes very important. Enzyme and substrate limitation are also more important at high than at low light levels. These two effects combine to produce the rather even spacing between the curves at high temperatures.

In Figs. 8a through d, external H_2S concentration S_a was varied as either V1 or V2, and photosynthesis was calculated using the short-term model. The same calculations were repeated using the long-term or seasonal model, and these results are shown in Figs. 8e through h. We see from Figs. 8a and e that changing H_2S concentration changes the slope of P_n as a function of C_a . Also evident is the large drop in P_n as S_a increases from 0.7 to 1.0 ppm H_2S . However, the shape of the curve does not change over the range of CO_2 shown. In Fig. 8b, we can see clearly that the increase in P_n with light intensity, when shifting from no H_2S to a fertilizing amount of H_2S , is greater at low light than at higher light intensities. As light intensity decreases, the maximum value of P_n with fertilization increases along the S_a axis. Likewise, the break-even point between H_2S fertilization and P_n depression increases along the S_a axis as light intensity decreases. In the seasonal calculations in Fig. 8f, the strong depressive effect in the long-term submodel shifts the maximum and break-even points to the left to lower S_a values. The sensitivities and order among the curves of constant light intensities remain unchanged in the range of S_a shown. In Fig. 8c, the effect of CO_2 on P_n response to H_2S is different. As CO_2 increases, the increase in maximum P_n due to H_2S fertilization increases faster than the increase in P_n with no H_2S ($S_a = 0.0$). As CO_2 increases, the ratio of H_2S -fertilized photosynthesis to photosynthesis without H_2S increases faster than the relative increase of photosynthesis in the absence of H_2S . Thus, in addition to the normal increase in P_n due to CO_2 , there is an additional beneficial effect resulting from the competition of CO_2 with SO_3^{2-} for the active sites on RuDPCase. In contrast, in the seasonal model depicted by Fig. 8g, the increases due to H_2S fertilization are approximately of equal absolute magnitude. Thus, the relative increases due to H_2S fertilization decrease as CO_2 increases. The long-term depressive effect of H_2S is very evident in comparing Figs. 8c and g. In Figs. 8a, c, d, e, g, and h, the light intensity was held constant at $130 \text{ nanoeinsteins cm}^{-2} \text{ s}^{-1}$. In Fig. 8d increasing stomatal resistance lowers the curves of photosynthesis as a function of H_2S concentration because of reduced CO_2 flow into the leaf. Simultaneous to this lowering, the peak in P_n due to H_2S fertilization falls even faster and also broadens. The faster rate of decrease in the peak corresponds to a reduction in both CO_2 and H_2S flow into the leaf. The broadening of the peak with increased r_s is caused by a reduced flow of H_2S into the leaf at equivalent external concentrations of H_2S levels. Thus, an equivalent effect, e.g., break-even between H_2S fertilization and P_n depression, is achieved at higher external H_2S . A mathematical example is the position of the inflection in Fig. 3. From Eqs. (31) and (34), we see that the inflection occurs at lower external H_2S concentrations with decreasing stomatal resistance. The relative order of the curves is constant in Fig. 8d over the range of S_a shown. In Fig. 8h, the remarks about peak width and height remain valid, but in the seasonal case depicted in Fig. 8h, another effect on the order of the curves occurs. At high S_a , the photosynthesis rate increases with stomatal resistance. At low S_a , the reverse is true. This is because at high S_a the inhibition by H_2S in the seasonal model dominates all other processes, and lower stomatal resistance (r_s) allows too much H_2S to enter the leaf. At low H_2S concentrations, H_2S and CO_2 fertilization occur, so at lower r_s greater photosynthesis occurs.

In Fig. 9, a different approach was taken. Figure 9 shows lines of constant photosynthesis for variations in two variables. In doing this, the balance between variables become very apparent. In Fig. 9a, all variables and model parameters are constant except C_a and r_s . The lines of constant photosynthesis are straight lines. Note that they are not parallel. If they were parallel, P_n would decrease linearly with r_s rather than as an inverse hyperbolic function. From Fig. 9a, we have strong evidence that

Fig. 8. Model predictions for the short-term model in (a) through (d). The long-term model results are plotted in (e) through (h). In (a) and (e), $V1 = \text{CO}_2$, $V2 = \text{H}_2\text{S}$; (b) and (f) H_2S , and I ; (c) and (g) H_2S , CO_2 ; (d) and (h) H_2S , r_s .

Fig. 9. Lines of constant photosynthesis (n moles cm⁻² s⁻¹) (indicated on lines) for short-term calculations of (a) C_a vs r_s, (b) ψ_s vs H₂S, (c) I vs H₂S, (d) CO₂ vs H₂S, (e) I vs CO₂, (f) CO₂ vs T, and (g) I vs T. The long-term model is plotted for CO₂ vs H₂S in (h).

$$C_a = a P_n r_s + b P_n + c \quad , \quad (56a)$$

or

$$P_n = \frac{\frac{1}{a} (C_a - c)}{r_s + b/a} \quad . \quad (56b)$$

Figure 9b is generated by assuming that stomatal resistance is related to soil-water conditions averaged over a sufficiently long time. Using Brown and Rosenberg's (1970) data for sugar beets, we fit a_3 in Eq. (37):

$$a_3 = 0.91 \text{ s cm}^{-1} + a_4 \psi_s^2 \quad , \quad (57)$$

where ψ_s is the soil water potential. The parameter a_4 was found to be $3.82 \text{ s cm}^{-1} \text{ bars}^{-2}$. Figure 9b illustrates several points. At very low H_2S concentrations and at very low $|\psi_s|$, small increases in H_2S (fertilization) can compensate for small increases in $|\psi_s|$. In general, at moderate to low $|\psi_s|$, increasing soil-water content (decreasing $|\psi_s|$) can compensate for deleterious effects of H_2S . At high values of $|\psi_s|$, photosynthesis is relatively insensitive to changes in H_2S . This corresponds to high stomatal resistance to diffusion. It should be noted that the curves in Fig. 9b are calculated for short-term behavior and have not been verified by experimental evidence. Figure 9c shows the fertilization effect: at low H_2S , increasing H_2S can offset the effect of decreased light intensity. As S_a increases beyond the region of fertilization, light must increase to compensate for the deleterious effects of increasing H_2S . At high P_n , large increases in light intensity are required to offset relatively small increases in H_2S ; at low P_n , the opposite is true. In Fig. 9d at low S_a , the fertilization effect is evident. Here, at constant photosynthesis as H_2S increases, CO_2 decreases. Then the curves abruptly go through a stationary phase where CO_2 concentrations are constant with increases in H_2S concentrations. Beyond this point, the curves enter the region in which H_2S inhibits photosynthesis. That is, increases in H_2S must be compensated by increases in CO_2 to keep photosynthesis constant. In this region, the curves are straight lines and, in fact, are given by

