Tellus (1985), *37B*, 216–229

A classification of some inverse problems in geochemical modelling

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(Manuscript received April 11; in final form October 8, 1985)

ABSTRACT

A number of geochemical inversion problems are analysed with the aim of classifying the inherent degree of difficulty and numerical instability involved in the process of obtaining numerical solutions. The approach is to consider relatively abstract representations of the problems so as to concentrate attention on those aspects that cause numerical difficulties. The various geochemical inversion problems are related to numerical differentiation with the order of differentiation indicating the instability of the problem. The less stable problems place more stringent demands on the observational data that are being interpreted, and the results are also more sensitive to any limitations in the formulation of the inversion problem. The examples considered are the determination of CO_2 source strengths, the deconvolution of trace gas concentrations from polar ice and interpretation of CCl_3F observations. The calibration of global carbon cycle models is described schematically as a sequence of poorly-conditioned problems.

1. Introduction to some inverse problems

Inverse problems and inversion techniques have recently become of considerable interest in many branches of geophysics (Twomey, 1977; Wunsch, 1978; Parker, 1970). The terminology arises from the fact that such problems are the 'inverses' of the direct problems that are more commonly or more readily studied. Keller (1976) has emphasised that the relation between two problems will be reciprocal in that two problems are 'inverses of one another if the formulation of each involves all or part of the solution of the other'. He suggests that the question of which problem is regarded as the direct problem and which is the inverse problem is often the result of the historical order in which the problems were studied. Allison (1979) focused attention on unstable inverse problems, i.e. problems for which the solution is highly sensitive to uncertainty in the inputs that correspond to the solution of the direct problem.

Referring to the more stable of a pair of mutually inverse problems as the direct problem frequently corresponds to the same terminology as the historical usage because the difficulties of constructing acceptable solutions to unstable or ill-posed problems has meant that the direct problems were studied first.

Allison has suggested that the occurrence of unstable inverse problems in modelling studies is inevitable. Since a model represents a high degree of abstraction from the real world, it will only be useful if the outputs of the model are relatively insensitive to the details of the model, i.e., relatively large changes in model details (i.e. structure and parameters) lead to relatively small changes in the model outputs. It follows immediately that if this is the case then the inverse problem of trying to deduce the details of the model by comparing the model outputs to observations will mean that small errors in the observations will lead to large errors in the deductions concerning the model.

Problems in which errors in the results are highly sensitive to the data that are fitted will also tend to have the results being highly sensitive to errors in the problem formulation. This can be readily shown in terms of the simple linear problem of deducing a set of parameters $\boldsymbol{x}$ from a set of observations $\boldsymbol{y}$, given a linear relation

$$\boldsymbol{A}\boldsymbol{x} = \boldsymbol{y}. \tag{1.1}$$

Ideally

$$\boldsymbol{x} = \boldsymbol{A}^{-1}\boldsymbol{y}, \tag{1.2}$$

but if $\boldsymbol{A}$ is ill-conditioned then any data errors $\delta\boldsymbol{y}$ in $\boldsymbol{y}$ will be magnified. In the estimate $\hat{\boldsymbol{x}}$ given by

$$\begin{aligned}\hat{\boldsymbol{x}} &= \boldsymbol{A}^{-1}(\boldsymbol{y}_{\text{ideal}} + \delta\boldsymbol{y}) \\ &= \boldsymbol{x}_{\text{true}} + \boldsymbol{A}^{-1}\delta\boldsymbol{y},\end{aligned} \tag{1.3}$$

$\hat{\boldsymbol{x}}$ can contain large error contributions if $\boldsymbol{A}$ is nearly singular. The sensitivity to errors in the formulation of the problem is shown by considering the case when an approximate 'model' $\boldsymbol{A}_{\text{model}} = \boldsymbol{A}_{\text{true}} + \delta\boldsymbol{A}$ is used to construct $\hat{\boldsymbol{x}}$. In this case:

$$(\boldsymbol{A}_{\text{model}} - \delta\boldsymbol{A})\,\boldsymbol{x}_{\text{true}} = \boldsymbol{y} \tag{1.4}$$

but

$$\hat{\boldsymbol{x}} = \boldsymbol{A}_{\text{model}}^{-1}\boldsymbol{y} = \boldsymbol{x}_{\text{true}} - \boldsymbol{A}_{\text{model}}^{-1}\,\delta\boldsymbol{A}\,\boldsymbol{x}_{\text{true}}. \tag{1.5}$$

The errors in $\hat{\boldsymbol{x}}$ can be large if $\boldsymbol{A}_{\text{model}}$ and $\boldsymbol{A}$ are nearly singular. Thus the more ill-conditioned a problem, the more stringent are the requirements on both the accuracy of the data and the problem formulation if reasonable solutions are to be obtained.

This paper presents a number of inverse problems arising in atmospheric chemistry and biogeochemical modelling and classifies these problems according to their inherent degree of stability. For the most part the problems will be of the form of deriving one function from another, and generally only functions of a single variable will be considered. The discussion uses numerical differentiation, which tends to amplify errors, as the archetypal inverse problem with numerical integration as the corresponding direct problem.

The comparison with numerical differentiation is not appropriate for all of the inverse problems of current interest in geochemical modelling but it does cover a significant range such as the problems studied by Fraser et al. (1983), Bolin and Keeling, (1963), Pearman and Hyson (1980), Enting (1984), Peng et al. (1983) and Enting (1985b).

The layout of the remainder of this paper is as follows. Section 2 considers numerical differentiation and the extent to which this process amplifies noise in the input signal and gives examples from geochemical models. Section 3 considers derivatives as the solutions of integral equations and then discusses the solution of more general integral equations. The stability of a numerical solution is related to the smoothness of the kernel of the integral. The deconvolution of $\delta^{13}C$ from tree rings is used as an example of the application of integral equations in carbon cycle modelling. Section 4 considers the special class of kernels that are used to define integral and differential operators of fractional orders (Ross, 1974). The example of a problem corresponding to fractional differentiation considered here is the recovery of atmospheric trace gas concentrations from concentration of gas in ice bubbles using a model described by Enting (1985b).

Section 5 goes on to consider the case of incomplete inverse problems, i.e. those in which the full solution of the direct problem is not available. As an example, it considers the attempt by Fraser et al. (1983) to deduce corrections to the estimated releases of CCl_3F. Finally, Section 6 gives a schematic representation of the problems of calibrating global carbon cycle models and shows how, to a first approximation, the calibration problem can be regarded as a series of interlinked inverse problems of the types considered in earlier sections.

