



Table 1:

Equations of radioactive decay, removal rates ( $\lambda_R$ ) and residence times ( $\tau_R$ )

## a) General

A = Activity = number of disintegrating atoms (N) per unit time

$$A = dN/dt = \lambda \cdot N \quad (\lambda \leftarrow \text{decay constant}) \quad (1)$$

$$N = N_0 \exp(-\lambda t) \text{ or } A = A_0 \exp(-\lambda t) \quad (2)$$

$$t_{1/2} = \ln 2 / \lambda \quad (= \text{half-life}) \text{ or } \tau = 1/\lambda \quad (= \text{residence time}) \quad (3)$$

$$\text{Age} = t = \ln(A_0/A) / \lambda \quad (4)$$

b) Parent-daughter relationships ( $N_P \xrightarrow{\lambda_P} N_D \xrightarrow{\lambda_D} E$ )

$$dN_D / dt = \lambda_P \cdot N_P - \lambda_D \cdot N_D \quad (5)$$

$$N_D = (\lambda_P \cdot N_P) (\exp(-\lambda_P \cdot t) - \exp(-\lambda_D \cdot t)) / (\lambda_D - \lambda_P) \quad (6)$$

## c) Radioactive decay and chemical removal from system (steady state)

Production from radioactive decay of parent nuclide =  
radioactive decay of daughter nuclide + removal of daughter nuclide (7a)

$$\lambda_D \cdot A_P = \lambda_D \cdot A_D + \lambda_R \cdot A_D = A_D (\lambda_R + \lambda_D) \quad (7b)$$

$$\tau_R = 1/\lambda_R = \tau_D \cdot A_D / (A_P - A_D) \quad (8)$$

Examples:  $^{228}\text{Th} / ^{228}\text{Ra}$ ,  $^{234}\text{Th} / ^{238}\text{U}$ ,  $^{230}\text{Th} / ^{238}\text{U}$ ,  $^{231}\text{Pa} / ^{235}\text{U}$ ,  $^{210}\text{Pb} / ^{222}\text{Rn}$ 

## d) Removal of cosmic ray produced isotope (constant flux, steady state)

$$\text{Input flux} = F_1 = \text{radioactive decay} + \text{removal flux} (= F_2) \quad (9a)$$

 $\Sigma A$  = integrated activity in water column

$$F_1 = (\lambda_D \cdot \Sigma A_D) + (\lambda_R \cdot \Sigma A_D) \quad (9b)$$

$$\tau_R = \tau_D (F_1 - F_2) / F_2 \quad (10)$$

Example:  $^7\text{Be}$ 

Table 2: Example of radioisotopes used in aquatic sciences as tracers for processes with time scales of days to centuries

Radioisotopes produced by:	Tracer for:				
	Dating of Groundwater	Mixing of surface waters	Particle transport	Gas exchange	Biological Activity
U / Th decay		$^{222}\text{Rn}/^{226}\text{Ra}$ $^{226}\text{Ra}$ , ( $^{224}\text{Ra}$ )	$^{234}\text{Th}/^{238}\text{U}$ $^{228}\text{Th}/^{228}\text{Ra}$ $^{230}\text{Th}/^{234}\text{U}$ $^{210}\text{Pb}/^{222}\text{Rn}$ $^{231}\text{Pa}/^{235}\text{U}$	$^{222}\text{Rn}/^{226}\text{Ra}$	
Cosmic Radiation	$^3\text{H}$ , $^{14}\text{C}$ , $^{39}\text{Ar}$ ( $^{85}\text{Kr}$ ), $^{32}\text{Si}$	( $^3\text{H}/^3\text{He}$ ), ( $^{14}\text{C}$ ), $^{39}\text{Ar}$ , ( $^{85}\text{Kr}$ ), ( $^7\text{Be}$ )	$^7\text{Be}$	$^{39}\text{Ar}$	
Atomic Bomb Tests	$^3\text{H}$ , $^{14}\text{C}$	$^3\text{H}$ , $^{14}\text{C}$ , $^{90}\text{Sr}$ , $^{137}\text{Cs}$	$^{55}\text{Fe}$ , ( $^{137}\text{Cs}$ ), $^{144}\text{Ce}$ $^{241}\text{Am}$ , $^{239}$ , $^{240}\text{Pu}$	$^3\text{H}/^3\text{He}$ , $^{14}\text{C}$	
Reactors and Accelerators (artificially produced isotopes)	$^3\text{H}$ , $^{85}\text{Kr}$	$^3\text{H}$ , $^{22}\text{Na}$	$^{54}\text{Mn}$ , $^{59}\text{Fe}$ , $^{60}\text{Co}$ , $^{65}\text{Zn}$ , $^{113}\text{Sn}$ , $^{228}\text{Th}$ , ( $^{134}\text{Cs}$ )	$^{85}\text{Kr}$	$^{14}\text{C}$ , $^{32}\text{P}$ , ( $^{33}\text{P}$ )

( ) = isotopes set in brackets cannot generally be used, but are potentially useful.

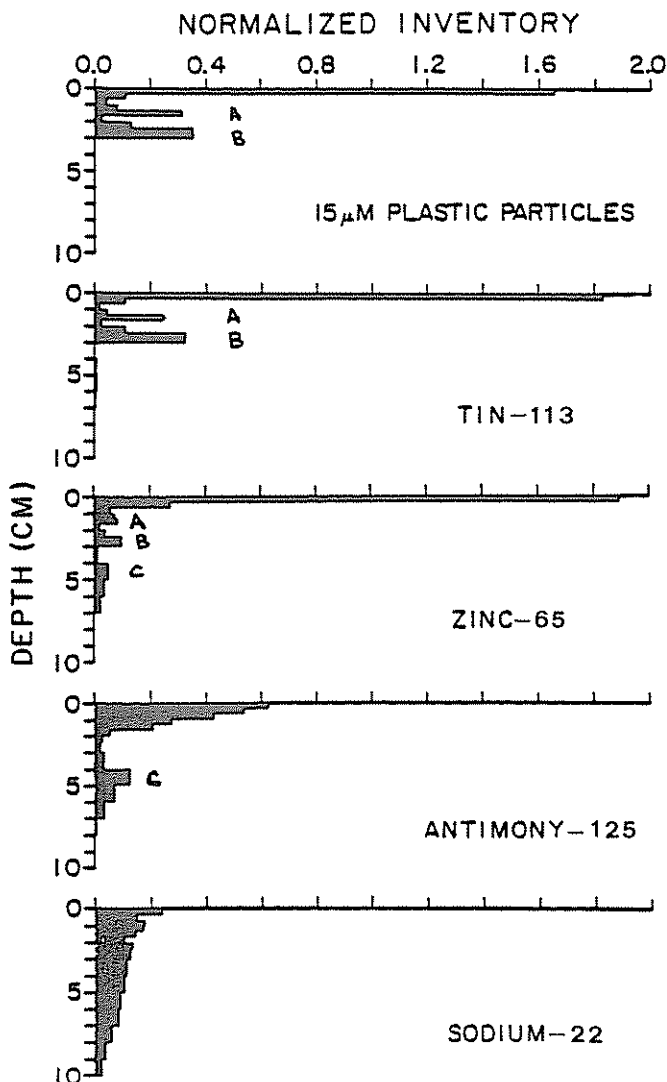


Figure 2:

Comparison of radionuclide profiles in marine sediments obtained from field or enclosure studies

a) This profile of natural ( $^{210}\text{Pb}_{xs}$  and  $^{234}\text{Th}_{xs}$  in dpm/g\*) and fallout radioisotopes ( $^{239, 240}\text{Pu}$  in 10 dpm/g) in a sediment core from the New York Bight, USA [1], shows the particle-associated radionuclide  $^{239, 240}\text{Pu}$  penetrating as deep as 30 cm where activities of excess  $^{210}\text{Pb}$  (=  $^{210}\text{Pb}$ - $^{226}\text{Ra}$ ) become insignificant. This indicates that benthic mixing caused by bioturbating benthic macrofauna is the primary cause for the penetration of these nuclides into the surface sediments. A numerical 3-layer mixing and sedimentation model can explain simultaneously the penetration of all 3 tracers which have either different half lives ( $t_{1/2}$ ) or times ( $\Delta t$ ) since addition to sediments ( $^{234}\text{Th}$ :  $t_{1/2} = 24$  days, is continuously produced by  $^{238}\text{U}$  decay in the water column and rapidly removed to sediments;  $^{210}\text{Pb}$ :  $t_{1/2} = 22$  years, supplied to the sediments by particles which continuously scavenge  $^{210}\text{Pb}$  originating from the decay of atmospheric  $^{222}\text{Rn}$ ;  $^{239, 240}\text{Pu}$ :  $\Delta t \sim 16$  years.) These coastal sediments thus acquire trace elements not mainly by sedimentation but by a combination of sediment resuspension and benthic mixing, which brings more adsorbing sediment surfaces into contact with the overlying water column.