$$P_n = \frac{C_s - c}{a S_a + b} \quad ,$$

where $a = 2.5 \text{ s cm}^{-1} \text{ ppm}^{-1}$, $b = 3.3 \text{ s cm}^{-1}$, and $c = 1.9 \text{ n mole cm}^{-3}$. In Fig. 9e at high light intensities, photosynthesis is relatively insensitive to light intensity, but very sensitive to CO_2 concentration with a large decrease in light intensity being required to offset a small increase in CO_2 concentration. At low light intensities, this is reversed; small decreases in light intensities require large increases in CO_2 concentration to maintain constant photosynthesis. The shapes of these curves indicate that to maintain constant photosynthesis, C_a must behave like $a/(I + b) + c$. Note that in all cases, light intensity increases are offset by decreases in CO_2 concentration along each curve of constant photosynthesis rate. For unit steps along these lines, the ratio of the CO_2 concentration to light intensity increases monotonically as the position on the curve moves from high to low intensity. In Fig 9f, the two variables are CO_2 concentration and temperature. At low temperatures, a large increase in temperature is offset by small decreases in CO_2 concentration to maintain a constant photosynthesis rate. At high CO_2 concentrations and low temperatures or low to moderate CO_2 concentrations and low to moderate temperatures, photosynthesis rate. At high temperatures, photosynthesis is very sensitive to temperature changes. In Fig. 9g, we high temperatures, a small increase in temperature requires a large increase in CO_2 to maintain a constant photosynthesis rate. At high temperatures, photosynthesis is very sensitive to temperature changes. In Fig. 9g, we plot curves of constant photosynthesis rates with varying light intensity and temperatures. At low temperatures and high light intensity, moderate decreases in temperature must be offset by moderate increases in light intensity. At low light intensity and low to moderate temperatures, photosynthesis is stable over wide variations in temperature. At high temperatures and high to moderate light intensities, moderate increases in temperature require moderate increases in light intensity to maintain a steady rate of photosynthesis. Figures 9a through g are calculated for the short-term model. A calculation for a long-term or seasonal model is shown in Fig. 9h, with CO_2 and H_2S as the two variables. Compare the equivalent short-term calculation in Fig. 9d. At low H_2S concentrations, a large

drop in CO_2 requires only a small increase in H_2S to maintain a constant photosynthesis rate (Fig. 9h). The CO_2 drop is larger in the seasonal than in the short-term model. As in Fig. 9d, a point exists at which a small change in S_a requires no change in CO_2 to maintain a constant photosynthesis rate. Beyond this stationary point at higher S_a , the curves abruptly enter a zone in which small increases in H_2S must be offset by large increases in CO_2 . Note that the slope of the curves in this region in the seasonal model are much greater than in the short-term model. Also note that the curves are straight in this region in the short-term model. In the long-term model, they curve because of the factor C_a^2 in Eq. (44).

In Fig. 10, we hold all input variables and model parameters fixed except one variable V1 plotted along the x axis. We plot the percentage change in photosynthesis for a 1% change in V1. This curve is plotted at several values of another variable V2; V2 is held constant in each curve. A percentage change greater than 1.1 means that V1 is extremely important in determining P_n at that value of V1 and V2, between 0.8 and 1.1 is very important, between 0.4 and 0.8 is moderately important, and between 0.0 and 0.4 is relatively unimportant. These divisions are arbitrary and are meant only as a guideline to interpret Fig. 10. Figure 10a shows that at high light intensities the CO_2 concentration is extremely important or very important in determining photosynthesis accurately. At low light intensities, CO_2 is very important to moderately important in determining photosynthesis rate. In Fig. 10b we see that at low temperatures CO_2 is extremely important. At high temperatures and at low CO_2 concentrations, CO_2 is moderately important; at high CO_2 concentrations, CO_2 is unimportant. Figure 10c shows that at all H_2S levels, CO_2 is extremely important or very important. The lines are very close together, so the importance of CO_2 does not vary much with changes in H_2S . In Fig. 10d we see that the higher the light intensity, the less important is temperature in determining photosynthesis, i.e., the size of the temperature region in which photosynthesis is stable against temperature fluctuation increases as light intensity increases. This is interesting from an evolutionary point of view because most of the photosynthesis occurs at high light intensities where it is in the plant's interest to keep photosynthetic output stable. Figure 10e shows that at high temperatures the importance of temperature increases with CO_2 concentration. At low temperatures, the opposite is true. At low temperatures, temperature is of low importance in determining photosynthesis rate; at high temperatures, changes in temperature cause large changes in photosynthesis. Figure 10f shows that as H_2S increases, the importance of H_2S increases from low to moderate or high. The moderate case is at high light intensity; the case of high importance is at low light intensity. Figure 10g shows that as stomatal resistance increases, the importance of stomatal resistance increases from low to moderate. As temperature increases, this is shifted to even lower importance along its entire length. At high temperatures, therefore, stomatal resistance is not important in controlling photosynthesis rates. This suggests that at high temperatures, a plant's stomatal resistance to prevent high evapotranspiration would decrease with little extra photosynthetic penalty. At lower temperatures, stomatal resistance is somewhat more important. Figure 10h shows that stomatal resistance increases from low to moderate importance as stomatal resistance increases and that this sensitivity is independent of CO_2 . Figure 10i shows that the equivalent change as light varies does depend on the light intensity. At high light intensities, the same change in sensitivity to stomatal resistance occurs. At low light intensities, P_n is even less dependent on r_s . Figure 10j shows that the sensitivity of P_n to r_s increases slightly from low to low or moderate values as r_s increases. The curves have shallow slopes and the sensitivity of P_n to r_s does not change much. The overall level of these lines varies such that P_n is more sensitive to changes in r_s at low than at high H_2S concentrations. In Fig. 10k, we show the sensitivity of P_n to changes in H_2S concentration at various levels of CO_2 for the short-term model. In Fig. 10l, we see the same for the seasonal model. Figure 10k shows an increase from no sensitivity at all to a moderate level of sensitivity to H_2S . No difference exists in sensitivity due to variations in CO_2 . The curves are identical. This is not true in the seasonal case. Here the sensitivity increases from zero to extremely high as H_2S concentration increases. Also, in the seasonal model, the sensitivity increases as CO_2 concentration decreases. A substantial difference exists among the curves as the CO_2 level, which is constant for each curve, varies. The implication of Figs. 10k and 10l is that the accuracy of the estimates of photosynthesis decreases in moving from the short-term to the long-term model unless the accuracy in measuring H_2S concentrations can be substantially increased.

