¹³C/¹²C Fractionation during CO₂ Transfer from Air to Sea

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ABSTRACT

Isotopic fractionation factors for the CO₂ transfer between atmosphere and ocean are calculated, taking into account equilibrium and kinetic fractionation. Diffusion of CO₂ into the water, which is rate limiting for mean oceanic conditions, fractionates the carbon isotopes only little. ¹³C/¹²C fractionations are found to be -1.8 to -2.3% for atmosphere-to-ocean transfer, and -9.7 to -10.2% for ocean-to-atmosphere transfer.

A different case is absorption by alkaline solutions which is controlled simultaneously by CO_2 diffusion and the reaction between CO_2 and OH^- . The reaction rate exhibits a fractionation for ${}^{13}C/{}^{12}C$ of about -27%.

1. INTRODUCTION

The fossil and the biospheric CO₂ that have been introduced into the atmosphere have a δ^{13} C of about -25% which is markedly different from the value of -7% characteristic for (present-day) atmospheric CO₂. Therefore, one can possibly estimate past CO₂ inputs into the atmosphere by reconstructing the atmospheric 13 C/ 12 C ratio from measurements on tree rings (Stuiver 1978).

The atmospheric CO_2 excess depends, besides the production rate, on the loss rate and therefore on the atmosphere – ocean transfer resistance. Since this resistance is not equal for the different isotopes, the transfer causes a kinetic isotope fractionation. For a quantitative consideration of the ¹³C history of atmospheric CO_2 by means of models for the global carbon cycle, the isotopic fractionation factors must be determined. This is the purpose of this paper.

2. EXCHANGE OF CO2 BETWEEN AIR AND SEA

 CO_2 exchange between atmosphere and ocean is mainly controlled by diffusion through a thin surface water layer, and we will first consider this process only, neglecting the influence of chemical reactions. The net air-sea exchange flux of CO_2 can then be written as

$$\mathbf{F} = \mathbf{F}_{as} - \mathbf{F}_{sa} = \mathbf{w}(\mathbf{c}_{o} - \mathbf{c}_{s}) = \mathbf{w}(\beta \mathbf{c}_{a} - \mathbf{c}_{s})$$

where $c_a = CO_2$ concentration in the atmosphere; $c_o, c_s = CO_2$ concentrations in surface ocean water (dissolved CO_2 gas only), at the interface (c_o) and in the bulk of the water (c_s); β = solubility of CO_2 ; w = transfer velocity for gas exchange. Solution equilibrium at the interface is assumed, $c_o = \beta c_a$, which is valid because the interfacial resistance is negligible (see section 3). For ¹³CO₂ this must be modified:

$$F^{13} = w^{13} \alpha_{\beta} \beta R_{a}^{13} c_{a} - w^{13} \alpha_{\Sigma} R_{\Sigma}^{13} c_{s}$$
(1)

where $R_a{}^{13}$, $R_{\Sigma}{}^{13} = {}^{13}C/{}^{12}C$ ratios in atmospheric CO₂ and in Σ CO₂ (= CO₂ + HCO₃⁻ + CO₃⁻) in sea water (${}^{13}C/{}^{12}C$ of dissolved CO₂ gas is not measured directly); $\alpha_{\beta} = \beta^{13}/\beta$ = equilibrium fractionation factor between ${}^{13}C$ and ${}^{12}C$ for CO₂ solubility,

 $\alpha_{\beta} = 0.9989$ at 20°C (Vogel et al. 1970);

 α_{Σ} = equilibrium fractionation factor between dissolved CO₂ gas and Σ CO₂.

