Letters to the Editor

K. C. JONES: Observations of Long-Term Air-Soil Exchange of Organic Contaminants, ESPR 1 (3), 172 – 177 (1994)

In his review article on the long-term air-soil exchange of organic contaminants, K. C. JONES [1] commented – among others – data on the soil concentration changes of 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) and octachlorodibenzo-p-dioxin (OCDD) between 1856 and 1986. Both compounds were regarded as having a "low" or "negligible" volatilisation potential and are "very slowly" biodegradable in the soil. This is certainly true and results in long residence times in soils.

JONES concluded that – sonce these compounds are of anthropogenic origin – their "concentrations have either continued to increase up to the present or have stabilized". He did not discuss, however, the photochemical degradation potential of those compounds, which has been shown by MILLER and coworkers [2, 3]. This process may indeed be negligible for most substances, but in the case of the dioxins, the OCDD concentration is 250 – 500 times higher than that of 2,3,7,8-TCDD, so that a reaction rate of only 0.1 – 1 percent enhances the concentrations of the degradation products as, e.g., of 2,3,7,8-TCDD [4], appreciably.

Considering this, one may speculate that the photochemical degradation on soil surfaces may as secondary source be responsible for the continuous increase of the 2,3,7,8-TCDD soil concentrations from 40 pg/kg in 1944 and 60 pg/kg in 1966 up to 110 pg/kg in 1986, despite its (slight) potential for volatilisation. OCDD concentrations increased only between 1944 and 1966 (from 10 000 to 32 000 pg/kg), but not between 1966 and 1986 (32 000 and 25 000 pg/kg, respectively).

Of course, these discrepancies may be due to analytical or other uncertainties. On the other hand, if this process would be proved, it may lead to consequences with regard to the assessment of OCDD (with a low toxicity equivalent (TE) of 0.001 in contrast to the degradation products with TEs of up to 1) as a "persistent" source of 2,3,7,8-TCDD over centuries!

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Dr. Gerd Rippen
Trischler und Partner GmbH
D-64203 Darmstadt, Germany

Z. JAWOROWSKI: Ancient Atmosphere – Validity of Ice Records ESPR 1 (3) 161 – 171 (1994)

It is with great hesitation that I write in reply to the paper by JAWOROWSKI; this paper deserves little attention. But unfortunately, he has succeded in publishing similar articles in journals and thus has induced considerable confusion regarding the reconstruction of ancient atmospheric compositions by the analysis of air occluded in polar ice of known age. We hope that this reply will help to clarify the issue. JAWOROWSKI is correct in one point. The glacier studies of ice cores are fundamental for one of the most important issues of the century and are of great importance for succeeding centuries.

I have been personally involved in the development of this field since its inception. In the early stages I was involved directly in experiments; later the experimental and analysis work was conducted by my collaborators and students. If in this article I speak of "we", I refer to the ice core team at the University of Bern. In the following I first give a short overwiev of the history of ice core research.

Although we knew since the nineteen fifties that human activities might change the climate of the Earth, it was not until the mid seventies we realised that mankind was faced with a serious problem. Using a new model for the exchange of CO_2 between atmosphere and ocean, we were able to consistently describe the uptake excess of CO_2 by the ocean, as well as the distribution in the ocean of ^{14}C produced by cosmic radiation, and ^{14}C stemming from nuclear weapon tests. We became convinced that, for the expected future anthropogenic CO_2 emission, the atmospheric CO_2 concentration would rise in a predictable manner. (In fact, using the estimated actual fossil CO_2 emissions as input, the CO_2 increase of the past 20 years corresponds to within 10 % of the predictions based on such models.) At that time an urgent question concerned the preindustrial atmospheric CO_2 concentration and the early history of the CO_2 increase, but also the question of whether the atmospheric CO_2 concentration of the preindustrial time was stable or whether there were also natural variations in CO_2 concentration.

The US-CO_2 programme was planned at an ERDA meeting in Miami in the late seventies. At that time we proposed a reconstruction of the CO_2 history by measuring the gases trapped in polar ice. This idea was met with a great deal of scepticism and we were aware that the changes for success were limited because of a wide spectrum of problems, including those which JAWOROWSKI describes in his paper. On the other hand, we were aware of the urgency of the greenhouse problem and concerned that the science community would fail to conduct the most relevant studies aimed at the assessment of the rising greenhouse effect.