2. Numerical differentiation

The numerical differentiation of non-exact data has been discussed by Anderssen and Bloomfield (1974a, b). The fundamental property is that while numerical integration tends to smooth out errors in the operand data, the inverse operation of numerical differentiation tends to amplify errors in its operand. Thus repeated numerical differentiation will further amplify errors so that when a numerical problem is equivalent to a λth order differentiation in either an exact or approximate sense, 'the equivalent order of differentiation is often taken as a measure of improperly-posedness' (Anderssen and de Hoog, 1983). (Section 4 considers the case when λ, the order of differentiation, takes a non-integer value and gives an example of a possible application.)

The way in which numerical differentiation amplifies errors can be most readily seen by using a spectral representation. If

$$c_{\text{obs}}(t) = \int_{t_0}^{t} s_0(t')\,\mathrm{d}t' + \sum_n \varepsilon_n \sin(n\omega_0 t) \tag{2.1}$$

where the ε_n are 'error' terms, then

$$\frac{\mathrm{d}}{\mathrm{d}t} c_{\mathrm{obs}}(t) = s_0(t) + \sum_n n\omega_0 \varepsilon_n \cos(n\omega_0 t). \qquad (2.2)$$

Numerical differentiation enhances the higher frequency contributions to the 'error' by a factor of n; as n grows, this contribution may grow without limit. In order to obtain a derivative from observations that are subject to noise whose high frequency components do not decay sufficiently rapidly, it is necessary to suppress the high frequency behaviour by some form of filtering. This procedure can remove the effect of the high frequency contributions to the error but it will simultaneously suppress part of the 'true' derivative, $s_0(t)$. Only the low frequency contributions to the derivative remain beause the high frequency contributions can not be reliably estimated in the presence of the errors.

A more complete description of numerical differentiation has been given by Anderssen and Bloomfield (1974a, b); the following aspects are of particular importance. Firstly, the stability problems arise from the factor n that occurs in eq (2.2) since this gives the amplification of the errors. Secondly, the solution of a problem in which such an amplification occurs will necessitate either high quality data or some restrictions on the resolution of the solution. Thirdly, since practical problems are almost always subject to some inherent limitations on the resolution, the relevant quantity to consider is the degree of amplification over the scales that are of interest.

Numerical differentiation arises naturally when trying to deduce the source strengths of geochemical tracers from observed concentrations. The fundamental mass balance equation for $c(t)$ the amount of tracer in a system is

$$\frac{\partial c}{\partial t} = s(t). \qquad (2.3)$$

Thus an unknown source strength $s(t)$ is determined as a function of time by numerically differentiating the observed concentrations $c(t)$. This basic equation underlies a variety of more complicated forms. For example, the multi-reservoir form is

$$\frac{\partial c_i}{\partial t} = \sum_j L_{ij} c_j(t) + s_i(t), \qquad (2.4)$$

where the L_{ij} are transport terms giving the fluxes between the reservoirs. Again, an inherent instability in deducing the sources $s_i(t)$ arises from the fact that numerical differentiations of the concentrations are required when evaluating the $\partial c/\partial t$ terms.

An example of a source deduction problem of this type is the attempt described by Fraser et al. (1985) of deducing the release rates of chlorofluorocarbons into the atmosphere.

An aspect of the source deduction problem (2.4) that may be even more poorly-posed is the problem of deducing the spatial distribution of seasonal variations of surface sources, given observations of surface concentrations. For CO_2 this deduction has been attempted by Bolin and Keeling (1963), Pearman and Hyson (1980) and Enting (1984). The difficulties involved in this problem can be seen by considering the simple model used by Bolin and Keeling. They analysed tropospheric CO_2 concentration $c(\mu, t)$, as a function of time t and μ = sine of latitude, using the one-dimensional diffusion equation:

$$\frac{\partial c}{\partial t} = Q \frac{\partial}{\partial \mu} \left((1-\mu^2) \frac{\partial c}{\partial \mu} \right) + s(\mu, t). \qquad (2.5)$$

In terms of the analysis presented in this section, the difficulty is immediately obvious. Deducing $s(\mu, t)$ from $c(\mu, t)$ requires the evaluation of the second derivative $\partial^2 c/\partial \mu^2$. Solution of the more complicated advective-diffusion models used by Pearman, Hyson and Enting will encounter similar difficulties. The transport terms are a combination of terms involving first derivatives of concentrations $v \cdot \nabla c$ and second derivatives $\nabla \cdot \boldsymbol{Q} \nabla c$. This would indicate that the surface sources can be determined most accurately in regions where advective transports dominate, and are most poorly determined in regions where diffusive transports dominate. Preliminary calculations using the model described by Enting (1984) suggest that on a global scale the behaviour of the inversion is qualitatively similar to that of a first derivative.

It must be emphasised that not only is the problem of deducing the spatial distribution of CO_2 sources inherently less stable than the corresponding temporal problem, but the available data concerning spatial variations is of lower quality than data concerning temporal variations. A study of spatial variations involves comparisons between sites where observations are made with different

instruments, different calibration gases and different data selection criteria. In addition the spatial resolution is restricted to a few dozen sites globally.

3. Integral equations

The problem of numerical differentiation is precisely equivalent to that of numerically solving the integral equation:

$$c(t) - c(t_0) = \int_{t_0}^{t} s(t')\,\mathrm{d}t'. \tag{3.1}$$

A study of various classes of integral equations enables us to consider a wider class of poorly-posed inverse problems than those considered in the previous section.

The first generalisation which occurs in much geochemical modelling is to equations of the form

$$c(t) - c(t_0) = \int_{t_0}^{t} R(t-t')\,s(t')\,\mathrm{d}t'. \tag{3.2}$$

These examples are Volterra equations of the first kind, since the variable, t appearing on the left is equal to the upper limit of the integration. Here $s(t)$ represents an input whose influence on some observable quantity $c(t)$ decreases with time according to some response function $R(t)$. $R(t)$ is the amount of tracer present at a time t after its release. It is assumed that a steady state applies prior to time t_0. A specific problem which can be analysed in this way is the work of Peng et al. (1983) who deduced source strengths $s(t)$ of biospheric carbon from observations of $^{13}C:^{12}C$ ratios in tree-rings. The theory of response functions for isotopic perturbations has been described by Tans (1980). The actual approach used by Peng et al. (1983) was to work directly with a carbon cycle model to deduce isotopic responses rather than explicitly form a response function $R(t)$.

