

27/8-74

Det Norske Videnskaps-Akademi i Oslo

Geophysica Norvegica

GEOFYSISKE PUBLIKASJONER

EIGIL HESSTVEDT, SVEIN-ERIK HENRIKSEN & HREINN HJARTARSON
On the development of an aerobic atmosphere. A model experiment.

DET NORSKE METEOROLOGISKE INSTITUTT
BIBLIOTERET
BLINDERN, OSLO 8

VOL. 31 NO. 1. 1974
UNIVERSITETSFORLAGET

Geophysica Norvegica

is a journal of geophysics, issued under the auspices of the Norwegian Academy of Science and Letters in Oslo

EDITOR

Eigil Hesstvedt, Institutt for geofysikk, Universitetet i Oslo, Oslo 3, Norway.

EDITORIAL BOARD

Olaf Devik, Rektorhaugen 11, Oslo, Norway

Olav Holt, Nordlysobservatoriet, Universitetet i Tromsø, 9000 Tromsø, Norway

Håkon Mosby, Geofysisk institutt, Universitetet i Bergen, 5000 Bergen, Norway.

PUBLISHER

Universitetsforlaget: P. O. Box 307, Blindern, Oslo 3, Norway.

P. O. Box 142, Boston, Mass. 02113, U.S.A.

SUBSCRIPTION

Geophysica Norvegica (Geofysiske Publikasjoner) is published at irregular intervals. Order from the Publisher, Universitetsforlaget.

Geophysica Norvegica (Geofysiske Publikasjoner) is a series of scientific publications issued by the Norwegian Academy of Science and Letters in Oslo. The Geophysical Commission appoints an editor and editorial committee.

Manuscripts for publication in *Geophysica Norvegica* should be carefully prepared (see Instructions to Author on p. 3 of the cover) and sent to the editor. The next step is the manuscript's submission to the Academy by a competent member, who is responsible for ensuring that the paper meets a sufficiently high scientific standard. (Members of the Academy are allowed to submit their own papers.) The final decision as to whether the paper should be published is taken by the editor.

Geophysica Norvegica is mainly intended as a journal for Norwegian authors, but papers from other authors may be accepted provided that the work has been carried out at a Norwegian institution or its content has a special relevance to Norway.

On the development of an aerobic atmosphere.

A model experiment

EIGIL HESSTVEDT, SVEIN-ERIK HENRIKSEN, AND HREINN HJARTARSON
Institute of Geophysics, University of Oslo

Hesstvedt, E., Henriksen, S.-E. & Hjartarson, H. On the development of an aerobic atmosphere. A model experiment. *Geophysica Norvegica*, Vol. 31, No. 1, 1974.

Photochemical atmosphere models are used to compute vertical profiles of O_3 corresponding to O_2 contents ranging from 3×10^{-4} PAL to the present level. Two different models are presented: the first model is a static O-H model, where the effect of atmospheric transport is disregarded. In the second model, also an O-H model, vertical eddy transport is considered along with the photochemistry. There is only a little difference in ozone column density computed from the two models, but the vertical profiles look quite different. The resulting absorption of ultraviolet solar radiation due to O_2 , O_3 , and H_2O is computed. It is shown that an ozone layer develops as the oxygen content rises from 3×10^{-4} to 3×10^{-3} PAL. The latter value gives total absorption below 285 nm, except in the region 200–220 nm, where an efficient filter is provided by 2 m of water. With continuous escape of hydrogen, the oxygen content may in principle continue to grow to the present value by photodissociation of water vapor alone. A self-regulating process, limiting the oxygen content to about 10^{-3} PAL, as proposed in earlier works, does not seem to exist.

E. Hesstvedt, Institute of Geophysics, University of Oslo, P. O. Box 1022, Blindern, Oslo 3, Norway

INTRODUCTION

It seems to be generally accepted that upon its formation the Earth was without a significant atmosphere. It is believed that our atmosphere was initially formed by volcanic activity, where outbursts of solid material were accompanied by release of gases, presumably H_2O , CO_2 , N_2 , SO_2 , H_2 , and Cl_2 . However, no O_2 is released by volcanic activity.

In the primitive atmosphere, oxygen is believed to have originated by photodissociation of water vapor, supplied to the atmosphere by the oceans. If all other processes, such as escape of hydrogen to space or chemical interactions between atmos-

phere and lithosphere, are disregarded, photodissociation alone would rapidly lead to an oxygen concentration which is 10^{-6} to 10^{-5} times the present atmospheric level (PAL). Continued photodissociation would be compensated for by the back-reactions $2OH \rightarrow H_2O + O$ and $OH + H_2O \rightarrow H_2 + O_2$, whereby water vapor is reformed. An increase in the oxygen content can only take place if hydrogen is removed from the atmosphere, for instance by escape to space. It has been suggested (Patterson 1970) that our present atmosphere is subject to such a loss at a rate of $2.5 - 8 \times 10^7$ atoms $cm^{-2}s^{-1}$. Such a process may have been going on continuously since the Earth's formation, although the escape rate may have varied by orders of magnitude. The formation of an oxygenic atmosphere can in principle be explained by the combined effect of dissociation of water vapor and escape of hydrogen to space. This is in contradiction to the proposed

This paper was submitted to the Norwegian Academy of Science and Letters in Oslo, 16 March 1973 (revised 1 March 1974).

self-regulating process which sets an upper limit for the oxygen content which can be obtained by photochemistry alone (Urey 1959, Berkner & Marshall 1964, Johnson 1969). The argument for such a limitation is that the increase of oxygen will reduce the photodissociation of water vapor, which takes place at wavelengths where oxygen absorbs very strongly. One result of our computations is that such a limit does not exist, as has already been pointed out earlier (Brinkmann 1969, Hesstvedt 1971). The increase of oxygen beyond a limit estimated at 10^{-3} PAL can be explained without the production of oxygen from photosynthesis, which may, however, have changed the rate of increase of atmospheric oxygen. It is also true that atmospheric water vapor is broken down by reaction with excited atomic oxygen, $O(^1D)$, formed by photodissociation of ozone at wavelengths below about 310 nm. Such radiation is not affected by oxygen absorption, which ends at 242.4 nm. The importance of this reaction for our present problem has earlier been pointed out by two of the authors (Hesstvedt 1971, Henriksen 1972).