 α_{Σ} depends on the amounts of CO₃⁻ and HCO₃⁻ in sea water. There are roughly 1.65 mmoles/l of HCO₃⁻, 0.35 mmoles/l of CO₃ and 0.01 mmoles/l of CO₂ in warm surface water (Broecker 1974). The fractionation factors at 20°C are 0.9905 between dissolved CO₂ and HCO₃⁻ (Mook et al. 1974) and 0.9929 between dissolved CO₂ and CO₃⁻⁻ (Mook 1968), so that we get $\alpha_{\Sigma} = 0.9910 = 1 - 9.0\%$. Eq. (1) can be rewritten as follows:

$$F^{13} = \alpha_{as} F_{as} R_a^{13} - \alpha_{sa} F_{sa} R_{\Sigma}^{13}$$

With the (one-way) fractionation factors:

$$\alpha_{\rm as} = \alpha_{\beta} \, {\rm w}^{13} / {\rm w} \alpha_{\rm sa} = \alpha_{\Sigma} \, {\rm w}^{13} / {\rm w}$$
(2)

Here we used $F_{as}^{12} \cong F_{as}$, i.e. the flux of ${}^{12}CO_2$ approximately equals the total CO_2 flux. The errors of model computations due to this approximation are negligible (see Appendix).

For evaluating the fractionation factors we need the ratio of the transfer velocities for ${}^{13}CO_2$ and ${}^{12}CO_2$. They are governed by diffusion in the liquid boundary layer. According to currently accepted theoretical models for gas exchange (Deacon 1977; SFB Meeresforschung 1979), the CO₂ transfer velocity depends on the diffusion coefficient of CO₂ in water, D, as

$$v \sim D^n$$
, with $0.5 \le n \le 0.67$.

We will follow the surface renewal model of Danckwerts (1970) which predicts

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$$w = \sqrt{D/\tau}$$

where *r* is the average replacement time for a water parcel at the surface. The ratio w^{13}/w is then equal to $\sqrt{D^{13}/D^{12}}$. Schönleber, Münnich and Flothmann measured the ratio of the diffusion coefficients for ${}^{13}CO_2$ and ${}^{12}CO_2$ in water and obtained (Schönleber 1976)

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$$D^{13}/D^{12} = 0.9991 = 1 - 0.9\%$$
. (3)
 $w^{13}/w = 1 - 0.5\%$.

whence

Now the fractionation factors can be computed numerically from eqs. (2):

$$\alpha_{as} = 0.9984 = 1 - 1.6\%$$

 $\alpha_{sa} = 0.9905 = 1 - 9.5\%$

As a check, the ratio α_{sa}/α_{as} does equal the equilibrium fractionation factor between atmospheric CO₂ and Σ CO₂, $\alpha_{sa}/\alpha_{as} = 0.9921 = \alpha_{\Sigma}/\alpha_{\beta}$, as it must.

The downwards flux, from atmosphere to ocean, is only slightly fractionated. This result is very different from the value of 0.986 for α_{am} used by Keeling (1973). That value was obtained from experiments on the absorption of CO₂ by hydroxide solution which is considered in the next paragraph.

The above calculations are based on the assumption that diffusion alone is the rate-controlling step for the CO_2 transfer between atmosphere and ocean which is a good approximation under average oceanic conditions (Bolin 1960). The possible influence of CO_2 hydration within the diffusive liquid layer on the kinetic fractionation is discussed in the last paragraph.

3. ABSORPTION OF CO₂ BY A HYDROXIDE SOLUTION

Experiments by Baertschi (1952), Craig (1953, 1954) and Münnich and Vogel (1959) showed that CO_2 absorbed by an open surface of a hydroxide solution is depleted in ¹³C by about 15‰ compared to the CO_2 gas. Münnich and Vogel (1959) treated the absorption in hydroxide solution in a paper which, however, has never been published. Absorption by alkaline solution is completely different from absorption by sea water. As shown below, the competition between reaction and diffusion in the liquid is primarily responsible for the isotopic fractionation in this case.

 CO_2 and OH^- ions react according to $CO_2 + OH^- = HCO_3^-$, and the reaction rate is given by k[OH⁻] [CO₂] or k h c, introducing h = [OH⁻], c = [CO₂]. At steady state, the CO₂ concentration in the alkaline solution obeys the equation

$$\frac{\partial c}{\partial t} = 0 = D \cdot \frac{\partial^2 c}{\partial z^2} - k h c$$
(4)

For $h \approx$ constant, which is valid for atmospheric CO₂ concentrations, the solution is

$$c = c_o \cdot \exp\left(-\sqrt{\frac{kh}{D}z}\right)$$

and the transfer velocity for CO₂ (referring to liquid phase concentrations) by

$$w = \frac{-D \operatorname{grad} c}{c} \bigg|_{(z=0)} = \sqrt{kh D}$$
(5)

With $k = 5800 \text{ molar}^{-1} \text{ s}^{-1}$ at 20°C (Kern 1960), $D = 1.7 \times 10^{-5} \text{ cm}^2/\text{s}$ (for CO₂ in water) and h = 1 molar we get w = 0.31 cm/s, which compares well with the transfer velocities of about 0.1 to 0.2 cm/s obtained by Baertschi and by Münnich and Vogel for 1 to 5 normal NaOH solutions.