The form (3.2) can be transformed into

$$\frac{\partial c}{\partial t} = s(t)R(0) + \int_{t_0}^{t} s(t')\frac{\partial}{\partial t}[R(t-t')]\,\mathrm{d}t', \tag{3.3}$$

so that the solution of (3.2) requires a numerical differentiation of $c(t)$ followed by the solution of a Volterra equation of the second kind. The solution of Volterra equations of the second kind is a well-posed problem and there exists a stable iterative solution that will always converge (Ursell, 1974). Thus the difficulty in solving equation (3.2) numerically is dominated by the difficulty of obtaining $\partial c/\partial t$ numerically.

The more general form of Volterra equation of the first kind is

$$c(x) = \int_{a}^{x} K(x,x')\,s(x')\,\mathrm{d}x', \tag{3.4}$$

and a further generalization is to Fredholm equations of the first kind

$$c(x) = \int_{a}^{b} K(x,x')\,s(x')\,\mathrm{d}x'. \tag{3.5}$$

Equations of the Fredholm type are very common in remote sensing problems (see, for example Twomey (1977)), but they seem of less interest in geochemical problems and are introduced here for the purposes of discussing the relative difficulty of obtaining solutions.

Twomey has emphasised that the difficulty in solving integral equations of the Fredholm type increases as the kernel $K(x,x')$ becomes smoother. The comments on the order of numerical differentiation from the previous section can be seen to be a specific example of this effect of smoothness by using the relation (Ross, 1974)

$$\int_{c}^{x}\mathrm{d}x_1\int_{c}^{x_1}\mathrm{d}x_2\ldots\int_{c}^{x_{n-2}}\mathrm{d}x_{n-1}\int_{c}^{x_{n-1}}h(x_n)\,\mathrm{d}x_n$$

$$=\frac{1}{\Gamma(n)}\int_{c}^{x}(x-x_n)^{n-1}\,h(x_n)\,\mathrm{d}x_n. \tag{3.6}$$

Thus an n-fold repeated integration of h from c to x is equivalent to convolution of h with the Fredholm kernel $K(x,x')$ where

$$K(x,x') = \frac{1}{\Gamma(n)}(x-x')^{n-1} \quad \text{for } x > x' \tag{3.7a}$$

$$= 0 \text{ for } x < x' \tag{3.7b}$$

In these equations $\Gamma(n)$ is the gamma function, which is equal to $(n-1)!$ for integer n. Since convolution with the kernel (3.7) is equivalent to

n-fold integration the inverse operation of solving an integral equation with this kernel is equivalent to an n-fold differentiation. As n increases, the kernels become smoother in that all derivatives up to order $n-2$ (inclusive) are continuous at $x=x'$, thus illustrating the connection between the effective order of differentiation and the smoothness of the Fredholm kernel as measures of the difficulty of solving poorly-posed problems. It is generally true that if the kernel $K(x,x')$ has n continuous derivatives then the solution of the Fredholm equation is equivalent in difficulty to an nth order numerical differentiation.

Because of the poorly-posed nature of these integral equations special techniques called regularisations are used to obtain acceptable numerical solutions. It is necessary to solve an approximation to the original problem, i.e., to construct an approximate inverse to the integral operator such that the approximate inverse does not amplify errors in its operand to an unacceptable extent (see for example Allison (1979), Twomey (1977) and for greater generality Jackson (1972)). A typical approach is to solve eq. (3.5) for $s(x)$ by finding the function that minimises

$$\theta = \| \int_a^b K(x,x')\, s(x')\, \mathrm{d}x' - c(x) \|^2 + \alpha \|s(x)\|^2 \tag{3.8}$$

where the norm

$$\|h(x)\|^2 = \int_a^b h(x)^2\, \mathrm{d}x. \tag{3.9}$$

This scheme is of particular interest because it can be shown that for fixed α the solution $s(x)$ is the solution of a Fredholm equation of the second kind, for which the existence of a solution is guaranteed and, for sufficiently large α, an iterative solution converges (Ursell, 1974).

There are many variations on the minimisation (3.8). One possibility is to minimise the linear combination of the two norms rather than the squares of the norms. Other possibilities are to use norms other than the L_2 norm used in eq. (3.8), although Anderssen and de Hoog (1983) have pointed out that for practical computations the choice is essentially restricted to L_1, L_2 or L_∞. Another class of modifications of the scheme (3.8) is to replace $\|s(x)\|^2$ by some other function of s, e.g., $\|s\|^2 + \|\partial s/\partial x\|^2$. The literature on these various possibilities is extensive (see for example Twomey (1977), Golub et al. (1979) and references therein).

The various regularisations have the desirable mathematical property of transforming unstable problems into stable problems by filtering out the unstable parts of the solution. Anderssen and Bloomfield (1974a) explicitly discuss numerical differentiation in terms of filtering. However, these processes are subject to the very considerable difficulty that there are generally not any objective criteria for choosing either the regularisation scheme or the value of α that is most suitable for a particular problem.

Twomey (1977) has proposed one partial solution by recommending that α be chosen to be within the range in which the solution is insensitive to α so that the value of α is relatively unimportant. If there is no such region, he regards the regularisation constraint as being incompatible with the original problem. An alternative approach to regularisation schemes is through biased estimation or 'ridge regression' (Hoerl and Kennard, 1970). The basic principle is that in ill-conditioned linear least-squares problems, biased estimates exist that have smaller mean-square errors than unbiased estimates (Goldstein and Smith, 1974). These biased estimates correspond to the regularised solutions described above in that the solution of the ill-posed problem is biased towards the regularisation constraint. The utility of this approach is limited by the fact that the optimal value of the parameter α cannot normally be determined unless the 'true' solution of the problem is already known. In order to overcome this difficulty a number of approaches have been devised determining an α that is either approximately optimal or optimal in a statistical sense. The most notable is generalised-cross-validation (Golub et al. (1979); see references therein for other methods). This technique requires relatively large amounts of comparable data and so its utility in geochemical studies may be limited.

An alternative approach to regularisation that may sometimes be possible is to interpret the regularisation in terms of additional or prior information concerning the problem. Rodgers (1977) has argued that this is the proper way in which to interpret the statistics of any constrained inversion calculation. The use of prior information as a constraint has been applied to the calibration of carbon cycle models (Enting and Pearman, 1983, 1986, Enting, 1985a).