1. PHOTOCHEMICAL ATMOSPHERE MODEL

We have only sparse information about atmospheric composition at the earlier stages. Theories on atmospheric development must therefore rest upon assumptions which are often questionable. In the study of atmospheric composition it is often convenient to use photochemical atmospheric models. Such models represent simplified simulations of the atmosphere and can therefore never give a full description of atmospheric development. Nevertheless, such models have often proved very useful in studies of certain aspects of the chemistry of the atmosphere.

In the present study we are aiming at two specific goals, namely (a) to determine ozone profiles corresponding to given oxygen contents, and (b) to show that for any given oxygen content there exists a composition which is in photochemical equilibrium. Our basic model is a photochemical atmosphere model in which 38 reactions involving oxygen and hydrogen are considered. Computa-

tions are made from the ground to 40 km altitude for equatorial conditions. Our model represents a simplification of the real atmosphere; the validity of the results will therefore depend upon the assumptions made. The photochemical reactions considered here are given in Table 1. Ten components are considered: $O(^3P)$, $O(^1D)$, O_2 , O_3 , OH, HO_2 , H_2O_2 , H_2 , H_2O , and H. The vertical distribution of water vapor is taken as constant in our computations. One assumption is namely that the vertical temperature profile has always been the same. On this basis we estimate a water vapor profile corresponding to a relative humidity of 75% in the troposphere and a mixing ratio of 6×10^{-6} by volume in the stratosphere. For a surface temperature of 26.5°C , corresponding to present equatorial conditions, this gives a column density of 1.66×10^{23} molecules cm^{-2} for water vapor. The corresponding figure for a surface temperature of 0°C would be 2.9×10^{22} molecules cm^{-2} . Even this lower value is sufficient to shield the Earth's surface from solar radiation of wavelengths shorter than 197 nm. It is therefore probable that radiation below this limit has never reached the surface.

On the basis of the reactions in Table 1, the densities of the other nine components are computed, first assuming that the total amounts of hydrogen and oxygen atoms are in the ratio 2:1, expressing that all components are derived from photodissociation of water vapor. This would correspond to the initial stage when no escape of hydrogen had taken place. The oxygen content at this stage is very low, about 10^{-5} PAL. As hydrogen escaped, however, the hydrogen/oxygen ratio (water vapor itself excluded) decreased and the equilibrium concentration of oxygen increased. At the same time, the photochemical lifetime of oxygen increased, and at about 10^{-4} PAL it is realistic to assume that turbulent vertical exchange had become faster than the photochemistry of molecular oxygen. It is then convenient to assume constant mixing ratios with height for oxygen, ranging from 3×10^{-4} to 1 PAL, and compute the concentrations of the other components, assuming that the atmosphere is in a steady state. Two different models are computed. In both, transport is indirectly considered for O_2

and water vapor by assuming constant profiles as explained above. In one of the models the effect of transport has been disregarded in the computation of the other components, while vertical eddy diffusion has been considered in the second model. In the troposphere a value of $10^5 \text{ cm}^2\text{s}^{-1}$ has been taken for the vertical eddy diffusion coefficient, while in the stratosphere lower values are assumed, decreasing exponentially with height to $10^3 \text{ cm}^2\text{s}^{-1}$ from the tropopause to 30 km, then increasing exponentially with height to $5 \times 10^3 \text{ cm}^2\text{s}^{-1}$ at 40 km (Isaksen & Hesstvedt 1973).

The computations are carried out as follows:

For each model the oxygen mixing ratio and the water vapor profile are taken as constant. Number densities for the remaining eight components are computed on the basis of the reactions given in Table 1. Production and loss terms for each component are expressed in terms of reaction rate coefficients and number densities. The assumption of photochemical equilibrium defines a system of eight nonlinear equations which determine the atmospheric composition at a given level. An iterative method is used to solve the equations. Complete expressions for production and loss are used in the computations. However,