Ordinary gas exchange is controlled by boundary layer turbulence in the liquid with transfer velocities w_0 of roughly 10^{-4} to 10^{-3} cm/sec for a relatively quiet liquid (Jähne et al. 1979) which is much slower than the transfer velocity observed here. Obviously, liquid turbulence does not contribute to the CO₂ absorption by a strong alkaline solution.

Münnich and Vogel report an approximate square root dependence of the absorption rate on OH⁻ concentration up to about 1.5 molar, in agreement with eq. (5), then a decrease with a further increase in OH⁻ concentration. They suspect that the decrease is due to a decrease of CO₂ solubility, and therefore of c_0 , because of the rise in ionic strength and in temperature (warming due to reaction). Furthermore, the transfer resistance through the gas boundary film competes at a high overall transfer rate. For stagnant air, w_{gas} can be as low as 0.2 cm/s, as determined from evaporation experiments (Vogt 1976).*)

Baertschi (1952) supposed that a large fraction of the CO_2 molecules impinging on the liquid surface are reflected; this is most probably not the case. Transport of molecules of a gas (mole mass M) through the interface is given from kinetic theory by the transfer velocity*)

$$w_{I} = \gamma \sqrt{\frac{RT}{2\pi M}}$$
(6)

Thorough experimental studies with pure water only yielded a lower limit for the sticking coefficient $y: y > 10^{-3}$ (Harvey and Smith 1959, Raimondi and Toor 1959). According to eq. (6), then $w_I > 10$ cm/s at ambient temperatures, which is much larger than the observed transfer velocity for the absorption of CO₂. The interfacial resistance can therefore be neglected and solution equilibrium can safely be assumed right at the surface, even for the case of the very rapid absorption by NaOH solution. (Obviously, interfacial resistance is completely negligible for ordinary CO₂ exchange between atmosphere and ocean).

It is interesting to notice that the *surface* does not act as a perfect sink for CO_2 , as one might think at first in view of the vigorous absorption, but part of the CO_2 molecules having entered the solution do leave it again without having reacted. The reason is that the transfer rate through the interface is extremely high

The CO₂ flux into the solution is $F = (c_o - c_{bulk}) w = c_o w$, since $c_{bulk} = 0$. The ¹³C/ ¹²C ratio in the absorbed CO₂ is given by the ratio of the ¹³CO₂ and ¹²C₂ fluxes:

*) The transfer velocities w_{gas} and w_{I} refer to gas-phase concentrations, in contrast to the overall gas transfer velocity w. Since the solubility of CO₂ in water is about 1, the numerical values of gas-phase realated and liquid-phase related transfer resistances are roughly equal.

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$$R_{abs} = \frac{F^{13}}{F^{12}} = \frac{R_o^{13} c_o w^{13}}{c_o w} = \frac{\beta^{13} R_a^{13} c_a w^{12}}{\beta c_a w}$$

or, from eq. (5)

$$R_{abs} = \alpha_{\beta} \sqrt{\frac{k^{13} D^{13}}{k D} R_a}$$

With $R_{abs}/R_a \approx 1 - 15\%$, $\alpha_\beta = 1 - 1.1\%$ and $D^{13}/D = 1 - 0.9\%$ the ratio of the reaction rate constants for ${}^{13}CO_2$ and ${}^{12}CO_2$ must be about 1-27%:

 $k^{13}/k \approx 0.973$

For high CO_2 concentrations, the OH^- concentration can no longer be considered constant since reaction becomes faster than OH^- diffusion. Besides eq. (4) the balance for OH^- ions has then to be considered:

$$\frac{\partial \mathbf{h}}{\partial \mathbf{t}} = \mathbf{O} = \mathbf{D}_{\text{OH}} \frac{\partial^2 \mathbf{h}}{\partial \mathbf{z}^2} - \mathbf{k} \mathbf{c} \mathbf{h}$$
(7)

