Chapter III.1   In Situ Measurement of Oxygen Profiles in Lakes: Microstratifications, Oscillations, and the Limits of Comparison with Chemical Methods

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1 Introduction

Molecular oxygen is the substance most extensively monitored in scientific and rou-
tine investigations of aquatic ecosystems. Oxygen distributions in stratified lakes and
departures from atmospheric equilibrium concentrations provide more information on
lake characteristics and for water management than any other chemical parameter [8].
Accordingly, the most common application of POS in field ecology is the measure-
ment of dissolved oxygen concentrations along vertical or horizontal transects of
aquatic systems. The situation is reflected by the abundance of commercially available
in situ oxygen probes (e.g., Delta Scientific, Electronic Instruments Limited, Inter-
national Biophysics Corporation, Kahlsico International Corporation, Orbisphere Lab-
oratories, Wissenschaftlich-Technische Werkstätten, Yellow Springs Instruments).
These sensors incorporate macrocathodes and are commonly equipped with a simple
battery-operated stirring device, and most instructions leave no doubt about the ease
of the method.

The problem of measuring oxygen concentration in large bodies of water may ap-
pear simple, but, in fact, according to personal communications, difficulties with field
applications of POS are experienced by many investigators although seldom mention-
ed in the literature ([2, 10, 21, 30], Chap. I.9). This justifies the discussion of some
practical aspects which may be fundamental for reliable in situ oxygen measurements.

This contribution contains some guidelines for choosing between the chemical
Winkler titration method involving discrete sampling and in situ measurement with
polarographic oxygen sensors (POS). The unique advantages of the latter are demon-
strated by studies of the oxygen dynamics in Kalbelesee, a shallow, productive sub-
alpine lake. The high resolution of oxygen microstratification revealed the phenome-
non of "spring stratification" which is probably widespread in this type of lake during
the period after icebreak. Measurement of the small-scale patterns of oxygen in space
are complemented by continuous monitoring of dissolved oxygen during daily cycles.
The use of POS provides the most economic method for the study of physicochemical

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processes in aquatic systems, especially in combination with the automatic measurement of additional ecological parameters.

2 Instrumentation

2.1 In Situ Oxygen Measurement

A YSI 5700 dissolved oxygen probe was used with a 15 m electrode cable. The POS was mounted in a modified stirring chamber which was originally designed for large volume respirometers (Chaps. II.1, III.3). A perspex chamber (Fig. 1) with a rotating magnet acts as a centrifugal pump. The magnet is driven by a 6 V dc motor running on 4 V which represents a compromise between the danger of decoupling and high stirring and pumping rates. Water is drawn through the central inlet in the bottom and discharged through the peripheral slots in the upper part of the chamber. Thus stirring does not disturb the natural oxygen gradient at the depth of submersion, and, additionally, turbulences are prevented by the 20 × 30 cm mounting plate. Within the chamber the turbulence not only provides an optimum current across the membrane, but is intense enough to tear off gas bubbles that might, if they collected in the chamber or at the membrane, distort the sensitivity and response time of the POS. This function of the stirring device is generally important when the probe is immersed in water after contact with air, and is essential when measurements are made in supersaturated surface waters where spontaneous bubble formation might occur. The supraoptimally high current in the stirring chamber serves another important purpose in continuous in situ measurements by keeping the growth of bacteria and algae on the membrane within limits (Chaps. I.9, II.9). If only gently stirred, membranes start "fouling" and have to be replaced. In fast rivers and in aeration tanks of sewage works the water currents may be high enough to render such stirring unnecessary [20].

The YSI 5700 and many other POS designed for in situ measurements are pressure-compensated. This is important if the electrolyte is not entirely free of gas bubbles. A pressure-transducing membrane on the side of the sensor shaft offsets changes in hydrostatic pressure on the oxygen transducing membrane. However, the hydrodynamic pressure generated by natural currents or in the stirring chamber is not compensated. This imposes problems, especially if a centrifugal pump is used as the stirring device, and therefore POS without pressure compensation are preferable. The pressure-transducing membrane can also be replaced by a pressure-tight seal, in which case special care is required to exclude all air bubbles when applying the membrane (Chap. I.1). This is recommended in any case and a small magnifying lens should be used for inspecting the electrolyte and membrane before taking measurements in the field.