Table 1. Reactions and reaction rate coefficients

(1) $\text{O}(^3\text{P}) + \text{O}(^3\text{P}) + \text{M} \rightarrow \text{O}_2 + \text{M}$	$k_1 = 3.8 \times 10^{-30} T^{-1} \cdot \exp(-170/T)$
(2) $\text{O}(^3\text{P}) + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M}$	$k_2 = 1.07 \times 10^{-34} \exp(510/T)$
(3) $\text{O}(^3\text{P}) + \text{O}_3 \rightarrow 2\text{O}_2$	$k_3 = 1.9 \times 10^{-11} \exp(-2300/T)$
(4a) $\text{O}_2 + h\nu \rightarrow \text{O}(^3\text{P}) + \text{O}(^3\text{P})$	$175 \text{ nm} < \lambda < 242.4 \text{ nm}, J_{2a}$
(4b) $\text{O}_2 + h\nu \rightarrow \text{O}(^3\text{P}) + \text{O}(^1\text{D})$	$\lambda < 175 \text{ nm}, J_{2b}$
(5a) $\text{O}_3 + h\nu \rightarrow \text{O}(^3\text{P}) + \text{O}_2$	$\lambda > 310 \text{ nm}, J_{3a}$
(5b) $\text{O}_3 + h\nu \rightarrow \text{O}(^1\text{D}) + \text{O}_2$	$\lambda < 310 \text{ nm}, J_{3b}$
(6) $\text{OH} + \text{O}(^3\text{P}) \rightarrow \text{H} + \text{O}_2$	$k_6 = 4.2 \times 10^{-11}$
(7) $\text{HO}_2 + \text{O}(^3\text{P}) \rightarrow \text{OH} + \text{O}_2$	$k_7 = 7 \times 10^{-11}$
(8) $\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$	$k_8 = 2.08 \times 10^{-32} \exp(290/T)$
(9) $\text{H} + \text{O}_3 \rightarrow \text{OH} + \text{O}_2$	$k_9 = 2.6 \times 10^{-11}$
(10) $\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$	$k_{10} = 2 \times 10^{-10}$
(11) $\text{H}_2\text{O}_2 + h\nu \rightarrow 2\text{OH}$	$187.5 \text{ nm} < \lambda < 382.5 \text{ nm}, J_{\text{H}_2\text{O}_2}$
(12) $\text{O}(^3\text{P}) + \text{H}_2\text{O}_2 \rightarrow \text{OH} + \text{HO}_2$	$k_{12} = 3.6 \times 10^{-11} \exp(-2950/T)$
(13) $\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	$k_{13} = 3 \times 10^{-11} \exp(-500/T)$
(14) $\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2$	$k_{14} = 1.7 \times 10^{-11} \exp(-910/T)$
(15) $\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}(^3\text{P})$	$k_{15} = 10^{-11} \cdot \exp(-530/T)$
(16) $\text{H}_2\text{O} + h\nu \rightarrow \text{OH} + \text{H}$	$135 \text{ nm} < \lambda < 237.5 \text{ nm}, J_{\text{H}_2\text{O}}$
(17) $\text{H} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}(^3\text{P})$	$k_{17} = 8.3 \times 10^{-11} \cdot \exp(-500/T)$
(18) $\text{H} + \text{HO}_2 \rightarrow \text{H}_2 + \text{O}_2$	$k_{18} = 4.2 \times 10^{-11} \cdot \exp(-350/T)$
(19) $\text{H} + \text{H} + \text{M} \rightarrow \text{H}_2 + \text{M}$	$k_{19} = 8.3 \times 10^{-33}$
(20) $\text{O}(^1\text{D}) + \text{M} \rightarrow \text{O}(^3\text{P}) + \text{M}$	$k_{20} = 5.9 \times 10^{-11}$
(21) $\text{O}(^1\text{D}) + \text{H}_2 \rightarrow \text{OH} + \text{H}$	$k_{21} = 2.9 \times 10^{-10}$
(22) $\text{O}(^3\text{P}) + \text{H}_2 \rightarrow \text{OH} + \text{H}$	$k_{22} = 3 \times 10^{-14} \cdot T \cdot \exp(-4480/T)$
(23) $\text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + 2\text{O}_2$	$k_{23} = 10^{-13} \exp(-1250/T)$
(24) $\text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2$	$k_{24} = 1.6 \times 10^{-12} \exp(-1000/T)$
(25) $\text{H} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2 + \text{HO}_2$	$k_{25} = 2.8 \times 10^{-12} \exp(-1900/T)$
(26) $\text{H} + \text{O}(^3\text{P}) + \text{M} \rightarrow \text{OH} + \text{M}$	$k_{26} = 2 \times 10^{-32}$
(27) $\text{H} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}(^3\text{P})$	$k_{27} = 2 \times 10^{-10} \exp(-4/RT)$
(28) $\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}(^3\text{P})$	$k_{28} = 3.7 \times 10^{-10} \exp(-8450/T)$
(29) $\text{O}(^1\text{D}) + \text{H}_2\text{O} \rightarrow 2\text{OH}$	$k_{29} = 3.5 \times 10^{-10}$
(30) $\text{H} + \text{HO}_2 \rightarrow 2\text{OH}$	$k_{30} = 4.2 \times 10^{-10} \exp(-950/T)$
(31) $\text{H} + \text{OH} + \text{M} \rightarrow \text{H}_2\text{O} + \text{M}$	$k_{31} = 6.1 \times 10^{-26}/T^2$
(32) $\text{O}(^3\text{P}) + \text{OH} + \text{M} \rightarrow \text{HO}_2 + \text{M}$	$k_{32} = 1.4 \times 10^{-31}$
(33) $\text{H} + \text{OH} \rightarrow \text{H}_2 + \text{O}(^3\text{P})$	$k_{33} = 3 \times 10^{-14} \cdot T \cdot \exp(-4480/T)$
(34) $\text{H}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{H}$	$k_{34} = 10^{-10} \exp(-5.9/RT)$
(35) $\text{O}(^1\text{D}) + \text{O}_3 \rightarrow 2\text{O}_2$	$k_{35} = 5 \times 10^{-10}$
(36) $\text{HO}_2 + h\nu \rightarrow \text{OH} + \text{O}(^3\text{P})$	$J_{\text{HO}_2} \approx J_{\text{H}_2\text{O}_2}$

we get a better understanding of the chemistry if the expressions are simplified by disregarding terms which turn out to be unimportant. Starting with $O(^1D)$ we have, with a high degree of accuracy

$$[O(^1D)] \approx \frac{J_{3b}[O_3] + J_{2b}[O_2]}{k_{20}[M] + k_{29}[H_2O]}$$

for daytime conditions. (M denotes an arbitrary air molecule.) Similarly, we have for atomic oxygen in the ground state

$$[O] \approx \frac{J_3[O_3] + 2J_2[O_2] + k_{15}[OH]^2 + (k_{17}[H] + J_{H_2O})[HO_2] + k_{29}[O(^1D)]}{k_2[M][O_2] + k_6[OH] + k_7[HO_2]}$$

and for atomic hydrogen

$$[H] \approx \frac{k_6[O][OH] + J_{H_2O}[H_2O] + (k_{21}[O(^1D)] + k_{34}[OH])[H_2]}{k_8[M][O_2] + k_9[O_3] + (k_{17} + k_{18} + k_{30})[HO_2]}$$

These three components have very short photochemical lifetimes, sometimes up to a minute, but in general, fractions of a second. Atomic oxygen and hydrogen disappear at night. This makes the night-time chemistry in the model relatively simple.