In Fig. 11, we show the percentage change in photosynthesis for a 10% change in V2 as a function of V1. Thus, in Fig. 11a, a 13% increase in photosynthesis occurs with a 10% increase of CO_2 above the ambient level (325 ppm) at a temperature of 15°C . By 40°C , this increase in P_n has fallen to about 2%, with the largest drop occurring between 32 and 40°C . Thus, over a very wide temperature range (15 to 33°C) CO_2 is very important in determining photosynthesis.

Fig. 10A. The percentage change in net photosynthesis is shown for a 10% change in V_1 . This is plotted against V_1 at fixed values of V_2 . All are short-term calculations. In (a) $V_1 = \text{CO}_2$, $V_2 = I$; (b) CO_2 , T ; (c) CO_2 , H_2S ; (d) T , I ; (e) T , CO_2 ; (f) H_2S , I .

Fig. 10B. The percentage change in net photosynthesis is shown for a 10% change in V1. This is plotted against V1 at fixed values of V2. All are short-term calculations except (l). In (g) r_s , T ; (h) r_s , CO_2 ; (i) r_s , I ; (j) r_s , H_2S ; (k) and (l) H_2S , CO_2 .

Fig. 11. The percentage change in net photosynthesis with a 10% change in V_2 plotted over a continuous range of V_1 . All are short-term calculations except (h). In (a) $V_1 = T$, $V_2 = \text{CO}_2$ where CO_2 was increased 10% from a base value of 325 ppm. (b) T , I with a base of $125 \text{ ne cm}^{-2} \text{ s}^{-1}$; (c) CO_2 , T at 25°C ; (d) CO_2 , H_2S at the bases, 0.01, 0.1, and 1.0 ppm H_2S ; (e) H_2S , CO_2 at 325 ppm CO_2 ; (f) H_2S , $I = 125 \text{ ne cm}^{-2} \text{ s}^{-1}$; (g) H_2S , ψ_s at 0.01, 0.1, and 1.0 bars; and (h) (long-term model) and (i) (short-term model) H_2S , r_s at 1.0 s cm^{-1} .

In Fig. 11b, we see that photosynthesis is not very sensitive to variation in light between 15 to 30°C. Above 30°C, the sensitivity increases, reaching a value of 10% change in P_n with a 10% variation in light intensity at 40°C. In Fig. 11c, the sensitivity of P_n to a 10% temperature change increases linearly from -1% at 200 ppm CO_2 to -6% at 500 ppm CO_2 . Photosynthesis is not very sensitive to temperature changes in this region. Figure 11d shows that the sensitivity of P_n to a 10% change in H_2S at three H_2S concentrations (0.01, 0.1, and 1.0 ppm) as a function of CO_2 from 200 to 500 ppm. All three curves are flat. The concentration of H_2S is not important at 0.01 and 0.1 ppm H_2S . The sensitivity of P_n is only -4% at 1.0 ppm H_2S . Figure 11e shows the sensitivity of P_n to a 10% change in CO_2 concentration from 0.0 to 2.0 ppm H_2S . The curve is flat and shows a 11 or 12% change in P_n . Therefore, the CO_2 concentration is very important in predicting photosynthesis rate. This suggests that care must be taken in monitoring CO_2 when studying the effects of sulfur compounds. Figure 11f shows the sensitivity of P_n to light at H_2S concentrations from 0.0 to 2.0 ppm. The sensitivity at 0.0 ppm is only 3%, drops to 2% at 0.1 ppm, and gradually rises to about 5.5% at 2.0 ppm H_2S . At this light intensity (130 nanoeinsteins $\text{cm}^{-2} \text{s}^{-1}$), light is of low to moderate importance in determining photosynthesis rate. Figure 11g shows the sensitivity of P_n to soil water potential at three different soil water potentials, -0.01, -0.1, and -1.0 bar. At -0.01 and -0.1 bar, P_n is very insensitive to changes in ψ_s . At -1.0 bar, the change in P_n is -12% in the absence of H_2S . As H_2S concentration increases to 2.0 ppm, the change in P_n slowly decreases to -7.5% with a 10% increase in ψ_s . Thus, at high soil-moisture stress, P_n is very sensitive to variations in ψ_s . Figures 11h and i show a plot of the percentage change in P_n with a 10% change in r_s at H_2S concentrations of 0.0 to 2.0 ppm. Figure 11h illustrates the long-term or seasonal model, and Fig 11i the short-term model. In both cases, P_n is not very sensitive to changes in r_s . In the short-term model, increases in r_s cause decreases in P_n . However, this is not true in the seasonal model. At low H_2S concentrations, 10% increases in r_s lead to small decreases in P_n ; at high concentrations, increases in r_s lead to small increases (2%) in P_n . Thus, in the seasonal model, stomatal resistance acts as a protective mechanism at high H_2S levels. In the short-term model, lack of CO_2 outweighs the protective effect of decreased H_2S resulting from increased r_s . Thus, the net effect is small decreases in P_n in the short-term model.

Figure 12 shows the percentage change in photosynthesis with a 10% change in V2 plotted against a range of values for variable V1. In this case, all of the V2 parameters are one of the model parameters, e.g., k_1 and k_2 . In Fig. 12a, we see that the sensitivity of P_n to k_1 , is very small, less than a 1% change occurs per 10% change in k_1 , i.e., a sensitivity of less than 0.1. (A sensitivity of 1.0 corresponds to a 10% change in P_n resulting from a 10% change in V2.) This low sensitivity is consistent at all concentrations of CO_2 shown. Figure 12b shows the sensitivity of P_n , as calculated by the seasonal long-term model, to a 10% change in k_1 as a function of H_2S concentrations from 0.0 to 2.0 ppm. The sensitivity increases from a change of less than 1% at 0.0 ppm to a change of 20% at 1.7 ppm H_2S . So for the seasonal model at higher concentrations of H_2S , accurate measurements must be made to determine model parameters. Figure 12c shows the percentage change in P_n with a 10% change in k_2 . The pole at 2 nanoeinsteins $\text{cm}^{-2} \text{s}^{-1}$ is where the compensation point occurs and where P_n goes through zero. Because any change relative to zero is large, this pole should probably be considered as an overestimate of the importance of k_2 . At moderate light intensities, k_2 is only of moderate importance in determining P_n . At high light intensities, P_n is not very sensitive to k_2 because the sensitivity is about 0.13 at a light intensity of 150 nanoeinsteins $\text{cm}^{-2} \text{s}^{-1}$. Except for Fig. 12b, all parts of Fig. 12 illustrate the short-term model. In Fig. 12d, the sensitivity of P_n to k_3 increases from a low of 0.2 at 15°C to greater than 1.0 at 40°C. Most of the increase occurs between 30 and 40°C. Thus, in this range k_3 must be accurately characterized. Figures 12e, f, g, and h plot the percentage change of P_n with a 10% change in k_1 , k_2 , k_3 , and k_5 , respectively, and all four curves are plotted against H_2S concentrations from 0 to 2.0 ppm. In Fig. 12e, the sensitivity increases gradually from near zero to 0.6 as S_a increases from 0 to 2.0 ppm. In Fig. 12f, sensitivity to k_2 initially drops from 0.2 at 0.0 ppm H_2S to about 0.05 at 0.05 ppm and then rises gradually to about 0.47 at 2.0 ppm. In Fig. 12g, sensitivity to k_3 drops initially as in Fig. 12f, but rises slightly higher to a final value of 0.65. In Fig. 12h, sensitivity to k_5 changes from 0.0 at 0.0 ppm to -0.6 at 2.0 ppm H_2S . Figures 12e, f, g, and h suggest that k_1 , k_2 , k_3 , and k_5 are only of low to moderate importance in estimating P_n in the short-term model. As the H_2S level increases, so does its importance, so that at higher concentrations larger errors in P_n can occur in using these parameters. A possible approach to avoid this difficulty would be to redetermine parameters when moving into the domain in which their sensitivities becomes significant.