4. Fractional differentiation and an application

In the previous section we quoted the result connecting an n-fold integration to a single convolution with a Volterra type kernel. If the n-fold integration operation is denoted ${}_cI_x^n$ then eq. (3.6) can be written

$${}_cI_x^{\lambda}\, h(x) = \frac{1}{\Gamma(\lambda)} \int_c^x (x-y)^{\lambda-1}\, h(y)\, \mathrm{d}y. \qquad (4.1)$$

There is nothing about the right-hand side which restricts λ to be an integer and so, as reviewed by Ross (1974), eq. (4.1) can be used to define λ-fold integration for all real $\lambda > 0$. Ross defined the fractional differentiation operator $D^{m-\nu}$ by

$${}_cD_x^{m-\lambda}\, h(x) = \frac{\mathrm{d}^m}{\mathrm{d}x^m}\, {}_cI_x^{\lambda}\, h(n) \quad \text{for } 0 < \lambda < 1. \qquad (4.2)$$

Integrals of the form (4.1) with λ in the range 0 to 1 occur frequently in problems involving geometrical probability, particularly for $\lambda = \frac{1}{2}$ (Anderssen and de Hoog, 1983).

One example of an effective fractional integration in a geochemical problem is a simplified static model of gas bubble trapping in firn. Gas bubbles trapped in ice-cores from the Arctic and Antarctic have been analysed (Neftel et al., 1985) to determine the atmospheric CO_2 concentration since pre-industrial times. However, one difficulty in interpreting the results of such analyses is that bubbles in any single layer will have been trapped at a range of different times. This will become important when analysing air trapped at around 100 years ago since the question of whether concentrations were changing at the end of the nineteenth century is of considerable importance in interpreting current carbon cycle models.

The model will be expressed in terms of z which represents a negative time coordinate (relative to the present) and which is related to the depth below the surface. The observations are $q(z)$, the CO_2 concentration in air bubbles occurring in a layer of ice that was deposited (as snow) z years before present (B.P.). The atmospheric CO_2 concentration z years B.P. is denoted $c(z)$. When the snow was deposited z years B.P., very little air was trapped initially. Most of the bubbles contributing to $q(z)$ are from times $z' < z$. The trapping function $R(x)$ gives the proportion of air in a layer that was trapped x years after the snow was deposited, and is assumed to be normalised so that

$$\int_0^{\infty} R(x)\, \mathrm{d}x = 1, \qquad (4.3)$$

and therefore

$$q(z) = \int_0^z R(z-z')\, c(z')\, \mathrm{d}z'. \qquad (4.4)$$

Enting (1985b) described a simple static model of gas trapping based on the percolation model from lattice statistics (Shante and Kirkpatrick, 1971; Essam, 1972). The percolation model is concerned with connected clusters in a lattice in which connecting pathways are closed in a random manner. A key quantity in percolation theory is the percolation probability $P(p)$ expressed as a function of p, the proportion of pathway closures in the lattice. $P(p)$ is the probability that a given site is connected via open pathways to an infinite cluster of sites.

One result of percolation theory is that there is a critical probability p_c at which $P(p)$ goes to zero and that $P(p)$ has a singularity:

$$P(p) \sim (p_c - p)^{\beta} \qquad \text{as} \qquad p \to p_c^- \qquad (4.5a)$$

with

$$P(p) = 0 \qquad \text{for} \qquad p \geqslant p_c. \qquad (4.5b)$$

The critical probability p_c depends on the lattice but universality theory predicts that the critical exponent β will be independent of the lattice. Series expansions lead to estimates of $\beta \approx 0.454$ (Gaunt and Sykes, 1983), for three-dimensional systems.

The infinite cluster is interpreted as the set of sites connected to the atmosphere and so writing P as a function of z, the proportion of trapped sites is $1 - P(z)$.

Thus

$$R(z) = -\frac{\partial}{\partial z} P(z) \sim (z_c - z)^{\beta-1}. \qquad (4.6)$$

Using eq. (4.4) it will be seen that the singularity contributes to the observed concentrations as

$$q(z) \sim \int_{z-z_c}^{z} (z_c - z + z')^{\beta-1} c(z')\,dz',$$

or putting

$$t = z_c - z,$$

$$t' = -z',$$

$$q(z_c - t) = \int_{t-z_c}^{t} (t - t')^{\beta-1} c(-t')\,dt'. \tag{4.7}$$

Thus the gas-bubble concentrations are essentially an order-β integration of past atmospheric concentrations and the deduction of past concentrations from bubble concentrations is essentially a βth-order differentiation. With $\beta \approx 0.454$, the percolation model of bubble trapping would imply that the bubble deconvolution problem is less poorly-posed than the normal source deduction problems. The errors that seem most likely to limit the accuracy of the deconvolution are the errors in the trapping distribution due to natural fluctuations in snow deposition. This would mean that the 'true' trapping process would be described by the more general case of the Volterra integral eq. (3.4) rather than the special form (4.4).

The analysis by Enting (1985b) exemplifies the point that was made in Section 2 where it was pointed out that the comparison of orders of differentiation, i.e., the comparison of the way in which errors are amplified in different problems, must refer to those length or time scales that are relevant to the problem and not just to some idealised assymptotic limit. As described by Enting (1985b) universality theory from statistical mechanics would suggest that the exponent for percolation in the firn would behave assymptotically as a two-dimensional system and hence have $\beta = 5/36$. However this behaviour would only apply very close to z_c and for time scales of interest to bubble trapping the system would show a 'crossover' (Stanley 1974) to the three-dimensional behaviour characterised by $\beta \approx 0.454$.

Another inverse problem arising in connection with bubble trapping is to solve eq. (4.4) for the trapping distribution $R(z)$, using a tracer such as one of the halocarbons for which $c(z)$ is known reasonably well and for which $q(z)$ can be measured. From the discussion of smoothness in the previous section it will be seen that this problem is very poorly conditioned since a smooth kernel $c(z)$ is involved when fine details of $R(z)$ are required.

5. Incomplete problems

Implicit in the discussion in the previous sections has been the assumption that there was, in principle, enough information available to define a unique solution to the problem if the data was error-free. For example it can be shown that the Volterra integral equation

$$c(t) = c(t_0) + \int_{t_0}^{t} R(t - t')\, s(t')\,dt', \tag{5.1}$$

with a monotonically decreasing kernel R has a unique solution $s(t)$ for a given $c(t)$, subject to $c(t)$ being differentiable (see eq. (3.3)). The previous sections have been concerned with the difficulty of deducing $s(t)$ over the interval (t_0, t_1) given values of $c(t)$ over (t_0, t_1) which are subject to error.