For the other components the expressions are more complicated. For OH, which has a short lifetime and disappears at night, we have

$$[OH] \approx P_{OH}/Q_{OH}$$

where

$$P_{OH} = (2k_{29}[O(^1D)] + J_{H_2O})[H_2O] + (k_7[O] + 2k_{30}[H])[HO_2] + (k_9[H] + k_{23}[HO_2])[O_3] + J_{H_2O_2}[H_2O_2]$$

$$Q_{OH} = k_6[O] + k_{14}[H_2O_2] + 2k_{15}[OH] + k_{24}[O_3] + k_{34}[H_2]$$

$[HO_2]$, which also has a short lifetime, may be expressed as

$$[HO_2] \approx \frac{k_8[M][O_2][H_2] + (k_{14}[H_2O_2] + k_{24}[O_3])[OH]}{k_7[O] + k_{10}[OH] + (k_{17} + k_{18} + k_{30})[H] + 2k_{13}[HO_2] + k_{23}[O_3] + J_{HO_2}}$$

For H_2 and H_2O_2 we have

$$[H_2] \approx \frac{k_{18}[HO_2][H]}{k_{21}[O(^1D)] + k_{34}[OH]}$$

and

$$[H_2O_2] \approx \frac{k_{13}[HO_2]^2}{J_{H_2O_2} + k_{14}[OH]}$$

The equilibrium density of ozone is found from the production and loss terms of odd oxygen ($O + O_3$). The production term is, if small terms are disregarded,

$$2J_2[O_2] + k_{15}[OH]^2 + J_{HO_2}[HO_2] + k_{17}[H][HO_2]$$

and the loss term is

$$(2k_3[O_3] + k_6[OH] + k_7[HO_2])[O] + k_9[H] + k_{23}[HO_2] + k_{24}[OH][O_3] + (2k_{35}[O_3] + k_{29}[H_2O])[O(^1D)]$$

Since $[O(^1D)]$ and $[O] \approx [O(^3P)]$ are nearly proportional to $[O_3]$, $[O_3]$ is easily expressed in terms of $[OH]$, $[H]$, $[H_2O]$, and $[HO_2]$.

As mentioned above, $O(^1D)$, $O(^3P)$, H, and OH disappear at night, and HO_2 is also reduced by about one order of magnitude. The night-time photochemistry of H_2 , H_2O_2 , and O_3 is therefore very slow. Thus daytime composition is largely determined by daytime photochemistry. Daytime means may therefore be used for the dissociation rate coefficients.

Recent data on solar radiation and absorption cross-sections are used for the computations of the dissociation rate coefficients (Ackerman 1971, Kockarts 1971, Hudson & Johnson 1973). It is assumed that the pressure (apart from the increasing partial pressure of O_2) has not under-

gone significant changes over the last three billion years. It is emphasized that this is an essential assumption in our model, since the total number

density $[M]$ determines the production of ozone through the reaction $O + O_2 + M \rightarrow O_3 + M$.

In the model we have described above, O_3 , H_2 , and H_2O_2 were determined on the assumption of photochemical equilibrium. We shall refer to this model as the 'equilibrium model' (although vertical transport is considered for O_2 and H_2O). However, O_3 , H_2 , and H_2O_2 have, at least in a part of the height interval we consider, lifetimes long enough to make photochemistry less important than vertical exchange. We have therefore also computed a 'transport model', where vertical transport of O_3 , H_2 , and H_2O_2 has been considered together with photochemistry. As we shall see, the two models give widely different profiles of ozone below the ozone peak. However, the ozone column density is only insignificantly (for our problem) altered by the consideration of transport.

2. RESULTS

Vertical profiles of ozone, computed from the equilibrium profiles model, are shown in Fig. 1 for oxygen levels from 3×10^{-4} PAL to the present value. The first trace of an ozone layer seems to have occurred just before the oxygen level reached the value 10^{-3} PAL. From then on, the ozone layer developed rapidly and soon reached values which are not too much different from what we have in the present atmosphere.

The effect of vertical transport is clearly demonstrated in Fig. 2, which shows ozone profiles for the transport model. Generally speaking, vertical transport brings ozone down from the peak level around 18 km down into the troposphere. This rearrangement, however, does not alter the ozone column density significantly.