In Tables 1 and 2, we show the percentage change in net photosynthesis with a 10% change in each variable shown. All calculations are made at 30 and 150 nanoeinsteins $\text{cm}^{-2} \text{s}^{-1}$, 25°C at the low light level, 25 and

Fig. 12. The percentage change in net photosynthesis with a 10% change in V_2 over a continuous range of V_1 . All are calculations for the short-term model except (b). In (a), $V_1 = \text{CO}_2$, $V_2 = k_1$; (b) H_2S , k_1 ; (c) I , k_2 ; (d) T , k_3 ; (e) H_2S , k_1 ; (f) H_2S , k_2 ; (g) H_2S , k_3 ; and (h) H_2S , k_5 .

Table 1. Percentage change in P_n with a 10% change in variable in the short-term model.

Light ^a		30		150			
Temperature, °C		25		25		35	
H ₂ S, ppm		0	0.01	0	0.01	0	0.01
ΔH_L	27	-1.11×10^{-12}	-8.97×10^{-13}	0.00	-2.56×10^{-12}	2.52×10^{-1}	5.98
T	3	-1.26×10^{-1}	-6.69	-2.50	-1.91	-2.09×10^{-1}	-7.11
H ₃	28	0.00	0.00	0.00	0.00	1.96×10^{-1}	4.04
C _a	2	7.02	9.13	1.09×10^{-1}	1.14×10^{-1}	6.85	1.06×10^{-1}
I	1	8.24	7.66	2.58	1.97	4.99	2.06
ΔS	22	5.78	3.67	1.87	1.62	7.11	4.72
k ₃	9	6.23	3.73	1.29	4.79×10^{-1}	4.39	8.02×10^{-1}
ΔH	20	6.15	3.90	2.00	1.73	5.98	3.97
k ₂	8	6.15	3.66	1.21	4.19×10^{-1}	4.13	7.04×10^{-1}
r _p	17	-1.32	-2.00	-4.29	-4.69	-3.28	-5.19
a ₁	30	-1.96	-3.88	-1.43	-1.66	-7.89×10^{-1}	-1.45
r _s	5	7.14×10^{-1}	-3.59	-2.96	-3.39	-1.71	-2.97
k ₉	34	-2.09	-2.04	-1.70	-1.46	-1.43	-9.49×10^{-1}
a ₃	33	-3.99×10^{-1}	-8.19×10^{-1}	-1.41	-1.64	-7.80×10^{-1}	-1.43
k ₄	10	0.00	1.62	1.37×10^{-12}	2.99×10^{-1}	2.84×10^{-12}	5.07×10^{-1}
H ₉	35	0.00	0.00	0.00	0.00	1.37	8.85×10^{-1}
k ₁	7	1.19	9.57×10^{-1}	4.62×10^{-1}	2.10×10^{-1}	2.83×10^{-1}	1.45×10^{-1}
S _a	6	0.00	1.19	0.00	1.84×10^{-1}	0.00	2.82×10^{-1}
r _{sexp}	29	0.00	1.16	3.19×10^{-12}	1.70×10^{-1}	1.36×10^{-11}	2.60×10^{-1}
K	15	-7.10×10^{-11}	-1.14	3.19×10^{-12}	-1.78×10^{-1}	1.36×10^{-11}	-2.83×10^{-1}
k ₆	12	0.00	1.13	1.37×10^{-12}	1.65×10^{-1}	2.84×10^{-12}	2.83×10^{-1}
r _a	4	-2.45×10^{-1}	-3.82×10^{-1}	-8.71×10^{-1}	-9.85×10^{-1}	-4.79×10^{-1}	-8.00×10^{-1}
R	19	-7.41×10^{-1}	-4.70×10^{-1}	-2.38×10^{-1}	-2.06×10^{-1}	-7.28×10^{-1}	-4.79×10^{-1}
r _{cw}	18	-1.60×10^{-1}	-2.50×10^{-1}	-5.71×10^{-1}	-6.28×10^{-1}	-4.00×10^{-1}	-6.69×10^{-1}
H ₁	25	0.00	0.00	0.00	0.00	6.18×10^{-1}	2.24×10^{-1}
a ₂	31	6.34×10^{-2}	1.31×10^{-1}	9.60×10^{-3}	1.12×10^{-2}	5.23×10^{-3}	9.75×10^{-3}
$\Delta H'$	23	-6.95×10^{-3}	-4.41×10^{-3}	-2.24×10^{-3}	-1.94×10^{-3}	-1.26×10^{-1}	-8.29×10^{-2}
K ₂	16	0.00	7.07×10^{-2}	0.00	2.99×10^{-2}	0.00	4.65×10^{-2}
k ₅	11	0.00	-1.47×10^{-2}	0.00	-9.94×10^{-3}	0.00	-4.58×10^{-2}
ψ_s	37	-9.33×10^{-6}	-1.93×10^{-5}	-3.34×10^{-5}	-3.89×10^{-5}	-1.82×10^{-5}	-3.39×10^{-5}
a ₄	36	-4.44×10^{-6}	-9.19×10^{-6}	-1.59×10^{-5}	-1.85×10^{-5}	-8.66×10^{-6}	-1.62×10^{-5}
ΔS_L	26	-1.11×10^{-12}	-8.97×10^{-13}	0.00	-2.56×10^{-12}	-2.55×10^{-6}	-4.70×10^{-7}
k ₁₁	39	0.00	0.00	0.00	0.00	0.00	0.00
k ₁₀	38	0.00	0.00	0.00	0.00	0.00	0.00
n	14	0.00	0.00	0.00	0.00	0.00	0.00
k ₇	13	0.00	0.00	0.00	0.00	0.00	0.00

^a Light intensity in nanoeinsteins $\text{cm}^{-2} \text{s}^{-1}$.