In geochemical studies we are frequently confronted with the situation in which we only know $c(t)$ over a part of the interval (t_0, t_1) in which $s(t)$ is non-zero. As an example, consider the case in which $c(t)$ is known over such a small interval that the knowledge can be effectively summarised as a knowledge of a small number of derivatives of c at time t_1. In order to interpret this knowledge of the information about $s(t)$, (5.1) may be differentiated to give

$$\left.\frac{\partial c}{\partial t}\right|_{t_1} = \int_{t_0}^{t_1} R(t_1 - t') \frac{ds}{dt'}\,dt', \tag{5.2}$$

$$\left.\frac{\partial^2 c}{\partial t^2}\right|_{t_1} = \int_{t_0}^{t_1} R(t_1 - t') \frac{d^2 s}{dt'^2}\,dt', \tag{5.3}$$

and so on. Eq. (5.2) is obtained from (3.3) by integrating by parts.

While a knowledge of the derivatives gives very specific constraints on the function $s(t)$, these constraints are totally inadequate to determine the function. It may however be of interest to consider the solutions to a 'related' problem that has the formal appearance of the regularised problems described in Section 3. If we have a knowledge of n derivatives $c^{(0)}$ to $c^{(n)}$ then we seek the solution $s(t)$ that minimises the function

$$\theta = \sum_{m=0}^{n} \left| \left(c^{(m)} - \int_{t_0}^{t_1} R(t-t')\, s^{(m)}(t')\mathrm{d}t' \right) \right|^2 + \alpha \|s(t)\|^2, \quad (5.4)$$

As in the regularised solutions described in Section 3, variations on this approach can use powers other than 2 and any one of a variety of norms. The solution can be regarded as defining the 'smallest' function $s(t)$ that gives a specified degree of agreement with the knowledge of the derivatives $s^{(m)}(t)$. 'Smallest' is defined in terms of whatever norm is chosen.

The choice of norm and of the parameter α is subject to all the difficulties described in connection with regularisation but has been subject to very little study. The only justifiable approach seems to be in terms of prior information as described in Section 4.

While there is probably limited interest in looking for the 'smallest' solution to any geochemical problem, often one has an initial estimate $s_0(t)$ and it is possible to use the formalism of (5.4) to look for the solution $s(t)$ that has the smallest differences from $s_0(t)$.

Putting $s(t) = s_0(t) + \sigma(t)$, this requires the $\sigma(t)$ that minimises

$$\theta = \sum_{m=0}^{n} \left| c^{(m)} - \int_{t_0}^{t_1} R(t-t')\, s_0^{(m)}(t')\mathrm{d}t' - \int_{t_0}^{t_1} R(t-t')\, \sigma^{(m)}(t')\,\mathrm{d}t' \right|^2 + \alpha \|\sigma(t)\|^2, \quad (5.5)$$

which, regarded as an equation to be solved for $\sigma(t)$, is of the same form as (5.4).

The solution $s(t)$ can then be interpreted as the closest function to $s_0(t)$ to achieve a specified degree of agreement with the derivatives $c^{(m)}$. Any other function will either give a worse approximation to the $c^{(m)}$ or will be further away from $s_0(t)$ (or both).

This type of analysis has been applied to CCl_3F and CO_2. Fraser et al. (1983) analysed records for CCl_3F concentrations for 1976 to 1980 from Cape Grim, Tasmania and fitted the observations with a least-squares quadratic fit, thus defining $c^{(0)}$, $c^{(1)}$ and $c^{(2)}$. The response function $R(t)$ was obtained from the two-dimensional model of Hyson et al. (1980) with modifications as described by Fraser et al. The initial estimate of the CCl_3F release $s_0(t)$ was obtained from compilations produced by the Chemical Manufacturers Association (CMA, 1982). However the observed second derivative $c^{(2)}$ was more negative than calculated on the basis of $s_0(t)$. Referring back to (5.3), it will be seen that this discrepancy implies that there has been a time when $\partial^2/\partial t^2\, s(t)$ is more negative (or less positive) than $\partial^2/\partial t^2\, s_0(t)$. This interpretation must be regarded as a qualitative description applicable to some smoothed representation of the release since the small-scale details of $s_0(t)$ are not available and Fraser et al. (1983) used a piecewise-linear representation. The function $s_0(t)$ has a region in which the 'second derivative' is negative. This is around 1974, the time of the peak in the estimated release. The discrepancy with observations could imply that either this peak was larger than estimated or that it occurred more recently than 1974 so that it gives a larger negative contribution to the weighted integral (5.3).

Fraser et al. (1983) obtained a reconstructed release function $s(t) = s_0(t) + \sigma(t)$ using a formalism based on eq. (5.4). Where $\|\sigma\|^2$ appears in eq. 5.4 they used a constraint that reflected the uncertainties of current knowledge of $s_0(t)$.

This constraint was a sum of squares of amplitudes of basis functions used to expand $\sigma(t)$. One of the basis functions was $s_0(t)$—its inclusion allows for the possibility of errors with a constant multiplicative factor due to the uncertainties in the absolute calibration of the CCl_3F concentration scale. The other basis functions were 11 piecewise-linear pulses centred on years 1970 to 1980, since errors in estimates for earlier times will be essentially undetectable and any attempt to deduce such errors would be highly unstable. This is reasonable because the change in usage patterns of CCl_3F during the 1970's due to environmental concerns has changed the bulk of the release from aerosol propellants where the delay between production and release is well-known to refrigerants and insulating foam where the delay between production and release is poorly known. There was thus a valid reason for regarding the releases for 1970–1980 as the most uncertain part of $s(t)$.

Similar reconstructions of source strengths for CO_2 have been calculated by Enting and Pearman (1983, 1986). For CO_2 the release $s(t)$ is the sum of a fossil fuel component $f(t)$ that is believed to be well-known and a biospheric component $b(t)$ for which there are conflicting estimates. Current

observations of CO_2 define $c(t_1)$ but using this knowledge in eq. (5.1) does not constrain the release function $s(t)$ because $c(t_0)$ is not well-known. The CO_2 observations also define $\partial c/\partial t|_{t_1}$ and eq. (5.2) does provide a constraint on $s(t)$. Specifically, most carbon cycle models give response functions $R(t)$ that require

$$\int_{t_0}^{t_1} R(t_1 - t') \frac{db}{dt'} dt' < 0 \tag{5.6}$$

if eq. (5.2) is to be satisfied. The use of response functions to specify the discrepancies between carbon cycle models and biospheric release functions is due to Oeschger and Heimann (1983).