It is of biological interest to interpret the pro-

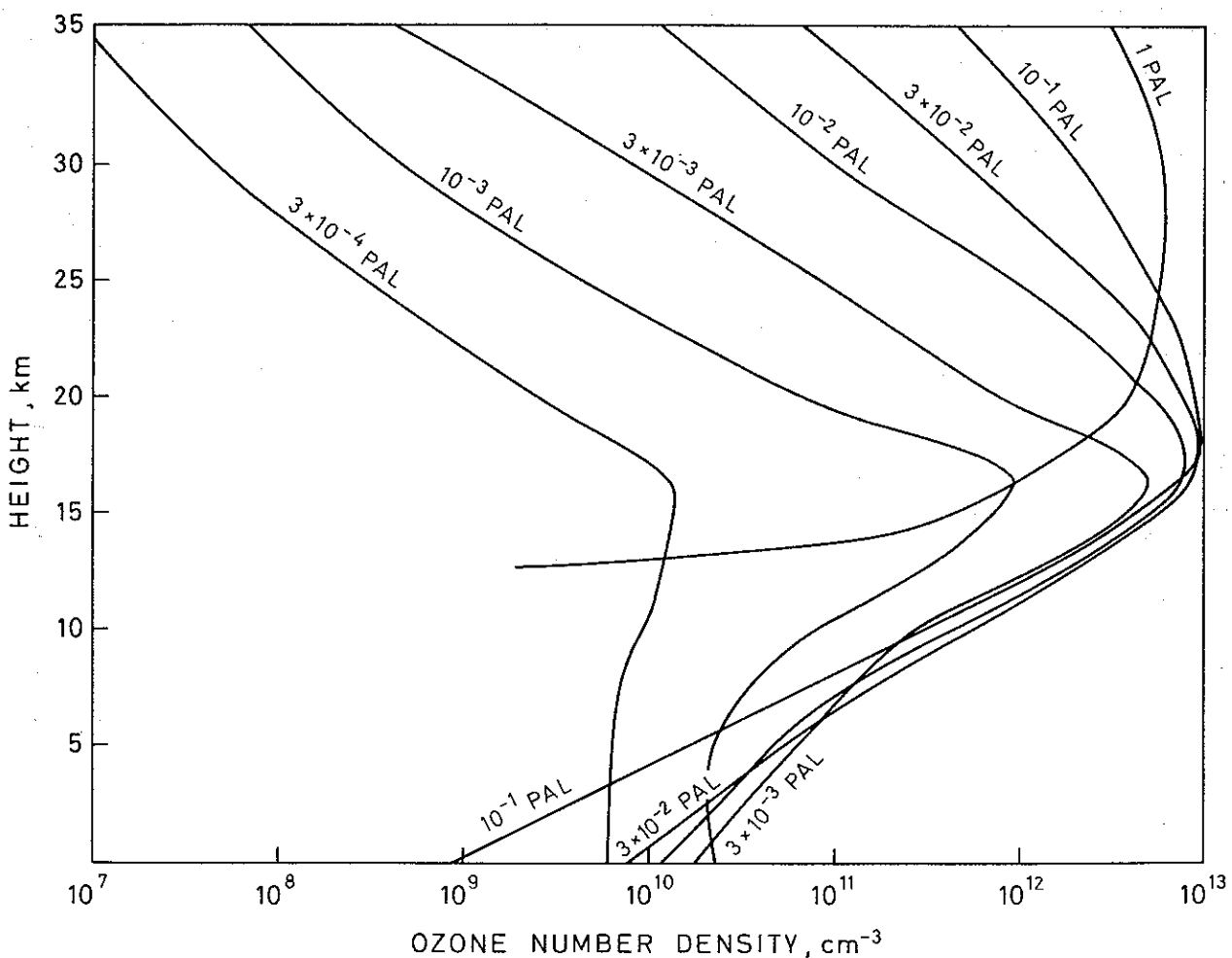


Figure 1. Vertical distribution of ozone for different oxygen levels, computed from a model where photochemical equilibrium was assumed for ozone.

files shown in Figs. 1 and 2 in terms of ultra-violet radiation penetrating to the Earth's surface. As already mentioned, water vapor is likely to absorb all radiation below about 200 nm. The most important absorbent in the interval 200–242 nm is molecular oxygen, and above 242 nm ozone. As one can see from Fig. 3, oxygen levels between 10^{-3} and 10^{-2} PAL still permit radiation at 210 nm to reach the surface. It should, however, be remembered that other absorbents, not considered in our model, may have been present in quantities large enough to filter out even this radiation. It is known that SO_2 , one of the more abundant volcanic gases, absorbs strongly between 200 and 220 nm; also in the region 260–310 nm the absorption is significant. SO_2 is a minor constituent of our present atmosphere (mixing ratio $\sim 3 \times 10^{-9}$), which reduces radiation at 210 nm by 12%; for other wavelengths the

reduction is less. If the mixing ratio in the primitive atmosphere were 10^{-7} , SO_2 would reduce the radiation at 210 nm by a factor of 60, while a mixing ratio of 10^{-6} would absorb all radiation in the interval 200–220 nm. Such a high SO_2 content would also absorb all radiation in the interval 260–310 nm. Clearly, since SO_2 is washed out of the atmosphere by precipitation, such high concentrations would result in a highly acidic environment on land.

It is further well known that water is an efficient absorbent of ultraviolet radiation (Dawson & Hulburt 1934). At 210 nm 2 m of water reduces the radiance by a factor of 5×10^{-5} , for 3 m of water the factor falls to 3×10^{-7} . The absorption coefficient decreases with increasing wavelength, and at 280 nm complete filtering requires a depth of 15 m of water. Combining these figures with the curves in Fig. 3, we may conclude that, for