Table 1 (cont.). Percentage change in P_n with a 10% change in variable in the short-term model.

Light ^a		30		150			
Temperature, °C		25		25		35	
H ₂ S, ppm		0.1	1.0	0.1	1.0	0.1	1.0
ΔH_L	27	0.00	0.00	4.73×10^{-12}	1.41×10^{-11}	1.47×10^1	2.48×10^2
H ₃	28	0.00	0.00	0.00	0.00	8.67	7.87×10^1
T	3	-1.44	-2.26×10^1	-3.06	-1.46×10^1	-1.14×10^1	-3.89×10^1
$\Delta S'$	22	2.00	9.11	1.64	3.38	5.34	2.26×10^1
ΔH	20	2.13	9.70	1.75	3.60	4.49	1.90×10^1
C _a	2	1.12×10^1	1.18×10^1	1.14×10^1	1.14×10^1	1.08×10^1	1.22×10^1
k ₃	9	9.91×10^{-1}	6.68	5.14×10^{-1}	3.90	1.43	8.34
S _a	6	1.22×10^{-1}	-6.87	-5.78×10^{-1}	-3.87	-2.00	-7.83
k ₁	7	4.39×10^{-1}	5.97	3.78×10^{-1}	3.64	1.03	7.64
k ₅	11	-1.12×10^{-1}	-5.80	-3.06×10^{-1}	-3.67	-1.06	-7.42
I	1	5.21	7.33	1.73	3.81	1.78	6.45
k ₂	8	9.43×10^{-1}	6.25	3.91×10^{-1}	2.92	1.09	6.20
k ₄	10	8.90×10^{-1}	6.25	3.89×10^{-1}	2.92	1.08	6.20
r _p	17	-2.81	-1.38	-4.67	-3.12	-4.89	-2.20
a ₁	30	-4.41	-9.66×10^{-1}	-1.42	-9.02×10^{-1}	-7.09×10^{-1}	-2.28×10^{-1}
r _s	5	-1.43	-4.60×10^{-1}	-2.94	-1.89	-1.54	-4.86×10^{-1}
R	19	-2.54×10^{-1}	-1.16	-2.08×10^{-1}	-4.30×10^{-1}	-5.43×10^{-1}	-2.29
k ₉	34	-1.59	-1.42	-1.35	-1.32	-7.15×10^{-1}	-7.06×10^{-1}
a ₃	33	-9.23×10^{-1}	-1.98×10^{-1}	-1.40	-8.91×10^{-1}	-7.01×10^{-1}	-2.26×10^{-1}
K	15	-2.02×10^{-1}	1.23	2.96×10^{-1}	2.28×10^{-1}	1.05	4.73×10^{-1}
r _{sexp}	29	1.18×10^{-1}	-1.09	-2.76×10^{-1}	-2.06×10^{-1}	-9.66×10^{-1}	-4.27×10^{-1}
K ₂	16	8.30×10^{-2}	-1.09	-2.58×10^{-1}	-2.05×10^{-1}	-9.04×10^{-1}	-4.25×10^{-1}
r _a	4	-5.51×10^{-1}	-2.47×10^{-1}	-9.55×10^{-1}	-6.17×10^{-1}	-7.48×10^{-1}	-2.82×10^{-1}
H ₉	35	0.00	0.00	0.00	0.00	6.62×10^{-1}	6.51×10^{-1}
r _{cw}	18	-3.61×10^{-1}	-1.61×10^{-1}	-6.26×10^{-1}	-4.04×10^{-1}	-6.26×10^{-1}	-2.36×10^{-1}
$\Delta H'$	23	-2.39×10^{-3}	-1.09×10^{-2}	-1.96×10^{-3}	-4.04×10^{-3}	-9.38×10^{-2}	-3.96×10^{-1}
k ₆	12	1.78×10^{-1}	9.48×10^{-3}	1.05×10^{-2}	4.02×10^{-3}	2.93×10^{-2}	8.34×10^{-3}
a ₂	31	1.48×10^{-1}	3.14×10^{-2}	9.53×10^{-3}	6.03×10^{-3}	4.70×10^{-3}	1.52×10^{-3}
H ₁	25	0.00	0.00	0.00	0.00	8.26×10^{-2}	3.06×10^{-2}
ψ_s	37	-2.17×10^{-5}	-4.62×10^{-6}	-3.32×10^{-5}	-2.10×10^{-5}	-1.64×10^{-5}	-5.28×10^{-6}
a ₄	36	-1.03×10^{-5}	-2.20×10^{-6}	-1.58×10^{-5}	-9.99×10^{-6}	-7.79×10^{-6}	-2.52×10^{-6}
ΔS_L	26	0.00	0.00	4.73×10^{-12}	1.41×10^{-11}	-8.03×10^{-7}	-4.39×10^{-6}
k ₁₁	39	0.00	0.00	0.00	0.00	0.00	0.00
k ₁₀	38	0.00	0.00	0.00	0.00	0.00	0.00
n	14	0.00	0.00	0.00	0.00	0.00	0.00
k ₇	13	0.00	0.00	0.00	0.00	0.00	0.00

Table 2. Percentage change in P_n with a 10% change in variable in the long-term model.