The signal of the POS was measured with a YSI model 51 or 54 dissolved oxygen meter or with a digital oxygen-temperature meter (Mountain and See Instruments) (Chap. I.10). For continuous registration of oxygen and other parameters, a six-channel strip chart recorder (Goerz, Miniscript 6D) was used. A 12 V rechargeable battery served as the power supply. At the lake the actual atmospheric pressure was measured with an altitude meter as necessary for calibrating the POS (Chap. I.2; App. A).
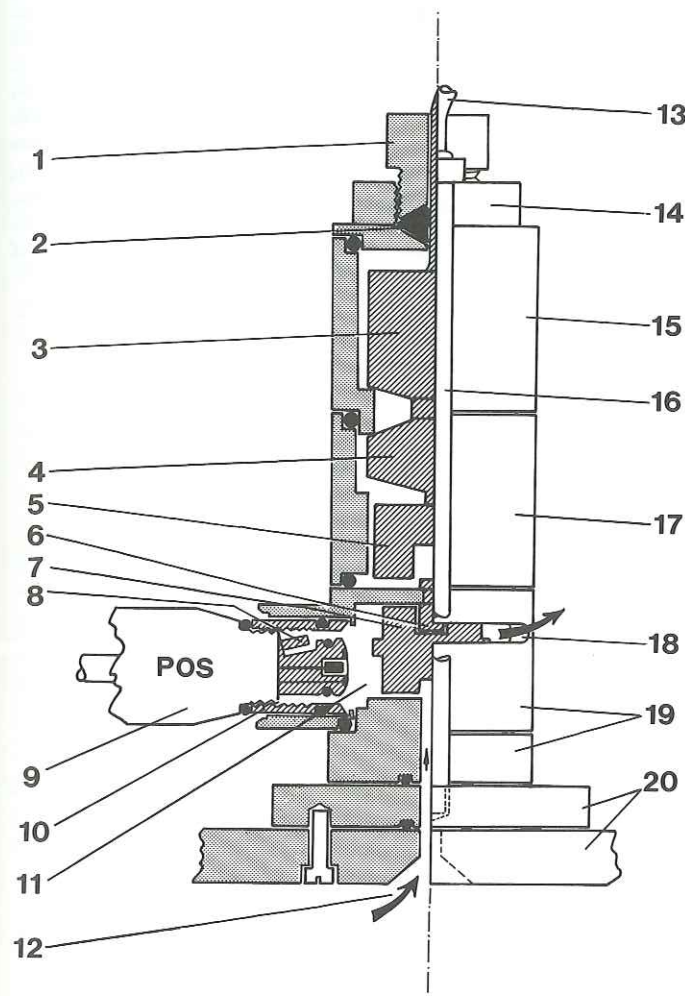

Fig. 1. The in situ stirring chamber for the POS; combined cross-section (*left*) and external view (*right*). *1* PVC screw, *2* conical rubber seal, *3* 6 V dc motor, *4* reduction gear, *5* drive magnet, *6* bearing pin, *7* magnetic follower, *8* thermistor, *9* POS, *10* stainless steel mounting sleeve, *11* stirring chamber, *12* inlet, *13* power supply cable for motor, *14* clamping plate, *15* perspex motor housing, *16* stainless steel mounting bolt, *17* perspex housing of drive magnet, *18* ejection slot, *19* perspex housing of stirring chamber, *20* lower mounting plate

2.2 Winkler Analysis

Water samples were collected with either a 2 dm³ Ruttner sampler or a 5 dm³, 0.5 m high Schindler sampler with built-in mercury thermometers calibrated at ± 0.05°C. Winkler reagents (App. D) were added immediately after filling 120 or 300 dm³ Winkler brown glass bottles. These were completely submersed in cool lake water for storage. In a field laboratory the samples were titrated according to the amperometric
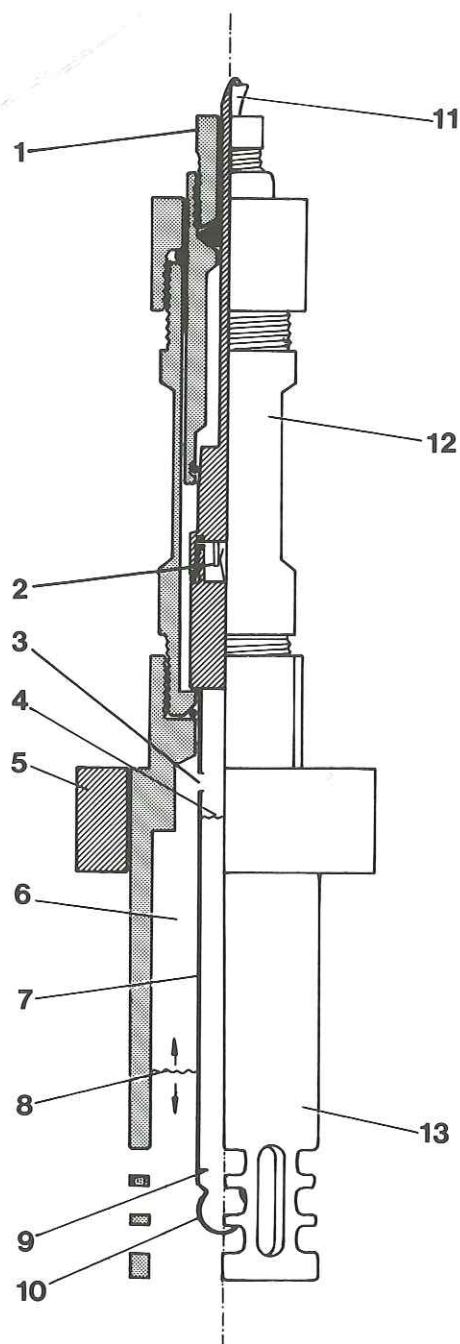
Fig. 2. Pressure compensation holder for the pH glass combination electrode; combined cross-section (*left*) and external view (*right*). *1* PVC screw, *2* Schott cable connection, *3* hole for electrolyte reservoir, *4* electrolyte level, *5* stabilizing weight, *6* pressure compensation air chamber, *7* pH electrode shaft, *8* water level rising with increasing depth, *9* diaphragm, *10* glass membrane, *11* electrode cable, *12* water- and pressure tight housing of cable connection, *13* electrode housing

method [12, 25] using the same voltmeter as used for the field pH-Eh measurements. Titrations were performed either with a 10 cm^3 automatic glass burette or with a 0.5 cm^3 microburette (Agla micrometer syringe, Burroughs Wellcome & Co., London) for near-zero oxygen concentrations.