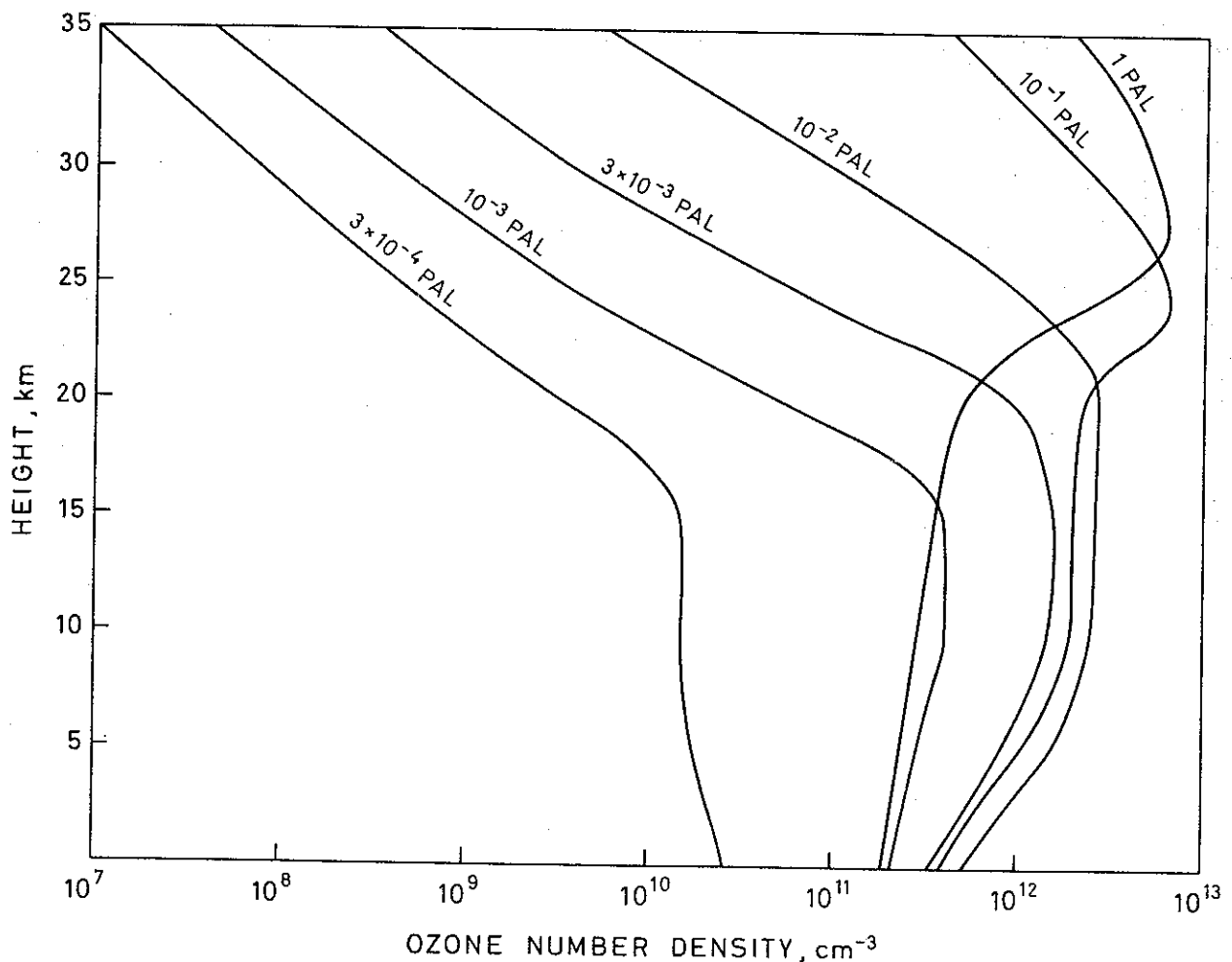


Figure 2. Vertical distribution of ozone for different oxygen levels, computed from a model where vertical eddy transport was considered for ozone.

an oxygen level of $2-3 \times 10^{-3}$ PAL and a depth of 2 m of water, all radiation below 280 nm is filtered out. Without water, i.e. on land, an oxygen level of 2×10^{-2} seems to be required for a complete absorption of the shorter wavelengths (below 290 nm).

Ozone profiles have also been computed for summer and winter conditions and for other latitudes than 0° . The results differ very little from those given in Figs. 1 and 2. The path length of ozone will vary with latitude owing to the decreasing elevation of the sun. This will, for the same amount of ozone, give an absorption which will be somewhat stronger than that shown in Fig. 2. For 60° latitude, summer and noon, the path length of ozone will be increased by a factor of 1.25 compared to the path length for overhead sun. However, this does not necessarily mean that the latitudinal variation in ultra-violet radiation at the surface is small. In our present atmosphere there is a marked increase in ozone as

we go towards higher latitudes. This increase is not attributed to photochemistry but rather to the general circulation of the stratosphere. Something similar may have occurred at earlier stages of the Earth's history. It is therefore not unlikely that Fig. 3 considerably underestimates the filtering effect of ozone in middle and high latitudes. But since no data for stratospheric transport in the past are available, it has not been possible to account for this effect, which may have been significant. In our present atmosphere the ozone column density at 45° (summer) is $\frac{1}{3}$ higher than at the Equator. Accounting for the sun's elevation, a curve for 10^{-3} PAL and 45° latitude should run close to that for 3×10^{-3} PAL computed for the Equator for wavelengths above 250 nm (Fig. 3).

According to our models, an equilibrium state exists for each oxygen level. An increase in oxygen requires a loss of hydrogen, which may have come about by escape of hydrogen to space.