The constraint (5.6) specifically excludes the case of $b(t) \equiv 0$ and also the releases proposed by Moore et al. (1981) and Houghton et al. (1983) that were increasing ($\partial b/\partial t > 0$) over virtually all of the last century, unless, of course, the models are giving $R(t)$ incorrectly. This latter possibility has led to a number of attempts to construct more detailed ocean models, a topic which is outside the scope of this paper.

The analysis undertaken by Enting and Pearman (1983, 1986) was along the lines described above for the CCl_3F analysis. The initial estimate $s_0(t)$ was taken as the sum of the fossil fuel release $f(t)$ from Rotty (1979) and the biospheric release $b_0(t)$ from Moore et al. (1981). The aim was to find a biospheric release $b_0(t) + \beta(t)$ which was as close as possible to the initial estimate $b_0(t)$ while still giving a specified degree of agreement with the observed $\partial c/\partial t$ and other relevant carbon cycle data.

While the outline above describes the basic principle of the reconstruction of $b(t)$, the actual procedure used by Enting and Pearman (1983, 1986) was more complicated in that the model parameters determining $R(t)$ were also allowed to vary subject to the constraint that other information such as ^{14}C distributions was reproduced satisfactorily. In other words the procedure for reconstructing $b(t)$ was embedded in the overall model calibration. This was performed using the constrained inversion techniques with prior information providing the constraint as described by Enting (1985a). In spite of this additional complexity the reconstructed release $b(t)$ can still be characterised very simply. Any other release function $b(t)$ (or more generally any other combination of $b(t)$ and model parameter values) will either differ more from $b_0(t)$ than $b(t)$ does or will involve larger discrepancies with carbon cycle observations (or both).

Another type of incomplete problem arises in the context of model calibration. In terms of the discussion in this paper this represents an attempt to deduce one or more response functions $R(t)$. For the simplest case where we have

$$c(t) = \int_0^t R(t - t')\, s(t')\, dt', \tag{5.7}$$

substituting $\tau = t - t'$ gives

$$c(t) = \int_0^t R(\tau)\, s(t - \tau)\, d\tau. \tag{5.8}$$

Thus the solution of this equation for $R(t)$, given the functions s and c, is equivalent in difficulty to a numerical differentiation of c as discussed in connection with eq. (3.3). However unless $R(t)$ goes to zero in a finite time t the solution of (5.8) will always be an incomplete problem since $c(t)$ and $s(t)$ will only be known up to a time t_{max} and eq. (5.8) will give no information concerning the behaviour of $R(t)$ for $t > t_{max}$.

In most modelling studies $R(t)$ is determined by the model parameters and the calibration procedure can attempt to estimate these parameters by fitting $R(t)$ for $t < t_{max}$. Regardless of whether this fitting is carried out explicitly by actually considering a function $R(t)$ or implicitly by using the mathematical model to relate $c(t)$ to $s(t)$, the success of the procedure will require that $c(t)$ is defined sufficiently well for $\partial c(t)/\partial t$ to be defined and that the interval $(0, t_{max})$ is long enough for all the relevant model parameters to be determined from R.

6. Calibration schemes for carbon cycle models

In this section we attempt to analyse the structure of the problem of calibrating an atmosphere-ocean model for the global carbon cycle. As in previous sections the aim is to obtain an indication of the inherent stability of the problem for the purpose of determining whether the available data is adequate for solving the problems of interest. For this reason we consider analytic representations that describe the dominant struc-

ture of the problem but which may be incomplete for performing actual carbon cycle calculations.

The calibration schemes analysed here uses ^{14}C from nuclear weapons testing to determine the rate at which the deeper layers of the ocean take up CO_2. The alternative procedure of using the natural ^{14}C distribution is subject to a number of difficulties, concerning time scales (Broecker et al. 1980) and biases due to the role of the detrital flux (Bacastow and Björkström, 1981, Enting, 1985a). For these and possibly other reasons, it appears that the use of natural ^{14}C in the calibration causes different models to have CO_2 uptakes that differ to a greater extent than would be the case if they were calibrated with anthropogenic ^{14}C. A comparison of Figs. 8 and 9 of Killough and Emanuel (1981) shows that in all cases except their very crudest model, the highest CO_2 uptakes occur in the models with the highest uptake of anthropogenic ^{14}C. This suggests that the use of anthropogenic ^{14}C to calibrate these models would improve the agreement of the CO_2 uptake.

For the present analysis we only explicitly consider the atmosphere and the ocean mixed layer and describe their contents of the three carbon isotopes as a_ν, m_ν respectively for $\nu = 12$, 13, and 14. The atmospheric source of isotope ν is denoted s_ν and the net flux from the atmosphere to the ocean is denoted ϕ_ν. The case of $\nu = 12$ is taken as being effectively equivalent to total carbon.

We begin by considering the response of the ocean mixed layer to a net input of isotope ν from the atmosphere. Assuming a linear ocean model we can write

$$m_\nu(t) = \int_{t_0}^{t} U(t-t')\,\phi_\nu(t')\,\mathrm{d}t'. \tag{6.1}$$

Here the response function $U(t)$ describes the dispersion of the perturbation into the deeper ocean layers. It is assumed that U is the same for all isotopes.

For total carbon, and effectively for ^{12}C, the equilibration between the atmosphere and the ocean mixed layer is rapid compared to the time-scales of interest. Sundquist and Plummer (1981) have suggested that for modelling purposes the atmosphere and the mixed layer should be regarded as being in exact equilibrium. For the purposes of the schematic argument of the present section, this assumption is certainly adequate and so we put

$$m_{12}(t) = \rho\, a_{12}(t). \tag{6.2}$$

For isotopic equilibrium the time scales are longer by a factor of about 10 (Broecker et al., 1980) and so it is necessary to model the air-sea flux directly as

$$\phi_\nu = k(a_\nu - m_\nu), \quad \nu = 13, 14, \tag{6.3}$$

if a_ν and m_ν are expressed as partial pressures. The coefficient k can be estimated in a variety of ways, such as the radon method (Broecker et al., 1980).

The atmosphere will also lose ^{14}C into the biosphere. We can define a response function B_{14} to describe the way in which the atmosphere responds to an isotopic perturbation by exchanging ^{14}C with the biosphere. Thus

$$a_{14}(t) = \int_{t_0}^{t} B_{14}(t-t')\,(s_{14}(t') - \phi_{14}(t'))\,\mathrm{d}t'. \tag{6.4}$$

This equation can be solved for $s_{14} - \phi_{14}$ and, as described in connection with eq. (3.3) this is equivalent in difficulty to differentiating $a_{14}(t)$. From a knowledge of $s_{14}(t)$, $\phi_{14}(t)$ can be extracted. Eqs. (6.1) and (6.3) then give

$$m_{14}(t) = \int_{t_0}^{t} U(t-t')\,\phi_{14}(t')\,\mathrm{d}t' \tag{6.5}$$

which is to be solved for $U(t)$.