\* xs = excess; dpm = disintegrations per minute

b) Radionuclide profiles in a sediment core from the MERL tank ecosystem, taken by Adler [14] 46 days after the addition of the radiotracers to the well mixed water column. Net sedimentation is low, and the particle pathways are primarily resuspension of surface sediment and benthic mixing. Different mobilities of radionuclides in the sediments are due to the presence of bioturbating benthic macrofauna, which mix sediment particles and pore waters differently in time and space. Over longer time scales the erratic mixing events should become more regular in space and time and become more amenable to eddydiffusional modelling.

by the radioactive decay of the atomic nucleus, which is independent of chemical and physical state, and independent of temperature and pressure. The age dating, evaluation of residence times and exchange rates (e.g. rates of adsorption, particle settling, sediment resuspension, mixing and accumulation, gas exchange, water mixing, etc.), are the primary applications of natural and fallout radionuclides (table 2). Fig. 1 exemplifies the processes of an aquatic ecosystem which are amenable to characterisation by radiotracers. In fig. 2a, natural and fallout radionuclides are shown to yield not only information on the influence of benthic mixing on the dating of sediments, but also on the mechanism of accumulation of trace elements in these sediments.

## 2. Artificial radionuclides: the need of enclosed experimental ecosystems

Not all processes in aquatic ecosystems can be studied equally well using as tracers those "natural" radioisotopes mentioned before. Often, it is desirable to use artificial radioisotopes, tailored specifically to the investigation of a certain chemical or biological process in an aquatic ecosystem. Yet, only rarely can artificial radionuclides be directly used to study these processes in the natural aquatic environment. In most cases, one needs an enclosed experimental ecosystem, which is replicating the natural system to a high degree. Such systems are also called "microcosms", "mesocosms", "limnocoralls", or simply: tanks, tubes, bags, bell-jars or aquaria. Such enclosures have been used by biologists

since several decades. However, only during the last decade or so have chemical limnologists and oceanographers made good use of such systems. The cooperative studies of heavy metal transport and effects inside the MELIMEX "limnocoralls" in Lake Baldegg, carried out by scientists of EAWAG (e.g. [2] and references therein) have to be mentioned here. Another example are the MERL mesocosms on the shores of Narragansett Bay, R.I., U.S.A. [3]. In these 12-14 tanks, studies of oil pollution, recovery of polluted marine sediments, and most recently, of eutrophication of coastal marine ecosystems have been carried out successfully in the last 7 years (e.g. articles [4,5] and references therein, and [6-8]). In this latter system, radiotracers have been utilized extensively to elucidate a number of transfer mechanisms and rates in this coastal marine ecosystem (e.g. [9-13]).

In experiments in controlled ecosystems, one only utilizes the tracer properties of the radionuclides, which are given by the easy means of detection of the gamma-ray emitting nuclides. The time parameter lies in the time course of the experiment itself.

The radiotracers in the controlled experimental ecosystem make it possible to identify the transport agent, the important reservoirs for the transport of a particular chemical substance and the determination of the rate limiting processes and its rate constant. Examples are given in table 2 and fig. 2b, 3a, 3b. In addition, the characterization of the biological activity (e.g.: primary production, respiration, accumulation or exchange of nutrients, trace metals or food

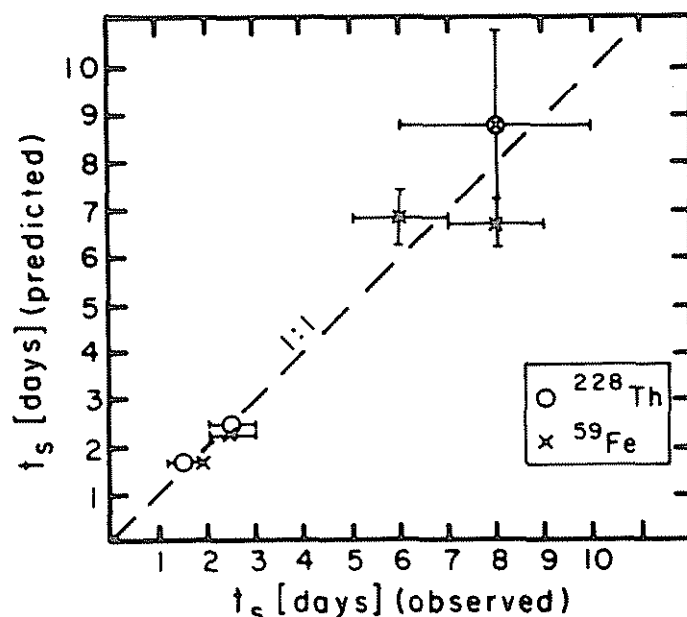
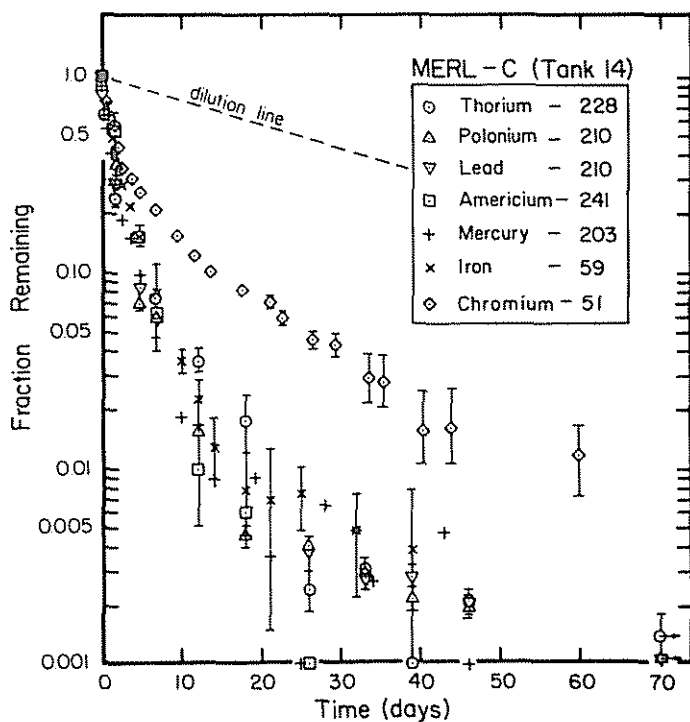


Figure 3:

Th as an analogue for removal of particle-reactive substances from aquatic ecosystems

a) Activities of Th, Po, Pb, Am, Hg, Fe and Cr isotopes in unfiltered water samples versus time in a MERL tank ecosystem (5 m deep, 13 m<sup>3</sup>, 30 cm sediments) during summer 1978 [12]: Initially, the isotopes are removed with half removal times of approximately 2 days caused by the adsorption onto falling particles. Later in the experiment, removal is controlled by the simultaneous action of resuspension and benthic mixing (bioturbation) of surface sediments. The slower removal of Cr after 3 days is due to oxidation of Cr(III) to Cr(VI). This figure then demonstrates that the above mentioned isotopes are removed at similar rates by the same mechanism. Th can thus serve as a suitable analogue for these particle-reactive pollutant trace metals in marine ecosystems.

b) The measured initial half-removal time  $t_s$  for <sup>228</sup>Th in the MERL tanks is plotted versus the predicted  $t_s$  from <sup>234</sup>Th/<sup>230</sup>U disequilibria in Narragansett Bay, R.I. This figure demonstrates that removal processes inside these model ecosystems are occurring at similar rates as in the natural ecosystem [12, 13].

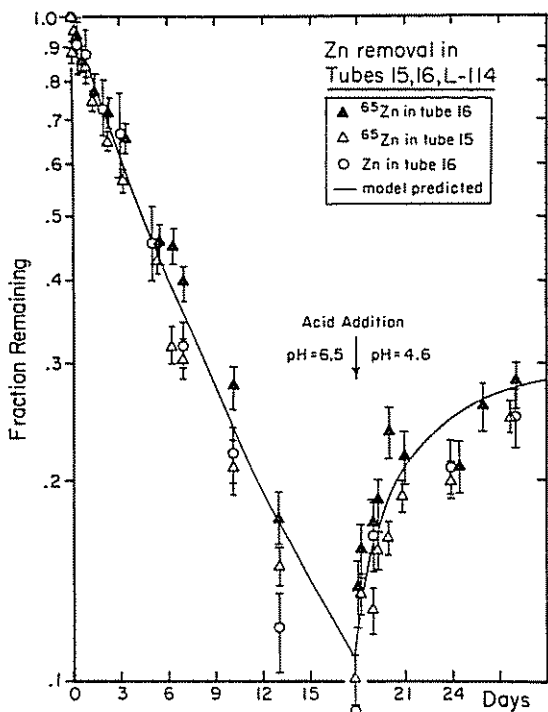


Figure 4:

Artificial radionuclides as analogues for the behaviour of stable elements in aquatic ecosystems

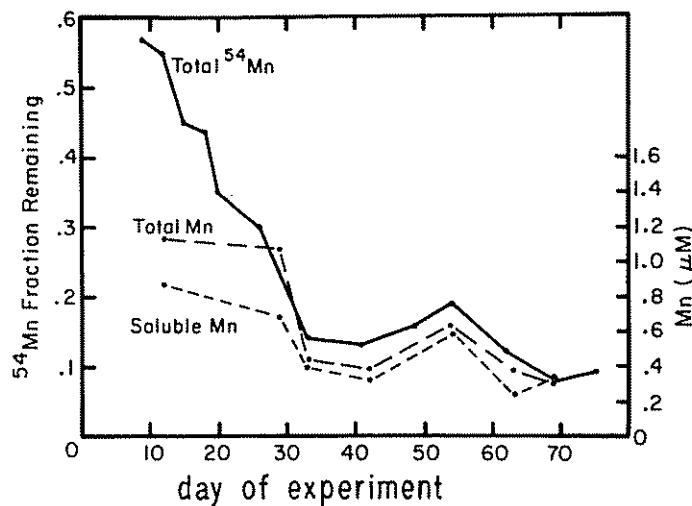
a)  $^{65}\text{Zn}$  and stable Zn, which were added initially at  $10^{-13}$  and  $10^{-6}\text{M}$  (tube 16), respectively, are removed from the water column of 1 m deep and 1m wide tubes in ELA-lake 114 (Northern Ontario, Canada) at similar rates, indicating that  $^{65}\text{Zn}$  is a reasonable analogue of stable Zn over a concentration range of 1–2 orders of magnitude [15]. Note that tube 15 has ambient concentrations of Zn (i.e.  $\leq 10^{-7}\text{M}$ ). The removal and backdiffusion of Zn (after HCl addition to  $\text{pH}=4.6$ ) can be predicted reasonably well by a numerical transport model and using measured parameters of distribution coefficients, particle flux, diffusive sublayer thickness and benthic mixing rates.

particles of planktonic or benthic organisms, etc.), the kinetics of the partitioning of elements into different soluble or particulate chemical forms, and sediment-water-air exchange processes are facilitated by using radiotracers.