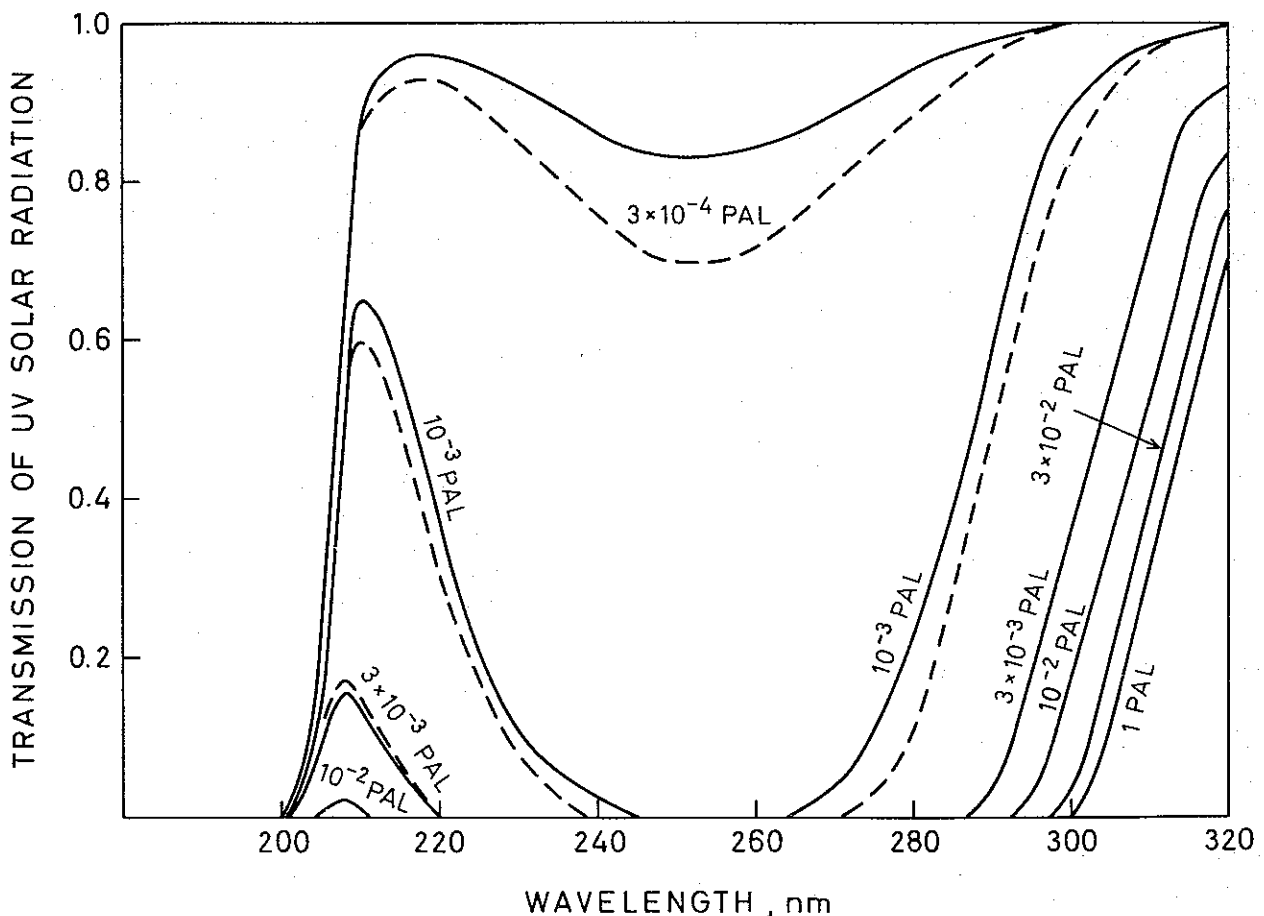


Figure 3. Transmission of UV-radiation to the Earth's surface (solid lines: transport model, broken lines: equilibrium model).

If no photosynthesis and no chemical interaction between lithosphere and atmosphere took place (which is certainly not true), the loss of hydrogen to space should approximately equal the total free oxygen content in the atmosphere. (An average loss rate of 1.3×10^8 hydrogen atoms $\text{cm}^{-2}\text{s}^{-2}$ would be sufficient to explain the production of today's oxygen level in our model.) Since the escape process must have been going on throughout the history of our planet, the conclusion must be that oxygen is bound to increase continuously even without the aid of photosynthesis. It appears, then, that photosynthesis is not necessary to explain the formation of an aerobic atmosphere.

The dissociation of water vapor is partly due to direct photodissociation, and partly due to reaction with $\text{O}(^1D)$, which is formed by photodissociation of ozone for wavelengths below 310 nm. At high levels, and for small oxygen (and ozone) contents, the former process is the more significant one. But in the troposphere and for oxygen levels above 10^{-3} PAL the latter reaction is largely dominating. Furthermore, when discussing photochemical production rates of oxygen, one should always have in mind that oxygen production goes on not only near the surface, but also at much higher levels. Turbulent transport will then bring the produced oxygen down to the surface and account for a constant mixing ratio with height.

The development of the stratospheric ozone layer has recently been studied by Ratner & Walker (1972). They used a pure oxygen equilibrium model and obtained quite different results from ours. Their profile for 1 PAL also differs from observed ones, not only at heights where hydrogen is known to reduce ozone, but also at heights where the pure oxygen model is believed to simulate the atmosphere fairly well. Part of the disagreement must therefore be sought elsewhere, for instance in the difference in data used for solar radiation and absorption.

It is true that the ozone content may also be influenced by other minor constituents, such as CO and nitrogen oxides. Since nothing is known about these gases at earlier stages of atmospheric development, models involving CO and nitrogen

oxides must be highly speculative. It may, however, be of interest to mention that for oxygen content around 10^{-3} PAL, the ozone will only be affected by nitrogen oxides if the mixing ratio is greater than 10^{-8} . This is comparable to, and at many heights higher than, the present value. Since stratospheric NO_x is formed by photodissociation of NO_2 produced by bacteria at the ground, such a high NO_x content is not very likely. On the other hand, the CO content may have been quite high in the stratosphere. This depends to a great extent upon the CO_2 content, since CO is formed by photodissociation of CO_2 and broken down by OH through the reaction $\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}$. If we assume the same CO_2 content as in the present atmosphere, we arrive at CO mixing ratios around 10^{-8} . CO will then destroy OH and thereby influence ozone. It should, however, be emphasized that even higher CO_2 levels would not make the results obtained here invalid; it is more a question of relatively small modifications.

REFERENCES

- Ackerman, M. 1971: p. 149 in *Mesospheric Models and Related Experiments*. D. Reidel Publishing Company, Dordrecht - Holland.
- Berkner, L. V. & Marshall, L. C. 1964: p. 122 in *Discussions of the Faraday Society*, No. 37.
- Brinkmann, R. T. 1969: *J. Geophys. Res.* 74, 5355-5368.
- Dawson, L. H. & Hulburt, E. D. 1934: *J. Optical Soc.* 24, 175-177.
- Henriksen, S.-E. 1972: Master's thesis, University of Oslo (in Norwegian).
- Hesstvedt, E. 1971: Internal Report, Institute of Geophysics, University of Oslo.
- Hudson, R. D. & Johnson, L. B. 1973: Paper presented at the IAGA Symposium, Kyoto, Japan.
- Isaksen, I. S. A. & Hesstvedt, E. 1973: NASA Contractor Report, NASA CR-2314, National Aeronautics and Space Administration, Washington, D. C.
- Johnson, F. S. 1969: p. 303 in *Space Science Reviews*, Vol. 9. D. Reidel Publishing Company, Dordrecht - Holland.
- Kockarts, G. 1971: p. 160 in *Mesospheric Models and Related Experiments*. D. Reidel Publishing Company, Dordrecht - Holland.
- Patterson, T. N. L. 1970: *Rev. of Geophys. and Space Phys.* 8, 461-467.
- Ratner, M. J. & Walker, J. C. G. 1972: *J. Atm. Sc.* 29, 803-808.
- Urey, H. C. 1959: p. 363 in *Handbuch der Physik*. Vol. L11, Springer-Verlag, Berlin.