Light ^a		30		150			
Temperature, °C		25		25		35	
H ₂ S, ppm		0	0.005	0	0.005	0	0.005
ΔH_L	27	0.00	-9.51×10^{-13}	0.00	0.00	2.52×10^1	7.78
T	3	-1.26×10^1	-8.52	-2.50	-1.93	-2.09×10^1	-8.36
H ₃	28	0.00	0.00	0.00	0.00	1.96×10^1	5.43
C _a	2	1.93×10^1	1.79×10^1	1.35×10^1	1.25×10^1	1.61×10^1	1.28×10^1
I	1	8.24	8.04	2.58	2.09	4.99	2.39
$\Delta S'$	22	5.78	4.23	1.87	1.66	7.11	4.93
k ₃	9	6.23	4.50	1.29	5.96×10^{-1}	4.39	1.13
ΔH	20	6.15	4.50	2.00	1.77	5.98	4.14
k ₂	8	6.15	4.42	1.21	5.38×10^{-1}	4.13	1.02
r _p	17	-1.32	-1.78	-4.29	-4.63	-3.28	-5.01
a ₁	30	-1.96	-3.45	-1.43	-1.65	-7.89×10^{-1}	-1.46
r _s	5	-7.14×10^{-1}	-3.42	-2.96	-3.37	-1.71	-2.98
k ₉	34	-2.09	-2.07	-1.70	-1.50	-1.43	-1.05
a ₃	33	-3.99×10^{-1}	-7.25×10^{-1}	-1.41	-1.63	-7.80×10^{-1}	-1.44
H ₉	35	0.00	0.00	0.00	0.00	1.37	9.86×10^{-1}
k ₄	10	0.00	1.22	0.00	2.88×10^{-1}	-5.68×10^{-13}	5.57×10^{-1}
k ₁	7	1.19	1.05	4.62×10^{-1}	2.51×10^{-1}	2.83×10^{-1}	1.60×10^{-1}
n	14	-3.90×10^{-4}	1.14	-8.44×10^{-5}	2.90×10^{-1}	-2.94×10^{-4}	5.61×10^{-1}
S _a	6	0.00	1.07	0.00	2.22×10^{-1}	0.00	4.14×10^{-1}
r _{sexp}	29	0.00	1.04	6.38×10^{-12}	2.06×10^{-1}	1.48×10^{-11}	3.85×10^{-1}
K	15	-8.38×10^{-11}	-9.96×10^{-1}	6.38×10^{-12}	-2.10×10^{-1}	1.48×10^{-11}	-4.05×10^{-1}
r _a	4	-2.45×10^{-1}	-3.38×10^{-1}	-8.71×10^{-1}	-9.45×10^{-1}	-4.79×10^{-1}	-7.69×10^{-1}
k ₆	12	0.00	9.11×10^{-1}	1.82×10^{-12}	1.91×10^{-1}	0.00	3.73×10^{-1}
R	19	-7.41×10^{-1}	-5.42×10^{-1}	-2.38×10^{-1}	-2.11×10^{-1}	-7.28×10^{-1}	-5.01×10^{-1}
r _{cw}	18	-1.60×10^{-1}	-2.21×10^{-1}	-5.71×10^{-1}	-6.20×10^{-1}	-4.00×10^{-1}	-6.43×10^{-1}
H ₁	25	0.00	0.00	0.00	0.00	6.18×10^{-1}	2.94×10^{-1}
k ₁₀	38	-4.81×10^{-5}	1.80×10^{-1}	-1.04×10^{-5}	4.61×10^{-2}	-3.63×10^{-5}	9.08×10^{-2}
k ₁₁	39	0.00	1.39×10^{-1}	0.00	2.13×10^{-2}	1.71×10^{-12}	4.21×10^{-2}
$\Delta H'$	23	-6.95×10^{-3}	-5.08×10^{-3}	-2.24×10^{-3}	-1.98×10^{-3}	-1.26×10^{-1}	-8.66×10^{-2}
a ₂	31	6.34×10^{-2}	1.16×10^{-1}	9.60×10^{-3}	1.12×10^{-2}	5.23×10^{-3}	9.84×10^{-3}
K ₂	16	0.00	3.13×10^{-2}	0.00	1.80×10^{-2}	0.00	3.41×10^{-2}
k ₅	11	0.00	-7.84×10^{-3}	0.00	-5.57×10^{-3}	0.00	-2.75×10^{-2}
k ₇	13	0.00	-5.12×10^{-3}	0.00	-2.05×10^{-3}	0.00	-4.06×10^{-3}
ψ_s	37	-9.33×10^{-6}	-1.71×10^{-5}	-3.34×10^{-5}	-3.88×10^{-5}	-1.82×10^{-5}	-3.43×10^{-5}
a ₄	36	-4.44×10^{-6}	-8.14×10^{-6}	-1.59×10^{-5}	-1.85×10^{-5}	-8.66×10^{-6}	-1.63×10^{-5}
ΔS_L	26	0.00	-9.51×10^{-13}	0.00	0.00	-2.55×10^{-6}	-6.69×10^{-7}

Table 2 (cont.). Percentage change in P_n with a 10% change in variable in the long-term model.