**3. Radiotracer mobility and behaviour of stable elements**

Can the observed mobility of a radiotracer in the environment be used to learn about the behaviour of stable chemical substances? The answer to this question could be yes and no. First, any fractionation effects during chemical reactions have to be negligible. This is usually the case for isotopes with atomic weights larger than 10. Second, chemical forms of radioactive and stable isotopes have to be similar. This is strictly only true if both isotopes are introduced in similar ways to the environment. Often, however, an equilibration with the principal phases lasting long enough is sufficient.

Some of the natural radionuclides originating from the U/Th decay series or cosmic radiation can directly act as analogues for the stable element under natural conditions, e.g.  $^{210}\text{Pb}$  for  $^{207}\text{Pb}$  (or  $^7\text{Be}$  for  $^9\text{Be}$ , or  $^{14}\text{CO}_2$  for  $^{12}\text{CO}_2$ ). Since they are introduced differently into the atmosphere and hydrosphere (e.g. Pb, mostly as Pb-halides and -sulfates from automobile exhausts,  $^{210}\text{Pb}$  produced by the decay of  $^{222}\text{Rn}$  in air and water), their distribution in the aquatic environment is similar but often not exactly the same. Another example are Th-nuclides, which do not have a stable isotope but which have been shown to act as analogues for a number of other "particle-reactive" elements in marine ecosystems [12]. This behaviour is further illustrated in Fig. 3.



b) A comparison of  $^{54}\text{Mn}$  activity and stable Mn concentrations of natural levels in the water column of a MERL tank is shown [10]. After 30 days  $^{54}\text{Mn}$  has reached a quasi-steady state with respect to removal and backdiffusion, with a concentration curve similar to that of stable Mn.

Some artificial radionuclides can also act as analogues for their stable elements under natural conditions, if care is taken to introduce the radiotracer in the predominant chemical form of the stable element. A comparison of  $^{65}\text{Zn}$  and Zn removal is given in fig. 4a.

However, the short-term behaviour of the radioactive isotope might not reveal the long term fate of the stable element. Radioactive and stable Fe would be a good example here. The slow aging processes of the amorphous Fe-oxhydroxides would not allow a rapid equilibration. If the observation time becomes comparable to the cycling time in the entire ecosystem, as is the case for  $^{54}\text{Mn}$  and Mn inside a MERL tank (fig. 4b), then both the radioactive and the stable element do acts similarly in a water column, even when in contact with sediments.

The mobility behaviour of a radionuclide under one set of environmental circumstances has then to be seen in the context of a thorough characterisation of the chemical properties of that system. Only then may we extrapolate the behaviour of the radioisotope to that of its stable element. The general applicability of results from radiochemical investigations depends thus heavily on a cooperative effort of physicists, chemists, biologists and geologists characterizing independently the same ecosystem.

Even though the examples given here are mostly taken from the experimental work carried out by the author and his colleagues in various projects in the U.S.A. and Canada, many of the techniques mentioned and questions raised here can also be relevant to EAWAG for the investigation of the mobility of pollutants in Swiss water ways and reservoirs.

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## Acid Precipitation and its Influence on Swiss Lakes

Jerald L. Schnoor, Laura Sigg, Werner Stumm, Jürg Zobrist

Even Swiss rain water is acid. Precipitation contains traces (mg/l) of sulfuric acid, nitric acid, heavy metals, and organic pollutants. As Zobrist and Stumm [1] have shown, based on routine analysis of precipitation, performed regularly by the EAWAG (Hydrologic Yearbook of Switzerland), Swiss rain water typically contains about 40–50 microequivalents per liter of acidity (free H<sup>+</sup> ions), with the exception of Alpine regions. Thus the pH in rain water is presently about 4.3. A pure water sample which is in equilibrium with atmospheric CO<sub>2</sub> would contain approximately 20 times less hydrogen ions (pH ~ 5.6).

### Genesis of Acid Precipitation

Most of the major and minor gaseous components of the atmosphere (O<sub>2</sub>, N<sub>2</sub>, CO<sub>2</sub>, CO, NO, NO<sub>2</sub>, SO<sub>2</sub>, CH<sub>4</sub>) participate in elemental cycles which are governed by oxidation-reduction reactions of biological origin—photosynthesis and respiration are major reactions in this cycle. These oxidation and reduction reactions both consume and produce the gases of the atmospheric reservoir, and steady-state concentrations are established over a period of millions of years for each component.

The atmosphere is more susceptible to anthropogenic emissions than the terrestrial or the aqueous environment because, from a quantitative point of view, the atmosphere is much smaller than the other reservoirs. Furthermore the time constants concerning atmospheric alterations are small in comparison to those of the seas and the lithosphere. When the rate of oxidation of carbon, nitrogen, and sulfur increases relative to the rate of reduction of CO<sub>2</sub>, nitrogen, oxides, SO<sub>2</sub> and H<sub>2</sub>SO<sub>4</sub> (which is caused by the activities of

civilization during the fossil fuel age), then the delicate balance is disturbed (Table 1). Accordingly, the concentration of CO<sub>2</sub> has increased globally, and the concentrations of SO<sub>2</sub>, H<sub>2</sub>SO<sub>4</sub>, NO, NO<sub>2</sub>, HNO<sub>2</sub> and HNO<sub>3</sub> have increased regionally. Buffering of these interactions in other reservoirs is very long. For example, the mixing time of the ocean is on the order of 1000 years.

In oxidation-reduction reactions, electron transfers (e<sup>-</sup>) are coupled with the transfer of protons (H<sup>+</sup>) to maintain a charge balance. A modification of the redox balance corresponds to a modification of the acid-base balance. Consequently, the potential acidity of the atmosphere increases vis-à-vis the bases (Figure 1, upper part). Resulting from the oxidation of sulfur and nitrogen in the atmosphere, the strong acids H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> are generated and are the main participants in the formation of acid rain. As H<sub>2</sub>CO<sub>3</sub> is a weak acid, the increase in the CO<sub>2</sub>-acidity over the last 100 years has an insignificant effect on the composition of precipitation.

A considerable part of the strong acids originate from the oxidation of sulfur in the combustion of fossil fuels and the "fixation" of nitrogen from the atmosphere to NO and NO<sub>2</sub> (during the combustion of gasoline in motor vehicles or other combustion processes of sufficiently high temperature). HCl results from the combustion and decomposition of organochlorine compounds, for example, in polyvinyl chloride plastics during incineration. But it should also be mentioned that there exist natural sources, resulting from volcanic activity and the oxidation of hydrogen sulfide from anaerobic sediments as well as dimethyl sulfide and OCS originating from the ocean. Bases originate in the atmo-