Formally, this could be regarded as a Volterra integral equation for $U(t)$ as described in the previous section in connection with eq. (5.8). It would thus be equivalent in difficulty to a numerical differentiation of $m_{14}(t)$ which (as shown by eq. 6.5) would require a second derivative of $a_{14}(t)$.

In actual fact the calibration problem is not as poorly-posed as this argument would suggest because the integral equation for $U(t)$ has in its kernel a contribution from $s_{14}(t)$. Since this represents the input of ^{14}C from nuclear testing it is not a smooth function and so a knowledge of $a_{14}(t)$ can lead to useful estimates of $U(t)$. Nonetheless, the problem is still incomplete in the sense described in the previous section because the data only cover a finite period.

Once a model has been calibrated using ^{14}C, several problems still remain. Firstly, the air-sea

flux of total carbon can be determined by mass balance for the atmosphere as

$$\boldsymbol{\phi} = \boldsymbol{s} - \dot{\boldsymbol{a}}.$$

Thus eqs. (6.1) and (6.2) give

$$\rho a_{12}(t) = \int_{t_0}^{t} U(t-t')\,(s(t) - \dot{a}(t))\,\mathrm{d}t'. \tag{6.6}$$

Alternatively, using an operator notation with $\boldsymbol{U}$, $\boldsymbol{s}$ etc. denoting functions and * denoting the convolution operation,

$$\rho \boldsymbol{a}_{12} = \boldsymbol{U}_{*}(\boldsymbol{s}_{12} - \dot{\boldsymbol{a}}_{12}) \tag{6.7}$$

whence

$$\rho \dot{\boldsymbol{a}}_{12} = U(0)\,(\boldsymbol{s}_{12} - \dot{\boldsymbol{a}}_{12}) + \boldsymbol{U}_{*}(\boldsymbol{s}_{12} - \dot{\boldsymbol{a}}_{12}),$$

$$(U(0) + \rho)(\boldsymbol{s}_{12} - \dot{\boldsymbol{a}}_{12}) = \rho\, \boldsymbol{s}_{12} + \boldsymbol{U}_{*}(\boldsymbol{s}_{12} - \dot{\boldsymbol{a}}_{12}).$$

Thus

$$(\boldsymbol{s}_{12} - \dot{\boldsymbol{a}}_{12}) = \frac{\rho}{U(0) + \rho}\,\boldsymbol{s}_{12} + \boldsymbol{V}_{*}(\boldsymbol{s}_{12} - \dot{\boldsymbol{a}}_{12}),$$

where

$$\boldsymbol{V} = \boldsymbol{U}'/[U(0) + \rho].$$

This gives

$$(\boldsymbol{s}_{12} - \dot{\boldsymbol{a}}_{12}) = \frac{\rho}{U(0) + \rho}\,(1 - \boldsymbol{V})^{-1}\,\boldsymbol{s}_{12}, \tag{6.8}$$

so from eq. (6.7),

$$\boldsymbol{a}_{12} = \frac{1}{U(0) + \rho}\,\boldsymbol{U}_{*}\,(1 - \boldsymbol{V})^{-1}{}_{*}\boldsymbol{s}_{12}. \tag{6.9}$$

The integral operator expressed as $(U(0) + \rho)^{-1}\,\boldsymbol{U}_{*}\,(1 - \boldsymbol{V})^{-1}$ which we denote $\boldsymbol{R}_{a}$ is, to within the approximations used here, the response to carbon inputs for the atmosphere in an atmosphere ocean system as defined by Oeschger and Heimann (1983) and as used in eq. (5.6).

At this point the approaches to interpreting carbon cycle models can take several different courses. One approach, described in the previous section, is to use $\boldsymbol{R}_{a}$ to place constraints on the biospheric release. An alternative is to use measurements of the ^{13}C content of tree-rings and then assume that they give an adequate representation of $a_{13}(t)$. The release $s_{13}(t)$ can then be obtained by solving

$$a_{13}(t) = \int_{t_0}^{t} R_{13}(t-t')\,s_{13}(t')\,\mathrm{d}t', \tag{6.10}$$

as described in Section 3 above in connection with the work of Peng et al. (1983). To a first approximation the source strength for the ^{13}C perturbation is proportional to the total source strength $s_{12}(t)$ which can thus be deduced from the solution of (6.10). Within the framework of the approximations used in this section the ^{13}C isotopic response function for the atmospheric component of an atmosphere/biosphere/ocean system can be obtained explicitly in terms of a biospheric ^{13}C response function $\boldsymbol{B}_{13}$ and the ocean response function $R(t)$.

$$\boldsymbol{m}_{13} = \boldsymbol{U}_{*}k(\boldsymbol{a}_{13} - \boldsymbol{m}_{13}),$$

$$\boldsymbol{a}_{13} = \boldsymbol{B}_{13*}(\boldsymbol{s}_{13} - k\boldsymbol{a}_{13} + k\boldsymbol{m}_{13}),$$

whence

$$(1 + k\boldsymbol{U})\boldsymbol{m}_{13} = \boldsymbol{U}_{*}k\,\boldsymbol{a}_{13})$$

$$(\boldsymbol{a}_{13} = \boldsymbol{B}_{13*}(\boldsymbol{s}_{13} - k\boldsymbol{a}_{13} + k(1 + k\,\boldsymbol{U})^{-1}{}_{*}\,\boldsymbol{U}_{*}\,\boldsymbol{a}_{13})$$

$$(1 + k\boldsymbol{B}_{13} - k\boldsymbol{B}_{13*}(1 + k\,\boldsymbol{U})^{-1}{}_{*}\,\boldsymbol{U})\,\boldsymbol{a}_{13} = \boldsymbol{B}_{13*}\,\boldsymbol{s}_{13},$$

or

$$\boldsymbol{a}_{13} = (1 + k\boldsymbol{B}_{13} - k\boldsymbol{B}_{13*}(1 + k\,\boldsymbol{U})^{-1}{}_{*}\,\boldsymbol{U})^{-1}\,\boldsymbol{B}_{13*}\,\boldsymbol{s}_{13}.$$

However this approximation will not be sufficiently accurate for the purposes of extracting $\boldsymbol{s}_{13}$ from the tree-ring record. Since the signal is very weak, the isotopic fractionation terms (Tans, 1980) that have been neglected in this analysis must be included if accurate results are to be obtained.