The project to reconstruct the history of the grennhouse gases was conducted; it was, and is, very successful – much above expectation. The CO_2 concentrations measured on the SIPLE core, Antarctica, serve as a measure of that success. They illustrate (JAWOROWSKI, *Fig. 5 a, p. 168*) the history of atmospheric CO_2 increase since the middle of the 18th century. Another important result was the observation of low CO_2 concentrations of the gases extracted from ice-age ice. The low glacial CO_2 concentrations have been confirmed in ice cores with different physical and chemical properties both from Greenland and Antarctica and independently from ^{13}C measurements on carbonate of foraminifera shells in ocean cores and, yet again, more recently in moss samples.

Now to the paper of JAWOROWSKI: For years he emphasizes only the difficulties of these studies, formulates the underlying assumptions which

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sometimes are only partly fulfilled and criticizes the work performed hitherto in an unscrupolous manner. He does this without any appreciation for the development of expertise in this field over several decades. Thus he extrapolates from contamination problems in improvised pioneering experiments in the late sixties to more recent (1992) similar experiments on the Greenland ice cap for which special equipment was developed. Some of his statements are drastically wrong from the physical point of view, e.g. the statement that CO_2 at 70 m depth in the ice begins to change into solid clathrates. Another example concerns the gas-occlusion process in firn and young ice. This process has been studied in detail theoretically and experimentally. The theory of diffusion of gases in firn and the occlusion at the firn-ice transition has been confirmed impressively by the detection of a gravitational enrichment of the heavier gases and of the heavier isotopes of a gas. This enrichment depends, in the first instance, on the depth of the firn-ice transition. It enables the reconstruction of the history of gas enclosure depth during the last glacial-interglacial cycle. But JAWOROSKI maintains that the age of the ice and that of the occluded gases are the same and shifts the CO_2 increase revealed from studies of the SIPLE core *(→ Fig. 5 a)* – which in the uppermost part overlaps convincingly with the atmospheric measurements – by ca. 100 years back in time (assuming identical ages for the ice and the gases in the ice). Fig. 5 b speaks for itself; why should there be such a drastic increase of CO_2 and of CH_4 *(→ Fig. 5 a)* in the middle of the 19th century?

The teams of researchers involved in ice core studies have a high standing within the scientific community. The early increases of the greenhouse gases are used to initiative the models simulating climatic change and help to understand the source and sink problem related to the greenhouse gas increases of the last 150 years. The low glacial greenhouse concentrations are an essential boundary condition for climate modelling experiments of the Earth during a glacial period. The papers by JAWOROWSKY, and the one by HEYKE quoted in this paper, are not taken seriously by the science community. The problem with these publications is that a broader circle of persons interested in the Global Change issue will receive the impression that the assessment of the problem is partly based on doubtful information, that there are serious weaknesses in experimental procedures, that the whole Global Change problem does not need to be taken so seriously and that there is no urgency regarding the control of CO_2 emission. The time lost now is crucial for attempts to limit the anthropogenic climatic change to a range with more absorbable negative consequences.

The study of the history of Earth system parameters is an on-going process; an increasing number of laboratories have become involved and interact with each other. As it is the case in any field of science, the state of art is continuously critically assessed and attempts are made to improve the quality of the research. Ice-core information is fundamental for the assessment of one of the most urgent problems of our time. Based on my experience during decades of involvement in this field, I consider the changes as very small that the major findings from greenhouse gas studies on ice cores are fundamentally wrong; and I find the publications of JAWOROWSKI not only to be incorrect, but irresponsible.

Hans Oeschger, Ph. D.
Professor of Physics
Physical Institute
University of Bern
CH-3012 Bern, Switzerland

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Editor-in-chief
Otto Hutzinger, Ph. D.
Professor of Ecological Chemistry
University of Bayreuth
D-95440 Bayreuth, Germany
Phone +49-921-55 22 54
Fax +49-921-55 23 34

Executive editor
Mrs. Almut Heinrich
ecomed publishers
Rudolf-Diesel-Straße 3
D-86899 Landsberg, Germany
Phone +49-81 91-125 469
Fax +49-81 91-125 600

Subscription Service, Circulation, Advertising
Mrs. Luitgard Ruile
ecomed publishers
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