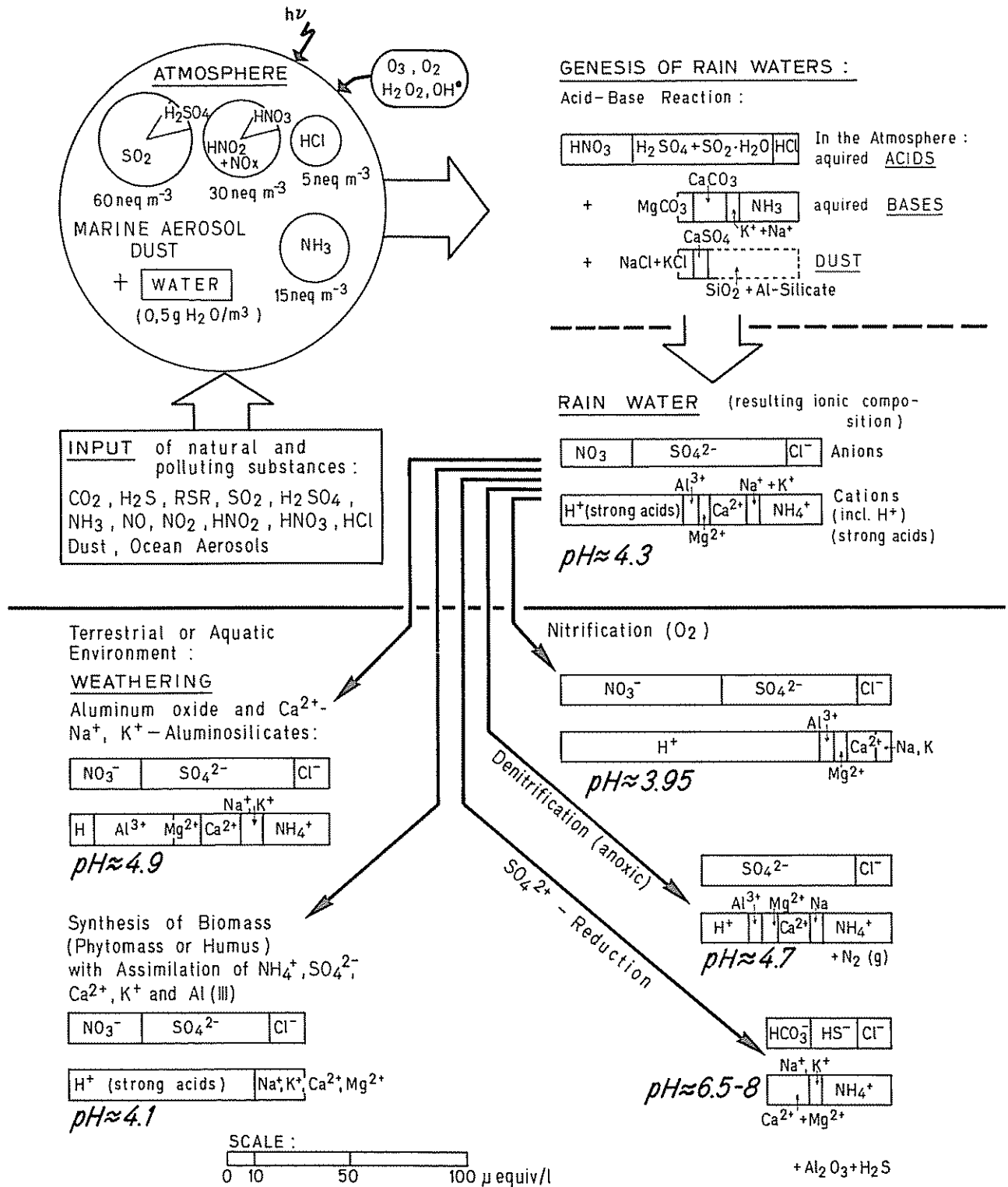


Figure 1

**Genesis of acid rain (from [2])**

From the oxidation of S and N during the combustion of fossil fuels, there is a build-up in the atmosphere (in the gas phase, aerosol particles, rain drops, snow flakes and fog) of  $CO_2$  and the oxides of S and N, which leads to acid-base interaction. The importance of absorption of gases into the various phases of gas, aerosol, and atmospheric water depends on a number of factors. (In this figure, we assume a yield of 50% for  $SO_4^{2-}$  and  $NO_3^-$ , of 80% for  $NH_3$  and of 100% for  $HCl$ .) The genesis of acid rain is shown on the upper right as an acid-base titration. Various interactions with the terrestrial and aquatic environment (see Table 1) are shown in the lower part of the figure.

Table 1: Processes which modify the H<sup>+</sup>-Balance in Waters [2]

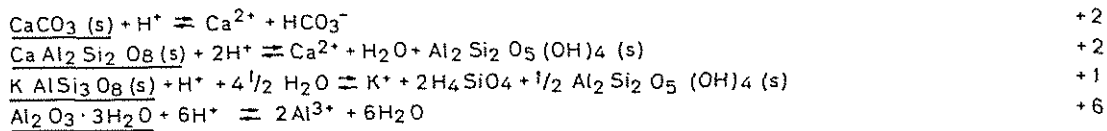
\* Alk = alkalinity = acid neutralizing capacity  
 H-Acy = Mineral acidity.

In the build-up of biomass (or the exchange of ions) the uptake of each equivalent of anions causes an equivalent increase in alkalinity, and each equivalent of cations which is taken up results in an equivalent decrease of alkalinity. One comes to the same conclusion as long as the biomass or humus is formed of neutral components  $\{(CH_2O)_a(NH_3)_b(H_3PO_4)_c(H_2SO_4)_d \dots (Ca(OH)_2)_g (Mg(OH)_2)_h (KOH)_i (NaOH)_l (H_2O)_m\}$  and provided that one has written the corresponding stoichiometric equations for formation and decomposition.

$$\Delta [Alk] = - \Delta [H-Acy]$$

Equivalents per mole reacted (reactant is underlined)\*

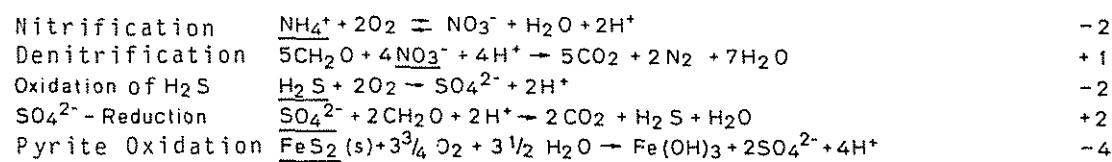
1a) Weathering Reactions



1b) Ion Exchange

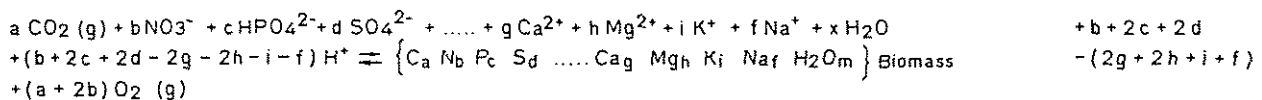


2) Redox Processes (Microbial Mediation)

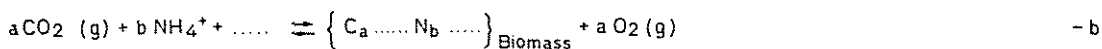


3) Synthesis (→) and Decomposition (←) of Biomass and of Humus

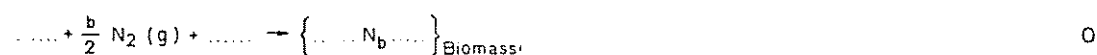
Photosynthesis with NO<sub>3</sub>-Assimilation (→), Aerobic Respiration (←)



NH<sub>4</sub>-Assimilation (→); Anaerobic Mineralization (back reaction)



N<sub>2</sub>-Fixation (half-reaction)



sphere as the carbonates of wind-blown dust and from ammonia, generally of natural origin. The  $\text{NH}_3$  originates from  $\text{NH}_4^+$  ions and from the decomposition of urea found in soil environments. Redox and acid-base reactions occur in the gas phase, in aerosols, in rain drops, cloud droplets and fog. The reactions for oxidation of  $\text{SO}_2$  in the atmosphere yield a sulfur residence time of several days at the very most; this corresponds to a transport distance of hundreds to a thousand kilometers. The formation of  $\text{HNO}_3$  by oxidation is more rapid, and compared to  $\text{H}_2\text{SO}_4$ , this results in a shorter travel distance from the emission source.  $\text{H}_2\text{SO}_4$  can also react with  $\text{NH}_3$  to form  $\text{NH}_4\text{HSO}_4$  or  $(\text{NH}_4)_2\text{SO}_4$  aerosols. In addition, the  $\text{NH}_4\text{NO}_3$  aerosols are in equilibrium with  $\text{NH}_3(\text{g})$  and  $\text{HNO}_3(\text{g})$ . The importance of gas and aerosol scavenging by atmospheric condensates and rain drops depends on many factors.

### Interaction with the environment

The chemical or ecological effect of acid rain depends directly on the concentration of  $\text{H}^+$  ions (or more precisely on their activity). Thus the solubility of dust mixed with rain, the dissolution of minerals (weathering rate), the release of cations by the soil (ion exchange), and the effects on biological processes are all influenced by the pH. The pH can also have an indirect effect because it determines the chemical speciation of solutes. For example, the proportion of free metal ions increases as the pH decreases, due to less complexation of metals with other inorganic and organic ligands (e.g.  $\text{OH}^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{RCOO}^-$ ) or due to decreased complexation at solid surfaces. Thus one supposes that the ecological effects of acid waters on vegetation or the toxic effects on fish or the failure of reproduction of fish are due, in large part, to an increased concentration of metal ions, especially  $\text{Al}^{3+}$ . Even more important for the trees and the plants is the direct absorption of  $\text{SO}_2(\text{g})$ .

After the deposition of acid precipitation, the minerals and the aquatic and terrestrial ecosystems modify the pH, i.e. the acidity and alkalinity of the rain water. The interactions with rocks can be represented, as a first approximation, as acid titration of bases in the rocks ( $\text{CO}_3^{2-}$ , oxides, silicates). The reactions with carbonates (limestone and dolomite) is very rapid, but with oxides (e.g. aluminium oxide) and aluminosilicates, it is not so rapid. In non-calcareous soils,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  are less available for dissolution, and thus the release of  $\text{Al}^{3+}$  occurs (fig. 1, lower part). The terrestrial and aquatic ecosystems are able to buffer and mitigate the effects of acid rain to some extent. On the other hand, biologically induced processes may even increase the acidity of rain wa-

ters. In principle, acidic surface waters can result without acid rain [2] (see Table 1).

Every temporal or spatial decoupling of the production and mineralisation of biomass leads to a modification of the  $\text{H}^+$  balance in the environment. This is a result of intensive agricultural and forestry practices and of seasonal fluctuations. The production of biomass (plants, phytoplankton, and humus) through the fixation of  $\text{CO}_2$ , the assimilation of  $\text{NH}_4^+$ , and the uptake of  $\text{Ca}^{2+}$  and  $\text{K}^+$ , all together lead to the subsequent acidification of water and soil. The absorption of more cations than anions must be compensated by the absorption of  $\text{OH}^-$  or the loss of  $\text{H}^+$  to the environment. This leads to leaching of cations from the soil and to podsolization. Humus and peat can likewise become very acid and deliver some humic acids to the water.