Light ^a		30		150			
Temperature, °C		25		25		35	
H ₂ S, ppm		0.05	0.5	0.05	0.5	0.05	0.5
ΔH_L	27	0.00	-5.31×10^{-12}	4.62×10^{-12}	0.00	4.92	7.51×10^2
H ₃	28	0.00	0.00	0.00	0.00	3.03	1.52×10^2
T	3	-1.45	-2.85×10^1	-2.13	-2.12×10^1	-6.92	-6.26×10^1
$\Delta S'$	22	2.11	1.59×10^1	1.56	6.21	4.57	6.01×10^1
ΔH	20	2.24	1.69×10^1	1.67	6.62	3.84	5.05×10^1
C _a	2	1.37×10^1	3.16×10^1	1.20×10^1	2.57×10^1	1.20×10^1	4.53×10^1
S _a	6	5.05×10^{-1}	-1.82×10^1	-1.71×10^{-1}	-1.15×10^1	-6.48×10^{-1}	-2.28×10^1
k ₃	9	1.20	9.10	2.88×10^{-1}	6.63	5.33×10^{-1}	1.38×10^1
n	14	9.02×10^{-1}	7.98	2.48×10^{-1}	5.82	4.59×10^{-1}	1.21×10^1
k ₁	7	4.63×10^{-1}	6.75	1.62×10^{-1}	5.43	2.72×10^{-1}	1.11×10^1
k ₅	11	-4.36×10^{-2}	-6.32	-6.51×10^{-2}	-5.19	-2.50×10^{-1}	-1.06×10^1
k ₇	13	-1.87×10^{-2}	-6.65	-2.53×10^{-2}	-5.26	-4.75×10^{-2}	-1.05×10^1
k ₂	8	1.16	8.51	2.24×10^{-1}	4.94	4.16×10^{-1}	1.02×10^1
k ₄	10	9.73×10^{-1}	8.50	2.17×10^{-1}	4.93	4.04×10^{-1}	1.02×10^1
I	1	5.63	4.70	1.67	4.92	1.47	9.09
K	15	-5.37×10^{-1}	6.94	9.41×10^{-2}	1.40	3.95×10^{-1}	2.88
R	19	-2.69×10^{-1}	-2.02	-1.99×10^{-1}	-7.90×10^{-1}	-4.64×10^{-1}	-6.10
r _{sexp}	29	4.89×10^{-1}	-5.89	-1.27×10^{-1}	-1.25	-4.86×10^{-1}	-2.56
K ₂	16	1.56×10^{-1}	-5.83	-9.23×10^{-2}	-1.24	-3.56×10^{-1}	-2.54
r _p	17	-2.75	-9.31×10^{-1}	-4.78	-2.00	-5.34	-1.39
a ₁	30	-4.56	4.38	-1.55	6.90×10^{-2}	-1.15	1.21
r _s	5	-2.63	2.11	-3.23	1.27×10^{-1}	-2.51	2.58
k ₁₀	38	1.44×10^{-1}	1.20	3.94×10^{-2}	8.84×10^{-1}	7.37×10^{-2}	1.80
k ₉	34	-1.67	-1.56	-1.36	-1.40	-7.43×10^{-1}	-9.27×10^{-1}
a ₃	33	-9.61×10^{-1}	8.80×10^{-1}	-1.53	6.82×10^{-2}	-1.13	1.20
$\Delta H'$	23	-2.52×10^{-3}	-1.90×10^{-2}	-1.87×10^{-3}	-7.41×10^{-3}	-8.02×10^{-2}	-1.05
r _a	4	-5.37×10^{-1}	-1.54×10^{-1}	-9.78×10^{-1}	-3.78×10^{-1}	-8.26×10^{-1}	-1.35×10^{-1}
H ₉	35	0.00	0.00	0.00	0.00	6.88×10^{-1}	8.55×10^{-1}
r _{cw}	18	-3.52×10^{-1}	-1.01×10^{-1}	-6.42×10^{-1}	-2.47×10^{-1}	-6.91×10^{-1}	-1.13×10^{-1}
k ₆	12	4.03×10^{-1}	3.16×10^{-2}	2.58×10^{-2}	1.42×10^{-2}	4.84×10^{-2}	2.88×10^{-2}
a ₂	31	1.54×10^{-1}	-1.39×10^{-1}	1.04×10^{-2}	-4.73×10^{-4}	7.55×10^{-3}	-8.00×10^{-3}
H ₁	25	0.00	0.00	0.00	0.00	9.56×10^{-2}	9.36×10^{-2}
k ₁₁	39	2.12×10^{-2}	9.38×10^{-4}	1.06×10^{-3}	5.22×10^{-4}	1.99×10^{-3}	1.06×10^{-3}
ψ_s	37	-2.27×10^{-5}	2.05×10^{-5}	-3.62×10^{-5}	1.65×10^{-6}	-2.63×10^{-5}	2.78×10^{-5}
a ₄	36	-1.08×10^{-5}	9.75×10^{-6}	-1.72×10^{-5}	7.83×10^{-7}	-1.25×10^{-5}	1.33×10^{-5}
ΔS_L	26	0.00	-5.31×10^{-12}	4.62×10^{-12}	0.00	-3.05×10^{-7}	-7.14×10^{-6}

^a Light intensity in nanoeinsteins $\text{cm}^{-2} \text{s}^{-1}$.

35°C at the high light level, 0.0, 0.01, 0.1, and 1.0 ppm H₂S for the short-term model, and 0.0, 0.005, 0.05, and 0.5 ppm H₂S for the long-term calculation. These values are divided into two sets (see Tables 1 and 2) with 0.0 and 0.01 ppm H₂S (or 0.0 and 0.005 ppm in long-term model) for one set and 0.1 and 1.0 ppm H₂S (or 0.05 and 0.5 ppm in long-term model) for the other. Within each set the changes are ranked in decreasing order of importance. This is done by finding the maximum value in the six categories and then ranking accordingly. Table 1 gives calculations for the short-term model and Table 2 for the long-term model. It is clear in Table 1 that the highest sensitivities are those associated with temperature and the temperature dependence of P_n. The other sensitive parameter is CO₂. At high H₂S levels, H₂S concentration is important. The parameters for the biochemistry, k₁, k₂, k₃, k₄, and k₅ are grouped together at relatively high importance at high H₂S levels. In fact, the increase in the importance of k₅ was the largest increase as pollutant level increased. We see from Table 1 that a great deal of stability exists with changes in parameters. The most important exception to this is in the temperature-dependent parameters. Thus, these parameters must be determined from reliable experimental observations. In Table 2, the same general pattern occurs except the numbers are often larger, and the parameters that are unique to the long-term model (k₇, k₈, etc.) have high importance, especially at higher H₂S concentrations. Once again, CO₂ and parameters associated with temperature dependence are very important. The parameter associated with temperature-dependent respiration is important at low or at high H₂S levels where P_g is depressed. We also see that the sensitivity to H₂S is larger in the long-term model than in the short-term model. Thus, the sensitivity to H₂S must be specified accurately in long-term experiments in which H₂S is held constant. The biochemical parameters are grouped together in importance at high H₂S concentrations. The parameter k₆ is insignificant at moderate or high light intensities. The parameter for light respiration is also not very important. The parameter k₁₀ is important only at high light, high temperature, and high H₂S. The parameter k₁₁ is unimportant. The various resistances, r_s, r_p, r_{cw}, and r_a, are relatively unimportant in determining photosynthesis rate. Thus, accuracy in these measurements, although important, is not critical for model functioning. The sensitivity to water stress was very low, because the water stress was initially low. At higher stress, the sensitivity increases as seen in the Fig. 11g.

CONCLUSIONS

We have developed a model of leaf photosynthesis under pollutant stress and have examined some of the properties of this model. We can make several conclusions regarding these results that fall in three broad categories: missing data and needed experiments, predictions including those parameters with highest and lowest sensitivities, and implications for setting standards. In the category of missing data, clearly data are needed on the full range of responses to light, temperature, and CO₂ and H₂S concentrations. That is, data are needed for the response of P_n to H₂S concentration at several light intensities other than the one used in Fig. 6. Data are also needed to determine P_n as a function of temperature at many H₂S concentrations. This would determine the differences in the exponent in Eq. (24a) and Eq. (24b). As further validation, measurements of P_n as a function of CO₂ concentration at several temperatures, light levels, etc. are desirable. Such experiments would confirm the curves in Figs. 7, 8, and 9. An important, but difficult, experiment would be to confirm or reject the sulfur submodel as in Eq. (31). In particular, the determination of the accuracy of Eq. (30) would be valuable. If S_c could be measured, it would be interesting to see if Eq. (31) changes appropriately with stomatal resistance. This remains a challenge. Finally, as an assessment tool, the validity of the long-term effects model should be established, or a more realistic one should be formulated and verified. This cannot be done without further research on the changes that occur in moving from short-term to long-term exposures. In particular, we need measurements of the photosynthesis response at different times during the growing season with experimental fumigation with both CO₂ and H₂S.