Eqs. (4) and (7) correspond to a nonlinear second order differential equation for c (or h) which cannot be solved explicitly⁽¹⁾. Figure 1 gives a qualitative picture of c and h as a function of depth. In the (fictitious) boundary film of thickness $z_o = D/w_o$, transport is by diffusion only and an OH⁻ gradient exists ($w_o =$ transfer velocity for surface renewal). Below z_o , the gradient vanishes due to turbulent mixing. The OH⁻ deficit:

$$h_{\infty} - h_{o} \approx z_{o} \frac{\partial h}{\partial z} (z_{o}) \approx - z_{o} \frac{\partial c}{\partial z} (z = 0)$$

is negligible for atmospheric CO₂ pressures, which justifies the assumption $h \approx \text{constant}$, but not for pure CO₂.

In this general case, the only parameters which the CO₂ concentration c can depend on are k, D_{CO_2} and D_{OH} , and the carbon isotope fractionation is directly dependent only on k and D_{CO_2} . Since diffusion is hardly fractionating, it is still essentially k, that is the reaction kinetics of CO₂ with the OH⁻ ions, that causes the isotope effect. However, with varying CO₂ concentration, the ratio of the two resistances-reaction and OH⁻ diffusion-changes. Baertschi (1952) observed a smaller ¹³C fractionation with pure CO₂ (11 ± 1‰) than with a N₂ - CO₂ mixture containing 2.6% CO₂ (fractionation 14±2‰). This is to be expected since with pure CO₂, diffusion of OH⁻ ions, which is not fractionating, contributes to the total resistance.

(1) The solutions of this differential equation are called Painlevé's functions (Kamke 1967)

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4. DISCUSSION

In addition to the equilibrium isotope fractionation between atmospheric CO₂ and total CO₂ in sea water, kinetic fractionation is effective as long as equilibrium is not established. This kinetic fractionation is mainly due to a (small) difference in the diffusion coefficients for ¹²CO₂ and ¹³CO₂ in water. On the other hand, absorption by a strong alkaline solution is controlled simultaneously by CO₂ diffusion and by the reaction between CO₂ and OH⁻ which obviously strongly fractionates the carbon isotopes. In sea water, the CO₂ – OH⁻ reaction is insignificant, as the following estimate shows. The OH⁻ concentration is about 10⁻⁶ moles/l which corresponds to a mean lifetime of a CO₂ molecule with respect to reaction with OH⁻ of about 170 s. This is long compared to the Danckwerts-renewal time of ~ 2 s for mean oceanic conditions. In the Danckwerts picture, we can consider surface renewal (characteristic time τ_0) and chemical reaction as statistical processes, so that the total lifetime is obtained by reciprocal addition, $1/\tau_{\text{total}} = 1/\tau_0 + 1/\tau_{\text{reaction}}$ (Danckwerts 1970, p. 109).

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The total transfer velocity is then given by

$$v_{total} = \sqrt{D (1/\tau_0 + 1/\tau_{reaction})} = \sqrt{D/\tau_0 (1 + \tau_0 k h)}$$

Correspondingly the fractionation due to this reaction is about $1/2 \times 2 \text{ s}/170 \text{ s} \times 27\%$ = 0.2\%

The hydration of CO₂ might also contribute to the total isotope fractionation; the calculation is analogous to that for the reaction with OH⁻. At 20°C, the CO₂ lifetime for hydration is ~ 50 s (K ern 1960), or 25 times longer than for surface renewal. The unknown kinetic fractionation by the hydration reaction is therefore to be divided by 25 to obtain its contribution to the total. If the fractionation in the hydration were as large as the one in the OH⁻ attachment, it would make up about $1/2 \times 27\%/25 = 0.5\%$. Assuming that this is the upper limit and zero permil is the lower limit, we finally get for the total fractionation factors:

$$\alpha_{\rm as} = 0.9982 \text{ to } 0.9977 = 1 - 1.8\% \text{ to } 1 - 2.3\%$$

$$\alpha_{\rm as} = 0.9903 \text{ to } 0.9898 = 1 - 9.7\% \text{ to } 1 - 10.2\%$$
(8)

The true fractionation in the hydration process is still to be determined experimentally.