### Acid Lakes in the Tessin Mountains

Although the concentration of free acidity in Swiss rain has approached that of Scandinavia, the consequences of acid rain have been minimal compared to those of Scandinavia and North America, because the soils and sediments contain relatively great amounts of carbonates (predominantly in calcareous soil) which provide rapid neutralization of excess acids. This is not the case for some lakes in non-calcareous mountainous regions. South of the Alps, there is an area of mountain lakes situated essentially in the vicinity of the watersheds of the Maggialtal in the Verzasca Valley where one finds exclusively crystalline rock. In chemical weathering of these crystalline rocks (granite, gneiss, and mica schist), i.e. the reaction of free acidity with the bases of the rocks is much slower than the dissolution of carbonates. Therefore, there are acid lakes in this area although precipitation analyses by the EAWAG show that the precipitation is not as acid as in the lowlands of Switzerland. Such lakes are acid when the residence time of acid rain or snowmelt in soils and the watershed is relatively short. Since the soils in question are very thin with exposed and weathered rocks and only little fine material available, the water has little time to react with the minerals. Also, any buffering effect of trees or thick vegetation is lacking at these altitudes. As analyses by the Office of Water Protection of the Canton of Tessin have shown [3], there are 20 small lakes in the mountains with pH values less than 6 (10 lakes have pH less than 5.5; the lowest pH measured was 4.6). In a first approximation, acidity is highest in those lakes with very small surface and catchment areas and the shortest residence times in the watershed. If the lakes receive runoff and snowmelt water very rapidly, then the acidity of its water is not greatly different from that of the snow.

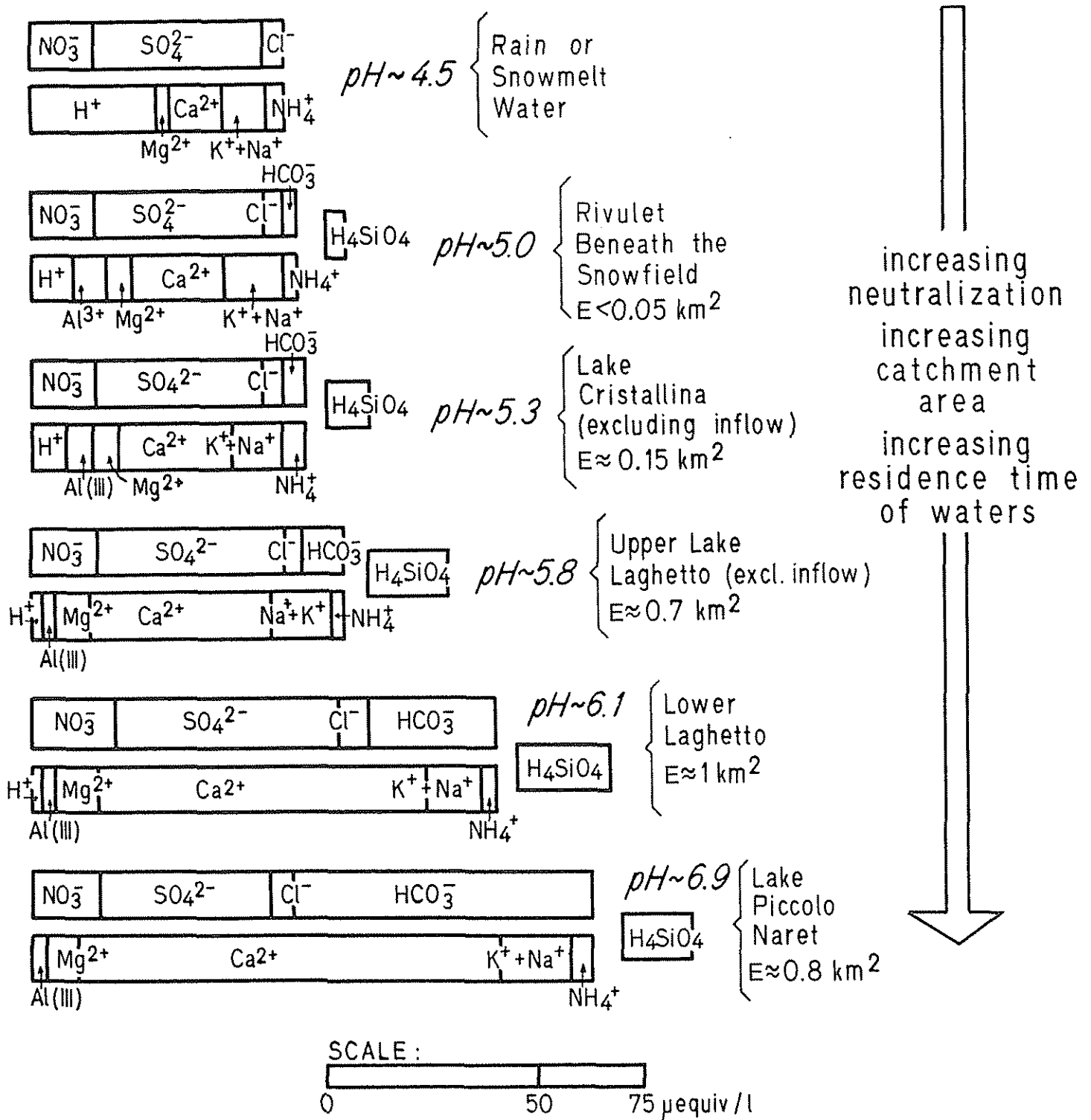


Figure 2:

Chemical composition of several waters in a drainage pattern in the area of the upper Maggia valley (in the vicinity of the Naret dam, at 2100-2500 m)

The extent of acid neutralization of rain or snowmelt water (chemical weathering) increases with the relative catchment area,  $E$ , and thus the residence time of the waters.

This neutralization is accompanied by increases in pH, silicic acid concentration ( $\text{H}_4\text{SiO}_4$ ), and by the liberation of cations from dissolution. Because of hydrologic changes from snowmelt, there are seasonal variations. This figure gives the condition from measurement at the of end July, 1982.

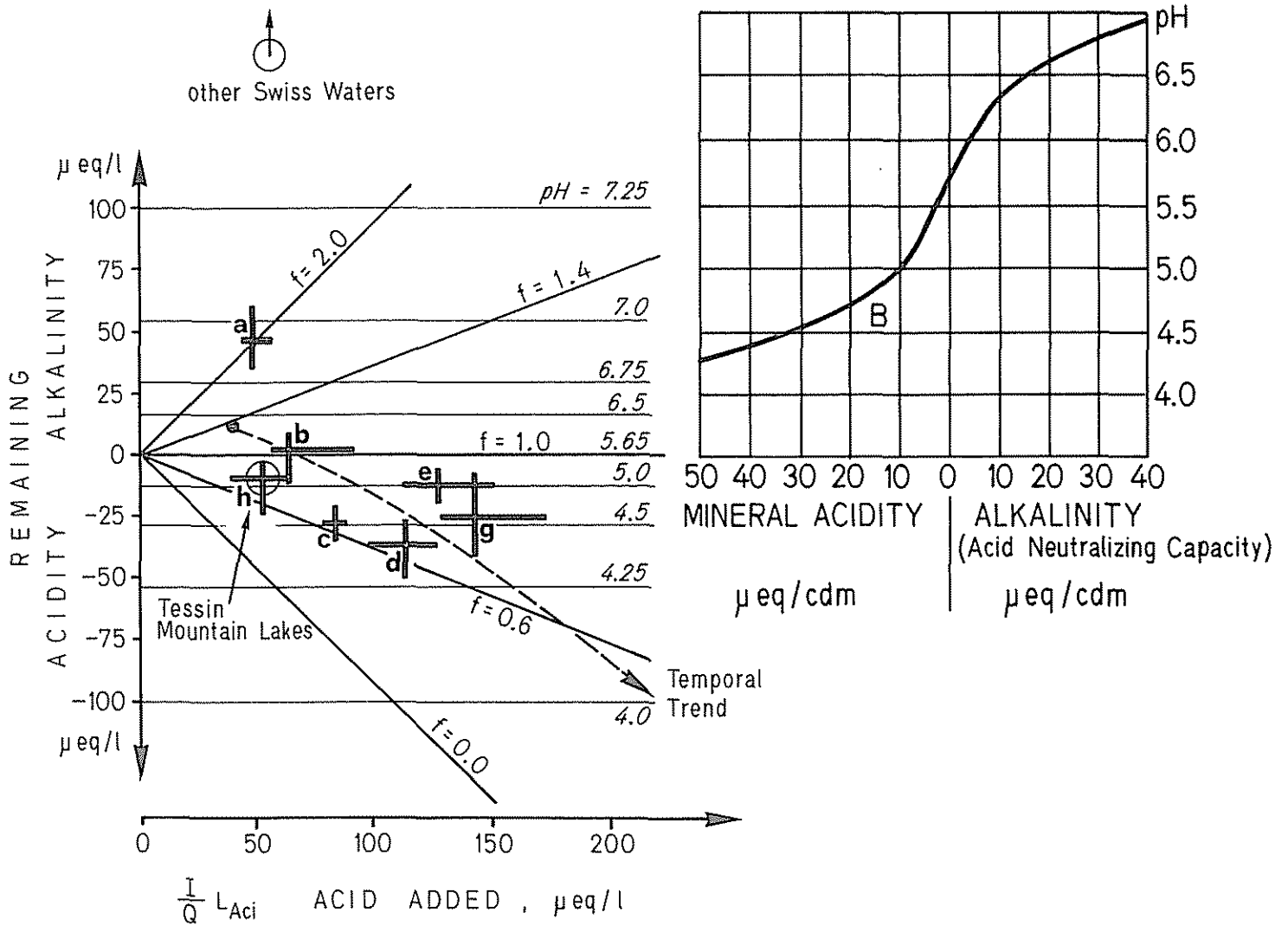


Figure 3:  
Alkalinity of natural waters as a function of Acid Loading (modified from [5]).