We have predicted model behavior under several conditions with special consideration given to the sensitivity to the various parameters and variables. We can summarize by pointing out a few that seem to be the most important or striking. The concentration of CO₂ and temperature are the most critical variables in determining P_n. Light at high temperatures is important, and H₂S is important at high concentrations. Less sensitive are the biochemical parameters, k₁, k₂, etc. Photosynthesis is insensitive to parameters related to diffusion resistance, r_s, r_a, etc. The verification of changes in the sensitivity to CO₂ with temperature, to light intensity with

temperature, and to stomatal resistance with light would be of interest. In other words, Figs. 7d, h, and e are very interesting and should be verified.

For purposes of setting standards, Fig. 8 suggests that short-term experiments alone are inadequate. For example, the break-even point between fertilization and depression of photosynthesis in Figs. 8c and g at 325 ppm CO_2 shifts from approximately 0.25 to 0.16 ppm H_2S . Thus, it would seem that either the long-term fumigation model should be used or a correction factor applied to short-term experiments. Of interest in Fig. 8d is that the curves of different stomatal resistances do not overlap in the entire range of H_2S concentrations, whereas in Fig. 8h, the curves are not well separated at high concentrations. In experiments designed to set standards, accurate measurements of r_s at low H_2S concentrations should be made; at high concentrations, r_s is much less significant.

Finally, in setting standards, Fig. 9 suggests that the standard be set with due regard for the expected ambient level of CO_2 , soil water conditions, etc. A damaging level of H_2S under one set of conditions is not damaging under others. Hence, standards could take these interactions into account so that different environments would have different permissible pollutant levels that would provide the same degree of protection to vegetation.

For assessment purposes, we reiterate that this model will be used as a submodel in a growth model for sugar beets, BEETGROW2. As of this writing, model development is complete, and a final determination of parameters is underway. Assessments will begin shortly. However, the results in this report can be used to make crude assessments at this time. In doing so, Figs. 8 and 9 are the most useful. Sugar beets prefer a well-watered environment, and under those conditions, are the most sensitive to H_2S . However, the expected CO_2 emissions may well have an ameliorative effect on any harmful effects that might occur. The magnitude of these effects must await detailed calculations using the full growth model.

ACKNOWLEDGMENT

I would like to thank Joseph Shinn for supplying unpublished data on sugar beet photosynthesis under H_2S fumigation.

REFERENCES

- Brown, K. W. (1976). Sugar beet and potatoes. *Vegetation and the Atmosphere*. (Ed. by J. L. Monteith), pp. 65-86. Academic Press, New York.
- Brown, K. W. and Rosenberg, N. J. (1970). Effect of windbreaks and soil water potential on stomatal diffusion resistance and photosynthetic rate of sugar beets (*Beta vulgaris*). *Agron. J.*, 62, 4-8.
- Chartier, Ph. (1970). A model of CO₂ assimilation in the leaf. *Prediction and Measurement of Photosynthetic Productivity* (Ed. by I. Malek), pp. 307-315. Proceedings of the IBP/PP Technical Meeting, Trebon 1969. Centre for Agricultural Publishing and Documentation, Wageningen.
- Fick, G. W. (1971). *Analysis and Simulation of the Growth of Sugar Beet (Beta vulgaris L.)*. Ph.D. dissertation, University of California, Davis, 71-25097 University Microfilms, Ann Arbor.
- Hall, A. E. (1970). *Photosynthetic Capabilities of Healthy and Beet Yellow Virus Infected Sugar Beets (Beta vulgaris L.)*. Ph.D. dissertation, University of California, Davis. 71-20384 University Microfilms, Ann Arbor.
- Hall, A. E. (1971). A model of leaf photosynthesis and respiration. *Carnegie Inst. Wash. Yearbook*, 70, 530-540.
- Hall, A. E. and Björkman, O. (1975). Model of leaf photosynthesis and respiration. *Perspectives of Biophysical Ecology*. (Ed. by D. M. Gates and R. B. Schmerl), pp. 55-72. Springer-Verlag, New York.
- Hofstra, G. and Hesketh, J. D. (1969). Effects of temperature on the gas exchange of leaves in the light and dark. *Planta* 85, 228-237.
- Johnson, F. H., Eyring, H., and Polissar, M. J. (1954). *The Kinetic Basis of Molecular Biology*. John Wiley, New York. 874 pp.
- Kanemasu, E. T., Thurtell, G. W., and Tanner, C. B. (1969). Design, calibration, and field use of a stomatal diffusion porometer. *Plant Physiol.* 44, 881-885.
- Kercher, J. R. (1978). A model of plant growth for assessing effects of simple gaseous sulfur compounds on sugar beets, *Beta vulgaris*. (manuscript in preparation.)
- Malhotra, S. S. and Hocking, D. (1976). Biochemical and cytological effects of sulfur dioxide on plant metabolism. *New Phytol.* 76, 227-237.
- Moore, D. (1976). *LSPFIT: A least-squares fit program with penalty function*. Lawrence Livermore Laboratory, Livermore, Calif., UCIR-1015.
- Nevins, D. J. (1965). *Influence of Leaf Age and Nitrogen Deficiency on Photosynthesis in Sugar Beet (Beta vulgaris) leaves*. Ph. D. dissertation, University of California, Davis, 66-2390 University Microfilms, Ann Arbor.
- Nevins, D. J. and Loomis, R. S. (1970). A method for determining net photosynthesis and transpiration of plant leaves. *Crop Sci.* 10, 3-6.
- Segal, I. H. (1975). *Enzyme Kinetics*. Wiley-Interscience, New York, 957 pp.
- Shinn, J. H., Clegg, B. R., Stuart, M. L. and Thompson, S. E. (1976). Exposures of field-grown lettuce to geothermal air pollution—photosynthetic and stomatal response. *J. Environ. Sci. Health A11*, 603-612.
- Sinclair, T. R. (1972). *A Leaf Photosynthesis Submodel for Use in General Growth Models*, Triangle Research Site, Eastern Deciduous Forest Biome, U. S. International Biological Program, Duke University, Durham, N. C. Memo Rept. 72-14.
- Stewart, D. W. (1970). *A Simulation of Net Photosynthesis of Field Corn*, Ph.D. dissertation, Cornell University. University Microfilms, Ann Arbor.
- Thompson, C. R. and Kats, G. (1978). Effects of continuous H₂S fumigation on crop and forest plants. *Environ. Sci. Technol.* 12, 550-553.
- Ziegler, I. (1973). The effect of air-polluting gases on plant metabolism. *Environmental Quality and Safety* 2, 182-208. *Global Aspects of Chemistry, Toxicology and Technology as Applied to the Environment*. Academic Press, New York.
- Ziegler, I. (1975). The effect of SO₂ pollution on plant metabolism. *Residue Rev.* 56, 79-105.