In order to see the significance of these numerical values, the atmospheric ${}^{13}\text{C}/{}^{12}\text{C}$ depression due to the fossil CO₂ input was computed by means of a box-diffusion model for the global carbon cycle (Oeschger *et al.* 1975), assuming a constant biomass (see also Siegenthaler *et al.* 1978). Using $\alpha_{as} = 0.9982$ and $\alpha_{sa} = 0.9903$, the resulting ${}^{13}\text{C}/{}^{12}\text{C}$ depression in 1970 is 0.74‰, while with the fractionation factors used by Keeling (1973) ($\alpha_{as} = 0.986$, $\alpha_{sa} = 0.977$) it is 0.61‰. The difference is significant, which shows the importance of the kinetic fractionation for the present atmospheric ${}^{13}\text{C}/{}^{12}\text{C}$ ratio.

For ${}^{14}C/{}^{12}C$ the fractionation factors are simply the square of those for ${}^{13}C/{}^{12}C$. For ${}^{13}C$, the fractionation is important since the observed variations in atmospheric air or in tree rings are of the order of 0.1 to 1‰. For the ${}^{14}C$ Suess effect, on the other hand, isotopic fractionation can well be corrected by means of normalizing to a common $\delta^{13}C$ value, except for second-order effects due to radioactive decay which are, however, negligible. The precise values of the fractionation factors are, therefore, not important for calculating ${}^{14}C$ variations.

APPENDIX

Consider the ¹³CO₂ balance of the atmosphere (a) in exchange with the surface ocean (s), with a CO₂ production rate P(t). If N_a = atmospheric CO₂ mass and the other symbols are as in section 2:

$$\frac{d N_a^{13}}{dt} = \frac{d}{dt} R_a^{13} N_a^{12} = -\alpha_{as} F_{as}^{12} R_a^{13} + \alpha_{sa} F_{sa}^{12} R_s^{13} + P^{12} R_p^{13}$$
(9)

We want to show that this exact equation is very well approximated by consistently replacing F_{ij}^{12} by the total CO₂ flux F_{ij} , and N_a^{12} by the total atmospheric CO₂ mass N_a (more generally, N_i^{12} by N_i for reservoir i), that is by

$$\frac{d}{dt} R_a^{13} N_a = - \alpha_{as} F_{as} R_a^{13} + \alpha_{sa} F_{sa} R_s^{13} + P R_p^{13}$$
(10)

The mass of ${}^{13}CO_2$ in the atmosphere is given by

$$N_a{}^{13} = R_a{}^{13} N_a{}^{12} = \frac{R_a{}^{13} N_a}{1 + R_a{}^{13}}$$

Similarly:

$$F_{as}^{13} = \alpha_{as} F_{as}^{12} R_{a}^{13} = \frac{\alpha_{as} F_{as} R_{a}^{13}}{1 + f_{as} R_{a}^{13}}$$
(11)

Using (11) and analogous expressions and by multiplying with $(1 + R_{ao})$, where R_{ao} is the ¹³C/¹²C ratio for the undisturbed atmosphere, we get from (9)

$$\frac{d}{dt} \cdot R_{a}^{13} N_{a} \cdot \frac{1 + R_{ao}^{13}}{1 + R_{a}^{13}} = -\alpha_{as} F_{as} R_{a}^{13} \cdot \frac{1 + R_{ao}^{13}}{1 + f_{as} R_{a}^{13}} + \alpha_{sa} F_{sa} R_{s}^{13} \frac{1 + R_{ao}}{1 + f_{sa} R_{a}^{13}} + P \cdot R_{p}^{13} \cdot \frac{1 + R_{ao}}{1 + R_{a}^{13}}$$
(12)

Eq. (12) is exact. The relative ¹³C concentrations are given by $\delta_s \approx +1\%$, $\delta_p \approx -25\%$ and the absolute ¹³C/¹²C ratio $R_{ao} \approx 0.011$. The numerical values of the fractions in eq. (12) deviate from 1 by $2 \cdot 10^{-4}$ or 0.2‰ at most, which is about 1 percent of the differences occurring (~ 20‰, between atmospheric and fossil CO₂). It is therefore a good approximation to set the fractions in (12) equal to unity, which directly gives eq. (10).