The acid deposition in the drainage area of lakes is neutralized by chemical weathering (the reaction with bases contained in rocks and minerals).  $f$  is the equivalents of acid neutralized by weathering ( $f = 0$  signifies no neutralization;  $f = 1$  corresponds to a perfect buffer;  $f > 1$  signifies an alkalization of the water, for example the dissolution of  $\text{CaCO}_3$  by  $\text{CO}_2$ ).

The difference between the acidity added and the resulting alkalinity corresponds to the degree of neutralization. Each lake would fol-

low a titration curve (similar to the one on the upper right) with progressive acid loadings. The dashed line represents the temporal trend or reaction pathway as more acid is added to the system. It corresponds to the titration curve.

a and b are lakes in Minnesota and Wisconsin (USA); c represents the Birkenes stream and two other lakes in southern Norway; d signifies 5 lakes in southwest Sweden; e are waters in New York and New Hampshire (USA); g represents 6 lakes in the La Cloche Mountains of southern Ontario, Canada; h indicates the Swiss Lakes in the upper Maggia valley of Tessin (in comparison to lowland Swiss lakes which have an alkalinity of more than 1000 eq/l).

Some typical waters in the Maggia Valley are schematically shown in fig. 2. It illustrates the successive reactions and neutralization of the source water as it flows; the concentration of cations ( $\text{Al}^{3+}$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^+$  and  $\text{Na}^+$ ) and silicic acid increases as the dissolution process occurs [4].

The concentration of free aluminum can only increase to the solubility of aluminum oxide: the lower the pH, the higher is the  $\text{Al}^{3+}$  concentration. Fish cannot reproduce in acid lakes; this is probably due to the high concentrations of the  $\text{Al}^{3+}$  and eventually also the concentrations of other heavy metals and free hydrogen ions rather than to the concentration of free acids. For the most part, the lakes are by no means sterile. But the supply of nutrients is extremely small—the water contains less than 5  $\mu\text{g}$  per liter—and thus the productivity is small too. The rate of chemical weathering in the watersheds of these lakes can be calculated on the basis of the

difference between precipitation acidity and that remaining in the lake; it amounts to 500 eq  $\text{ha}^{-1} \text{yr}^{-1}$  and is only about half of the rate of chemical weathering of aluminosilicate minerals in the alpine valley of the Rhine [6].

From a comparison of acid lakes in the mountains of Tessin with other acid lakes in Scandinavia and North America (fig. 3) [5], it seems that the Tessin lakes only recently ceased to be able to compensate for an increasing acid loading (5–10 years ago). The analysis of similar lakes by H. Marrer some ten years ago appears to confirm the decreasing trend in the pH of these Tessin mountain lakes. It is feared that the acidity of precipitation will continue to increase. If the concentration of  $\text{H}^+$  ions in precipitation were to double, the majority of lakes situated in the crystalline rock regions will probably have pH values of less than 5 [4].

## Early Warning Systems of Nature

The atmosphere is not only an important vehicle for the deposition of acid pollutants but also for a number of other substances which affect ecological systems, both aquatic and terrestrial. Atmospheric deposition accounts for about  $100 \text{ g ha}^{-1} \text{ yr}^{-1}$  of polyaromatic hydrocarbons in rural environments.

In populated regions, rain waters contain concentrations of heavy metals considered excessive for surface waters. Atmospheric deposition of heavy metals to Lake Constance

results in concentrations which are two orders of magnitude higher than those in the oceans. Acid lakes and crippled trees, therefore, are indicators of atmospheric pollution. They represent a warning system for anthropogenic perturbations of important hydrogeochemical cycles.

*Acknowledgement:* We thank Mr. J. Righetti of Dipartimento dell'ambiente, Sezione protezione acqua e aria, 6500 Bellinzona, for his help and valuable suggestions.

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## Denitrification by Methane-utilizing mixed Bacterial Cultures

Geoffrey Hamer and Klaus Mechsner

### Introduction

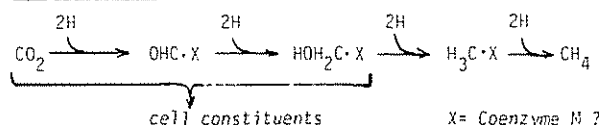
In aquatic and terrestrial environments the overall order of magnitude of *anaerobic production processes for methane (methanogenesis)* and that of *aerobic utilization processes for methane (methanotrophy)* can be predicted to be similar as only a small proportion of the methane produced by methanogenesis escapes to the atmosphere.

The processes provide two important stages in the global carbon cycle. The major elemental cycles are, of course, linked at many points but here only one aspect of linking between the methanotrophic stage of the carbon cycle and the nitrogen cycle will be discussed.

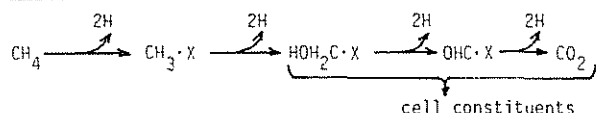
Methane, produced as a result of the degradation and mineralization of complex organic matter under anaerobic conditions (equation 1), is ubiquitous in both aquatic and terrestrial environments, and not unexpectedly, methane-oxidizing bacteria are widely distributed in such environments. *Methane-oxidizing* or methanotrophic bacteria are strictly aerobic and most species are obligate, being able to grow only on methane and a restricted number of single carbon atom compounds derived from methane, as carbon energy substrates (equation 2). Traditional techniques employed for the enumeration, enrichment and isolation of microorga-

### Equations

1) METHANOGENESIS (a strictly anaerobic process)

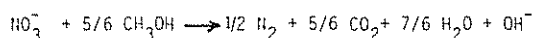


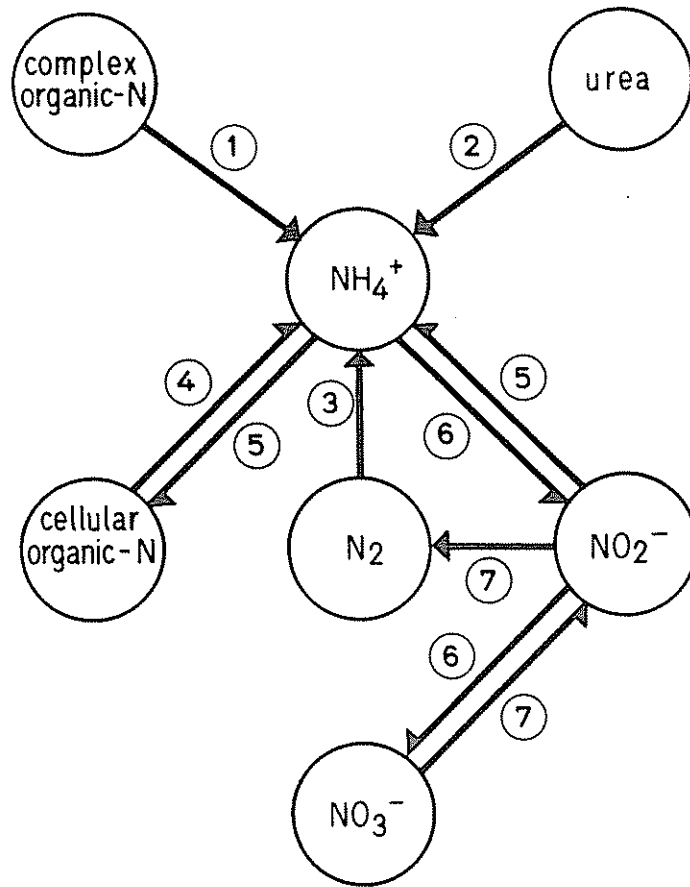
2) METHANOTROPHY AND METHYLOTROPHY (aerobic processes)



X =  $\cdot\text{OH}$ , and/or a pteridine derivative, and/or a folate, and/or glutathione