If the approach of obtaining $b(t)$ from tree-ring data is used then the appropriate final step is to check that the function $b(t)$ is consistent with the constraint that the derivative $\dot{a}_{12}(t)$ places on the release. While this step was not explicitly considered by Peng et al. (1983), the general form of their reconstruction is that $b(t)$ is tending to decrease in time and so qualitatively it appears to be consistent with the requirement (5.6).

7. Conclusions

The various sections of this paper have attempted to show how a comparison of the structures of biogeochemical problems can be used as a guide to the relative difficulty of solving them

numerically. The analyses have taken geochemical problems and then abstracted those aspects that lead to most difficulty in obtaining numerical solutions. In the problem of deducing tracer source strengths from observations of concentrations given a model of the tracer behaviour we have used a sequence of abstractions. If the model is fixed then its role can be represented by a response function either exactly, if the model is linear, or approximately if the non-linearities are weak. This abstraction shows that the source deduction is equivalent (or for weakly non-linear models essentially equivalent) to solving eq. (3.2), i.e., a Volterra integral equation of the first kind.

The transformation to eq. (3.3) is a further step that allows a more precise isolation of the difficulties. The solution requires a numerical differentiation (a 'difficult' and possibly unstable problem) followed by solution of a Volterra integral equation of the second kind (an 'easy' stable problem). The successive abstractions have isolated the difficult part of the problem as being one of numerical differentiation.

The analysis of the calibration of carbon cycle models using anthropogenic ^{14}C has made extensive use of a sequence of abstractions in order to show that what is involved is a sequence of poorly posed problems. When discussing the motivation for the use of constrained inversion techniques in the calibration of carbon cycle models, Enting (1985a) pointed out that a number of carbon cycle studies require some form of deconvolution (which can be poorly posed) superimposed on a poorly-posed calibration problem. The abstracted description in Section 6 shows more clearly how such a structure comes about.

It is suggested that any attempt to solve a geochemical inverse problem numerically should be preceded by an analysis of the inherent 'difficulty' or stability of the problem in order to determine whether the available data will support the type of solution that is sought. This is particularly important when solutions are obtained by involving computer packages as 'black boxes', since warnings of numerical difficulties may be easily overlooked in such cases.

8. Acknowledgements

The author wishes to thank Dr. Garry Newsam of the Center for Mathematical Analysis, Australian National University and Dr. Denis O'Brien of the Division of Atmospheric Research, CSIRO for helpful discussions.

9. Notation

Symbols such as $\boldsymbol{a}$ denote functions $a(t)$. Symbols such as $\boldsymbol{R}$ denote functions $R(t)$ used as integral operators so that $\boldsymbol{R}_*\boldsymbol{a}$ denotes the function of t given by

$$\int_{t_0}^{t} R(t-t')\,a(t')\,\mathrm{d}t'.$$

a	lower limit of integral used when writing typical examples of integral equations.
$\boldsymbol{a}_v$, $a_v(t)$	For $v = 12, 13, 14$ the perturbation of the atmospheric content of carbon isotope v. In all such uses, $v = 12$ is taken as synonymous with total carbon.
$\boldsymbol{A}$	Matrix defining an arbitrary linear model.
b	Upper limit of integral in general examples detached from specific contexts.
$\boldsymbol{b}$, $b(t)$	The release rate of biospheric carbon into the atmosphere.
$\boldsymbol{B}_v$, $B_v(t)$	The response function for the atmospheric part of an atmosphere/biosphere system to a perturbing input of isotope v. Only defined for a steady state biosphere and so not applicable for $v = 12$.
c	Lower limit of integrals used in definition of fractional integration.
$\boldsymbol{c}$, $c(t)$	Concentration of any geochemical constituent, especially for atmospheric concentration of CO_2 or CCl_3F.
${}_cD_x^\lambda$	Differential operator of order λ. Equivalent to d^λ/dx^λ for positive integer λ.
$\boldsymbol{f}$, $f(t)$	The release rate of fossil fuel carbon into the atmosphere.
$\boldsymbol{g}$, $\boldsymbol{h}$, $g(t)$, $h(t)$	General functions.
${}_cI_x^\lambda$	Integral operator of order λ.
k	Air-sea gas exchange rate.

$K(x,x')$	Kernel of an arbitrary integral equation.
$\boldsymbol{m}_v, m_v(t)$	For $v = 12, 13, 14$ the perturbation of the amount of carbon isotope v in the ocean mixed layer.
p	In percolation models, the probability of an elementary pathway being closed.
p_c	The value of p at which $P(p)$ vanishes.
$P(p)$	The percolation probability, i.e., the probability that a particular site is connected to an infinite cluster of other sites via open pathways.
$q(z)$	Concentration of CO_2 or other trace gas in gas bubbles in ice-cores.
Q	Mean meridional diffusion coefficient for the troposphere.
$\boldsymbol{Q}$	Diffusion tensor for atmospheric transport models.
$\boldsymbol{R}, R(t)$	General geochemical response function.
$\boldsymbol{R}_v, R_v(t)$	Response function of atmosphere in an atmosphere/ocean/biosphere system to perturbating inputs of isotope v. A steady state biosphere does not contribute to R_{12}.
$\boldsymbol{s}, s(t)$	A general geochemical source strength.
$\boldsymbol{s}, s_v(t)$	The source strength for carbon isotope v into the atmosphere $s_{12}(t) = f(t) + b(t)$.
t, t'	Time variables.
t_0	Initial time for a geochemical process—a steady state is assumed for $t < t_0$.
$\boldsymbol{T}, T(t)$	The age distribution function for bubble trapping in firn.
$\boldsymbol{U}, U(t)$	Response of mixed layer in an ocean model to a perturbating input from the atmosphere. Assumed to be the same for all tracers.
$\mathbf{v}$	Velocity vector in atmospheric transport models.
$\boldsymbol{V}, V(t)$	Operator used in defining atmospheric CO_2 response function. Proportional to $\partial U(t)/\partial t$.
x, y	Arbitrary variables used in integral equations.
z	Negative time variable, monotonically increasing with depth, for layers of firn.
α	Regularisation parameter.
β	Critical exponent for $P(p)$.
Γ	Gamma function.
θ	Sum of squares minimised in various regularisation schemes.
ϕ_v	Air-sea flux of carbon isotope v.
μ	Sine of latitude.
v	Carbon isotope index.
ρ	Sea-air CO_2 ratio assuming instant equilibrium.
$\sigma(t)$	Deviation from direct estimate of CCl_3F release rate.

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