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REFERENCES

- Baertschi, P., (1952). Die Fraktionierung der Kohlenstoffisotope bei der Absorption von Kohlendioxid. Helv. Chim. Acta, *35*, 1030–1036.
- Bolin, B., (1960). On the exchange of carbon dioxide between the atmosphere and the sea. Tellus, *12*, 274–281.
- Broecker, W.S., (1974). Chemical Oceanography. Harcourt Brace Jovanovich.
- Craig, H., (1953). The geochemistry of the stable carbon isotopes. Geochim. Cosmochim. Acta, *3*, 53–92.
- Craig, H., (1954). Carbon 13 in plants and the relationship between carbon 13 an carbon 14 variations in nature. J. Geology, *62*, 115–149.

Danckwerts, P.V., (1970). Gas-Liquid Reactions. McGraw-Hill.

- Deacon, E.L., (1977). Gas transfer to and across an air-water interface. Tellus, 29, 363-374.
- Harvey, E.A., and Smith, W., (1959). The absorption of carbon dioxide by a quiescent liquid. Chem. Engng. Sci., 10, 274–280.
- Jähne, B., Münnich, K.O. & Siegenthaler, U., (1979). Measurements of gas exchange and momentum transfer in a circular wind tunnel. Tellus, *31*, 321–329.
- Keeling, C.D., (1973). The carbon dioxide cycle: reservoir models to depict the exchange of atmospheric carbon dioxide with the oceans and land plants. In Chemistry of the lower atmosphere (ed. S.I. Rasool), 251–329.
- Kern, D.M., (1960). The hydration of carbon dioxide. J. Chem. Education, 37, 14-23.
- Landolt-Börnstein, (1968). Zahlenwerte und Funktionen, vol. II/5, 16 Springer.
- Mook, W.G., (1968). Geochemistry of the stable carbon and oxygen isotopes of natural waters in the Netherlands. Ph.D. Thesis, Groningen.
- Mook, W.G., Bommerson, J.C. & Stavermann, W.H., (1974). Carbon isotope fractionation between dissolved bicarbonate and gaseous carbon dioxide. Earth Planet. Sci. Letters, 22, 169–176.
- Münnich, K.O., & Vogel, J.C., (1959). Variations in ¹⁴C-content during the last years. Presented at Internat. ¹⁴C Symposium, Groningen; unpublished manuscript.
- Oeschger, H., Siegenthaler, U., Schotterer, U., & Gugelmann, A., (1975). A box diffusion model to study the carbon dioxide exchange in nature. Tellus, *27*, 168–192.
- Raimondi, P., & Toor, H.L., (1959). Interfacial resistance in gas absorption. A.I.Ch.E. Journal, *5*, 86–92.
- Schönleber, G., (1976). Messung der Isotopentrennung bei der Diffusion von ¹³CO₂ und ¹²CO₂ in Wasser. Diploma thesis, Institute for Environmental Physics, University of Heidelberg.
- SFB Meeresforschung, (1979). Symposium on Gas Exchange and Capillary Waves, Trier (Germany) July 1979. (Proceedings to be published by Sonderforschungsbereich Meeresforschung, University of Hamburg).
- Siegenthaler, U., Heimann, M., & Oeschger, H., (1978). Model Responses of the Atmospheric CO₂ Level and ¹³C/¹²C ratio to Biogenic CO₂ Input. In "Carbon Dioxide, Climate and Society", J. Williams, (ed.), 79–87 (Pergamon).
- Stuiver, M., (1978). Atmospheric carbon dioxide and carbon reservoir changes. Science, 199, 253-258.
- Vogel, J.C., Grootes, P.M., & Mook, W.G., (1970). Isotope fractionation between gaseous and dissolved carbon dioxide. Z. Physik, 230, 225–238.
- Vogt, H.-J., (1976). Isotopentrennung bei der Verdampfung von Wasser. Diploma-thesis, Institute for Environmental Physics, University of Heidelberg.