3) DENITRIFICATION WITH METHANOL

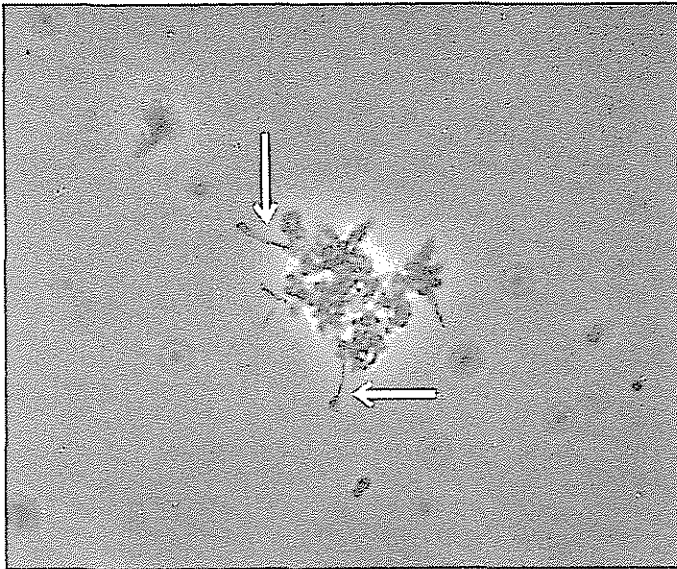




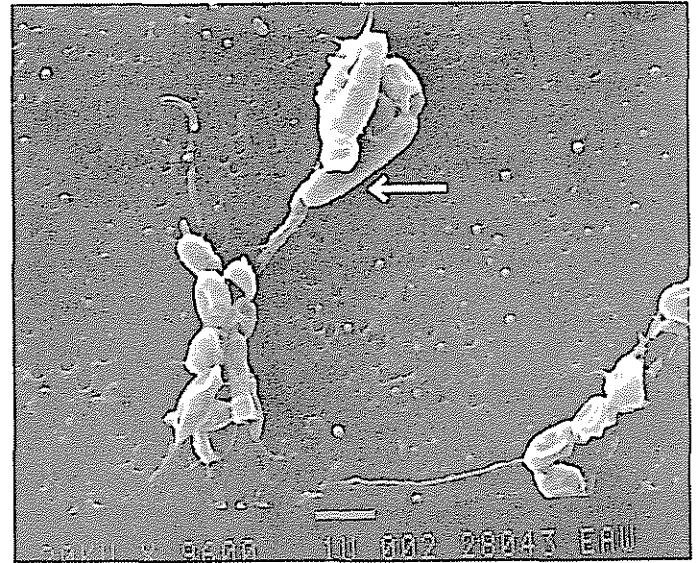
- ① deamination by heterotrophs
- ② hydrolysis by heterotrophs
- ③ fixation by methanotrophs
- ④ lysis and deamination by heterotrophs
- ⑤ assimilation
- ⑥ nitrification by methanotrophs
- ⑦ denitrification by hyphomicrobia

Figure 1:

The role of methane oxidizing mixed cultures in the nitrogen cycle. In natural environments, methane is utilized by mixed associations of bacteria that comprise a methane oxidizer, a methanol oxidizer (usually a *Hyphomicrobium* sp.) and several heterotrophs. Only the methane oxidizer utilizes methane as its carbon energy substrate. The other components of the mixed culture utilize either a by-product of methane oxidation (methanol) or lysis products to relieve inhibition of the methane oxidizer. The capabilities of the several components of such mixed cultures with respect to nitrogen compounds are extensive.



Light Micrograph  
Phase Contrast ca. 1500x



Scanning Electron Micrograph  
Scale bar: 1  $\mu\text{m}$

Figure 4:

- a) Light (phase contrast) Micrograph,  
b) Scanning Electron Micrograph of mixed methanotrophic / *Hyphomicrobium* sp. co-cultures.

† = *Hyphomicrobium* sp.

Typical structural characteristics of the *Hyphomicrobium* sp. (elongated bud and stem) are clearly evident, but the techniques used do not allow the typical membrane structure of methanotrophs to be seen. The micrographs were prepared by Messrs. H.R. Bürgi and H. Bachmann.

nisms in or from water and soil do not permit methanotrophic bacteria to assert themselves, and consequently, their role in the natural environmental process cycles involving carbon and nitrogen has been grossly underestimated. In natural environments, methanotrophic bacteria are invariably found in close association with *facultative methanol-oxidizing bacteria* of the genus *Hyphomicrobium* (see Fig. 4) and various heterotrophic bacteria. The primary reason that hyphomicrobia occur in natural associations with methanotrophic bacteria is that the latter bacteria, under sub-optimal growth conditions, produce excess methanol, which, if allowed to accumulate, will inhibit further methane oxidation. Hyphomicrobia are able to grow under both aerobic and anaerobic conditions with methanol as carbon energy substrate. The dominant role of hyphomicrobia in denitrification (equation 3), both in the natural environment and in wastewater treatment processes, is extensively documented. When assessing the role of various bacterial species in either environmental or technical processes, it is their role in association with other bacterial species functioning in particular micro- and macro-ecosystems that must be considered to be of primary importance. Here, it is the denitrification capacity of associations of methane-oxidizing bacteria with hyphomicrobia that is subject to examination. Prior to more detailed discussion, it is instructive to consider the probable roles of such associations in the overall nitrogen cycle, as illustrated in fig. 1. The key question of concern is the conditions under which the various process steps are able to occur.

#### Denitrification in heterogeneous microbial systems

In a completely homogeneous system, denitrification will occur only under anaerobic conditions. However, all microbial culture systems are markedly heterogeneous (see Fig. 4) with significant concentration gradients. In such systems, the detection of oxygen in the overall systems does not necessarily indicate an availability of oxygen at the sites of en-

zymic reaction within the microorganisms and the presence of oxygen gradients in such systems is almost certainly responsible for claims that denitrification occurs under apparently aerobic conditions. Several hypotheses concerning denitrification by methane-utilizing mixed cultures can be formulated for heterogeneous environments.

However, of the several hypotheses, those proposing complete denitrification by methanotrophic bacteria themselves are devoid of supporting evidence. Some potentially plausible hypotheses that remain include:

- (i) Denitrification in *flocculated* mixed cultures where the methanotrophic bacteria utilize methane and produce methanol under aerobic conditions, and the hyphomicrobia utilize methanol and simultaneously denitrify in the anaerobic regions of the flocs;
- (ii) Denitrification in *discretely dispersed* mixed cultures where the methanotrophic bacteria utilize methane and produce methanol and the hyphomicrobia utilize methanol and simultaneously denitrify in the overall presence of oxygen but where the hyphomicrobia have a relatively lower affinity for oxygen than do the methanotrophic bacteria and are, therefore, ineffective competitors for oxygen and are forced to use nitrate as an alternative electron acceptor;
- (iii) Denitrification in *discretely dispersed* mixed cultures where the methanotrophic bacteria utilize methane and produce methanol and the hyphomicrobia *simultaneously utilize methanol both aerobically and anaerobically* because of intra-cellular differences in oxygen availability.

One interesting implication of denitrification by methanotrophic/methylotrophic associations is that the denitrification could become dominant in environments that would normally be considered unsuitable for the process, i.e., where oxygen is present and conventional carbon substrates for microbial growth are deficient.

## Experiments and results

Experiments were undertaken using both mono-cultures (*Hyphomicrobium* sp.) and mixed cultures in stirred flasks. The mixed cultures contained a methanol-utilizing *Hyphomicrobium* sp. and either a pure culture of the methanotrophic bacterium *Methylococcus capsulatus* or enrichment cultures of methanotrophs.

### 1) Denitrification rates under anaerobic and under aerobic conditions

In a first series of experiments, batch mono-cultures of the *Hyphomicrobium* sp. were grown, with methanol and nitrate, under three sets of conditions, (i) where oxygen was present in the head-space of the flasks and oxygen transfer between the head-space and the liquid culture occurs, (ii) where strictly anaerobic conditions were maintained, and (iii) where anaerobic conditions were maintained until after the start of denitrification, where upon oxygen was introduced into the head-space and subsequent transfer to the liquid culture occurred. The results of these experiments are shown in fig. 2a, b and c where the head-space concentration of oxygen and nitrogen and the concentrations of nitrate and nitrogen and the dry weight of bacterial cells are plotted against elapsed time. The results shown in fig. 2a clearly indicate simultaneous oxygen uptake and nitrate reduction in a pure mono-culture of the *Hyphomicrobium* sp. and those in fig. 2b show nitrate reduction under typical anaerobic conditions with the pure mono-culture of the *Hyphomicrobium* sp. Under strictly anaerobic conditions, the observed rate of denitrification per unit dry weight of bacteria was somewhat less than the observed rate of denitrification in the presence of oxygen. On a unit liquid volume basis, the increased rate was even more apparent because of the significantly higher biomass yield coefficient and, hence, higher cell density, achieved under aerobic conditions. The results shown in fig. 2c indicate that no immediate inhibition of the rate of denitrification occurs when oxygen is introduced into an anaerobic denitrifying culture of the *Hyphomicrobium* sp., and, after a short lag, the rate of denitrification increased to approach the rate observed in experiments where oxygen was present throughout.