Instructions to Authors

GEOPHYSICA NORVEGICA

publishes papers in English. When preparing manuscripts for submission, authors should consult 1973 copies of the journal and follow its style as closely as possible.

MANUSCRIPTS

Manuscript must be typewritten, double spaced throughout, on one side of the paper, with a wide margin. Authors should submit the *original* manuscript (preferably with one copy) to the editor, whose address is shown on page 2 of the cover.

Separate sheets should be used for the following: 1) title page, with the author's name and institution, and, if the title is longer than 40 letters and spaces, a short title not exceeding this limit for use in the running heads; 2) an abstract not exceeding 12 lines (910 letters and spaces) with the name and full postal address underneath of the author to whom communications, proofs, and reprints are to be sent; 3) references; 4) Tables with their headings; 5) legends to Figures.

Brief *Acknowledgements* of grants and other assistance, if any, will be printed at the end of the text.

FIGURES, TABLES, AND MATHEMATICAL SYMBOLS

All illustrations are to be considered as Figures. Each graph, drawing, or photograph should be numbered in sequence with arabic numerals, and should be identified on the back by the name of the journal, the author's name, and the Figure number. The top should be indicated. The Figures should be the original drawing. The columns of *Geophysica Norvegica* are 67 mm broad, and the size of the original drawings should be in proportion. Lines must be thick enough to allow for reduction. Letters and numbers should not be less than 2 mm high in the printed illustration. Photographs should be submitted as unmounted glossy enlargements showing good details.

Tables are to be numbered consecutively with roman numerals. Each Table should be typed on a separate sheet, with a descriptive heading that makes the Table self-explanatory.

All Figures and Tables should be referred to in the text by their number. Their approximate position should be indicated in the margin of the manuscript.

All numbered equations and all unnumbered but complicated equations should be typed on separate lines. Equations should be punctuated.

All text material will be set in roman type unless otherwise marked. Hence, all variables and other characters to be set in italic type should be underlined once with a straight line. Vectors and other characters in boldface type should be indicated by underlining with a single wavy line.

No footnotes should be used.

REFERENCES TO LITERATURE

In the text, Brown (1957, p. 9), Brown & White (1961). If more than two authors, Brown et al. (1963). Multiple references: 'As several authors have reported (Brown 1967, Brown & White 1961, Green et al. 1963)', i. e. chronological order, no commas between names and year.

Lists of References are to be unnumbered and in alphabetical order. The international alphabetical order of Scandinavian and German vowels, should be observed: Å = AA, Æ and Ä = AE, Ø and Ö = OE, Ü = UE. Indicate 1st, 2nd, 3rd, etc. works by the same author in the same year by a, b, c, etc. (White 1966a). No ditto marks should be used. Titles of journals should be abbreviated according to *World List of Scientific Periodicals*.

Examples:

Cadle, R. D. 1966. p. 83 in *Particles in the Atmosphere and Space*. Reinhold Publishing Corporation, New York.

Craig, R. A. 1965. p. 161 in *The Upper Atmosphere. Meteorology and Physics*. International Geophysics Series, Vol. 8. Academic Press, New York and London.

Eliassen, A. & Kleinschmidt, E. 1957. p. 66 in *Handbuch der Physik*. Vol. 48, Part 2, edited by S. Flügge. Springer-Verlag, Berlin.

Junge, C. 1972. *Quart. J. R. Met. Soc.* 98, 711.

PROOFS

Two copies of the first proof will be sent (page proofs). One copy, duly corrected, should be returned to the editor with the least possible delay. All technical parts of the article, including references, names, figures (numbers, formulae), illustrations, etc. are the responsibility of the authors. Authors will be required to pay for any major alterations they may make.

REPRINTS

Fifty reprints of each article will be supplied free. Additional reprints can be ordered at a charge.

Biological and Geological Journals

<i>Title</i>	<i>Languages</i>	<i>Summary/ Abstract</i>	<i>Issues per volume</i>
AMBIO A journal of the Human Environment, Research and Management	English		6
ASTARTE Journal of Arctic Biology	English		2
BLYTTIA Journal of the Norwegian Botanical Association	Norwegian	English	4
BOREAS An International Journal of Quaternary Geology	English, French and German	English	4
LETHAIA An International Journal of Palaeontology and Stratigraphy	English, French and German	English	4
LITHOS An International Journal of Mineralogy, Petrology and Geochemistry	English, French and German	English	4
NORSK ENTOMOLOGISK TIDSSKRIFT Norwegian Journal of Entomology	English, Norwegian and German	English	2
NORSK GEOGRAFISK TIDSSKRIFT Norwegian Journal of Geography	English, Norwegian and German	English	4
NORSK GEOLOGISK TIDSSKRIFT Norwegian Journal of Geology	English, French and German		4
NORWEGIAN JOURNAL OF BOTANY	English, French and German	English	4
NORWEGIAN JOURNAL OF ZOOLOGY	English, French and German	English	4
ORNIS SCANDINAVICA	English		2

Periodicals

ACTA BOREALIA Journal of Arctic Botany, Geology and Zoology	English		
ASTROPHYSICA NORVEGICA Norwegian Journal of Theoretical Astrophysics	English		
FOLIA LIMNOLOGICA SCANDINAVICA Scandinavian Journal of Limnology	English		
GEOPHYSICA NORVEGICA Geofysiske Publikasjoner	English		
PHYSICA NORVEGICA Norwegian Journal of General Physics	English		4
SARSIA Journal of Marine Biology	English		