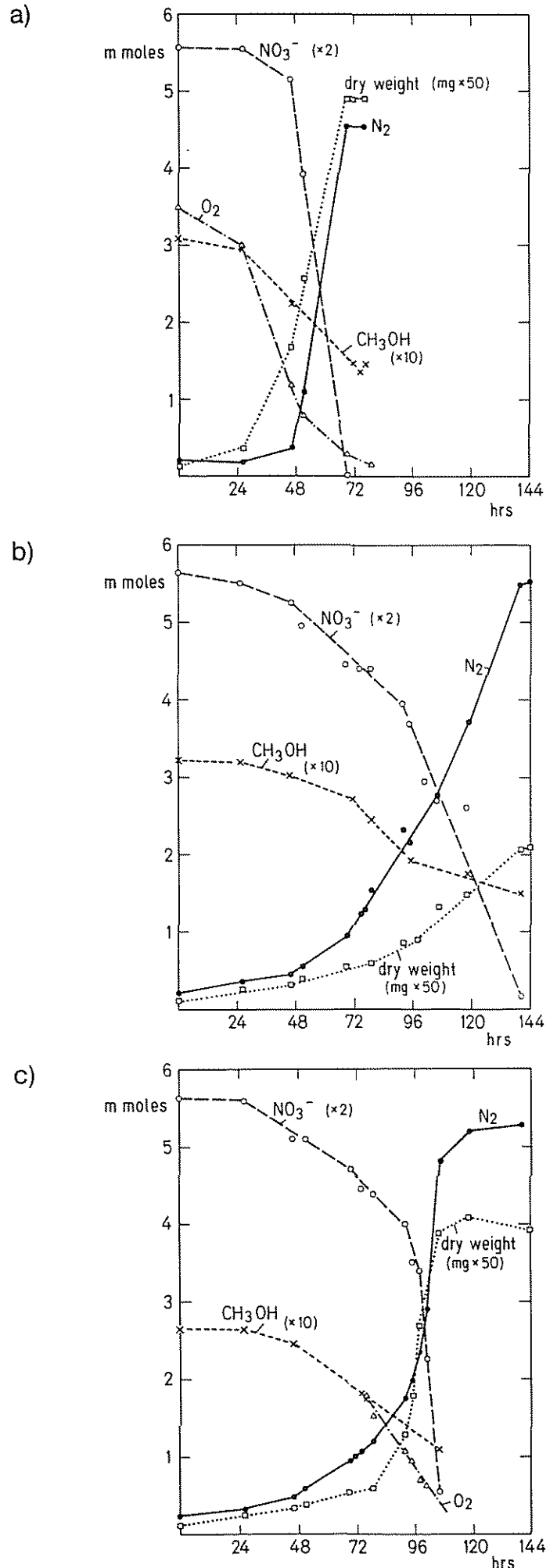
However, what still remains unclear from these experimental results is whether, under conditions where oxygen is present in the headspace and being continuously transferred to and utilized in the liquid culture medium, a significant dissolved oxygen concentration is maintained in the liquid culture medium or whether the dissolved oxygen concentration in the liquid medium approaches zero throughout the experiment. To elucidate this particular point requires *in situ* measurements of the dissolved oxygen concentration in the liquid medium. Such experiments are presently in progress.

Figure 2:

Typical consumption and production curves for a *Hyphomicrobium* sp. utilizing methanol

- a) in the presence of oxygen,
- b) in the presence of oxygen,
- c) initially in the absence of oxygen, but subsequently in the presence of oxygen.

Denitrification is clearly evident under all three conditions. In the presence of oxygen simultaneous denitrification and respiration are observed.



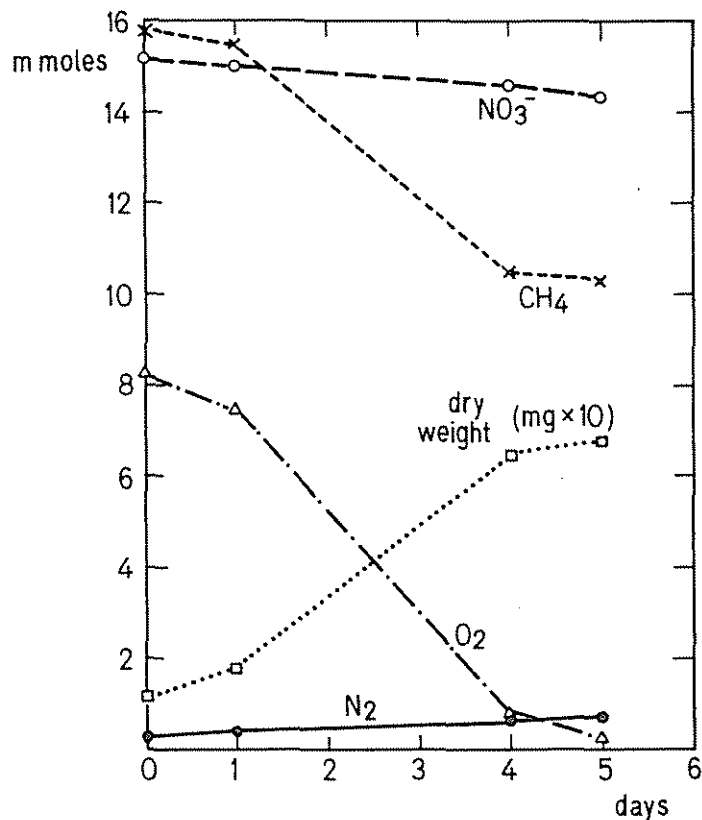


Figure 3:  
Typical consumption and production curves for a methanotrophic / Hyphomicrobium co-culture utilizing methane in the presence of oxygen.  
 The apparent low level of denitrification results from the low levels of methanol produced and a correspondingly low fraction of the *Hyphomicrobium* sp. in the mixed culture.

## 2) Mixed cultures

In order to determine the validity of the hypothesis that hyphomicrobia can denitrify in the presence of oxygen when their source of carbon substrate results from an overproduction of methanol during the aerobic growth of methanotrophic bacteria on methane, stirred flask experiments were undertaken in which co-cultures of either *Methylococcus capsulatus* or enrichment cultures of methanotrophs and the *Hyphomicrobium* sp. were grown with methane as sole carbon energy substrate in the presence of oxygen. For such a culture, the head-space concentrations of oxygen, methane and nitrogen and the concentration of nitrate and the dry weight of bacterial cells in the liquid culture medium with respect to elapsed time are shown in fig. 3. In such co-cultures the *Hyphomicrobium* sp. represents some 5 per cent of the culture. Light and electron micrographs of such cultures are shown in fig. 4a and b. The results shown in fig. 3 clearly indicate the onset of denitrification after the initial development of the methanotrophic population and associated carbon substrate production for the hyphomicrobia. The level of denitrifying activity per unit weight of bacteria present in the system is consistent with the fraction of hyphomicrobia present in the overall population.

## Conclusions

The results obtained from the experiments so far undertaken lend support to the hypothesis that denitrification occurs in mixed cultures containing methanotrophs and hyphomicrobia. The methanotrophs grow methane as a sole carbon source in the presence of oxygen. Methanol is a by-product of this process. Hyphomicrobia oxidize methanol by using oxygen and/or nitrate as electron acceptors.

However, the results do not discredit either the hypothesis concerning inter-species competition for oxygen or that based on marked segregation and associated oxygen gradients within the culture system.

As far as the application of these results is concerned, useful information is provided with respect to the nitrogen cycle during the summer stratification of lakes, on the one hand, and interesting possibilities are indicated for achieving denitrification during aerobic sewage treatment by the introduction of methane produced during anaerobic sludge digestion, thereby contributing to the overall integration of the unit processes used for sewage treatment, on the other hand.

## Radioisotopes in Aquatic Sciences

## Acid precipitation and its Influence on Swiss Lakes

## Denitrification by Methane-utilizing mixed Bacterial Cultures

## The Contributing Authors

*Dr. Peter Santschi* is a geochemist at Lamont-Doherty Geological Observatory, Columbia University (USA), doing very creative research especially on the role of sediments in natural waters. He is presently a visiting scientist at EAWAG. Very fortunately for EAWAG, Dr. Santschi has decided to accept a permanent position as a senior scientist at EAWAG.

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## News about EAWAG collaborators

*Dr. Dieter Imboden* has submitted a habilitation thesis «Tracers and Mixing in the Aquatic Environment» to the authorities of the Swiss Federal Institute of Technology. He is now Privatdocent for Aquatic Physics.

*Dr. Alexander J. B. Zehnder* who has been a research microbiologist in EAWAG's Technical Biology Department has been appointed professor in microbiology at the Agricultural University of Wageningen/Netherlands. Dr. Zehnder who obtained his Ph.D. (with Professor Wuhrmann) at Zurich was a postdoctoral fellow at the University of Wisconsin (Prof. T.D. Brock) and was an assistant professor at the Department of Civil Engineering at Stanford University before joining EAWAG.

*Dr. Christine Matter-Müller* who has been the editor of EAWAG News has left EAWAG to accept a major management task in a family-related enterprise. She got her Ph.D. at ETH Zurich and joined EAWAG after a postdoctoral fellow-

ship at Stanford University. She has been very influential in coordinating multidisciplinary projects at EAWAG. She is being replaced in some of her staff functions by *Dr. Peter Perret*, a biologist.

The editorship of EAWAG News has been taken over by *Diana Hornung*. She is a chemist with a degree from the University of Zurich with experience in research at Rensselaer Polytechnic Institute and in private industry and is a graduate of our postgraduate program in water pollution control and water technology.

*Professor Werner Stumm* was invited to the Chinese Academy in Peking. He gave a series of lectures at Academia Sinica's Institute of Environmental Chemistry.

A workshop conference on "Chemical Processes in Lakes" with ca. 50 Participants will be held in September. The proceedings of this conference will be published early in 1984 by Wiley Interscience, New York.

*Prof. Rudolf Braun* will resign from his position as head of the EAWAG Department of Solid Wastes in order to devote full time to his functions as a professor of solid wastes.

Prof. Braun has been building up the Department of Solid Wastes at EAWAG since 1955. Under his direction, his department has provided most useful services in the national interest and in the interest of environmental protection. EAWAG is most grateful to Prof. Braun for his dedicated engagement. EAWAG will continue to support Prof. Braun in his duties as a professor.

*Prof. Peter Baccini* will become new head of the Department of Solid Wastes (1st October 1983). Prof. Baccini will continue to serve as a professor of chemistry at the university of Neuchâtel.



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