2.3 In Situ Measurement of Temperature and pH

Temperature was measured with the thermistor of the YSI 5700 dissolved oxygen probe (YSI 400) and with separate thermistors (YSI 44006) linearized over 0° to 10°, 5° to 15°, or 10° to 20°C ranges (Chap. I.10).

While in situ determinations of redox potential and conductivity were performed only occasionally, pH was routinely measured to ± 0.01 pH units with a Radiometer specific ion meter (PHM 53) calibrated at 1 or 2 pH units full scale deflection. The Schott (N 62) pH combination glass electrode was mounted in a pressure compensation holder (Fig. 2). As the probe is lowered to greater depths, the water level within the holder rises and keeps the slight overpressure that is exerted by the electrolyte on the diaphragm constant. Two-point calibrations of the pH electrode at the temperature of the surface water rendered temperature corrections insignificant (< 0.01 pH units per °C). Special care is required in keeping the cable connections absolutely water tight. The mutual interference between the pH electrode and POS that was seen on a few occasions, was dependent on the distance between the two probes in the water. This might indicate defective insulation of the electrodes or cable connections.

3 Laboratory Tests

3.1 POS

Before commensing a field program, it is advisable to test the equipment under controlled laboratory conditions in order to gain some confidence in the method and to discover its limitations. Many commercial oxygen-temperature meters do not give an absolute accuracy of temperature measurements better than ± 0.5 to 1°C. This is definitely unsatisfactory for most applications and, due to a false account of the oxygen solubility and erroneous temperature compensation, will also adversely affect the oxygen measurements. With electronic linearization and digital display (Chap. I.10) improvement to ± 0.05°C was achieved by an additive correction term over the temperature range expected in the field (Table 1). Electronic temperature compensation of the oxygen solubility and membrane permeability should be tested for every combination of membrane, sensor, and electronic circuit (Chap. I.10). If these match, then the precision of oxygen determinations in the whole ecological temperature range is good (± 3 μmol dm^{-3} or 0.1 mg dm^{-3} at air saturation in pure water; Table 1), although conformity with absolute values may be less accurate (± 15 μmol dm^{-3} or 0.5 mg dm^{-3}) after simple calibration in air above the water surface (Chap. I.2).

The time course of the oxygen signal is determined by the water renewal time of the stirring chamber and by the time constant of the POS, as in respirometric systems

Table 1. Temperature compensation of a POS (YSI 5700) calibrated in air (17°C; $_bp$ = 95.2 kPa) and linearity of the YSI thermistor 400 measured with a digital oxygen-temperature meter (Mountain and Sea Instruments). The measured values and the deviations (ΔT, Δc_s) from the expected values are listed. For the deviations, the means (calibration errors) ± standard deviations (linearization errors) are given below

Temperature [°C]			Oxygen [μmol dm^{-3}]		
θ	Signal	ΔT	c_s	Signal	Δc_s
2.50	2.27	0.23	400	388	12
4.05	3.80	0.25	384	–	–
4.21	3.96	0.25	382	372	10
6.26	6.03	0.23	346	334	12
9.94	9.77	0.17	331	319	12
12.08	11.89	0.19	315	303	12
12.10	11.90	0.20	315	300	15
14.14	14.02	0.12	301	288	13
15.92	15.78	0.14	290	275	15
17.85	17.69	0.16	278	263	15
19.82	19.57	0.25	267	253	14
		0.20 ± 0.045			13.4 ± 2.0

(Chap. II.3). Since the response time is the first function of the sensor to be affected by aging and poisoning, the manufacturer's specifications should not be uncritically relied upon when applying a sensor for some period of time in the field. With the present system (Fig. 1) and with a sensor that has been periodically used for more than one year, the 95% response was 60 s for oxygen and 40 s for temperature. The steady state values, however, were reached only after 8 and 5 min respectively. An equilibration time of 120 s is sufficient for applications in the field.

3.2 The Winkler Method

Since Winkler dissolved oxygen analysis was chosen as a reference for the field measurements with POS, the accuracy of the chemical method was also tested under standardized conditions. After equilibrating thermostated tap water either with air or nitrogen for 1 h, samples were siphoned into Winkler bottles exactly as in the field. To reduce volatilization of iodine [25], a large fraction of the expected volume of thiosulfate was added directly to the previously acidified water sample. Amperometric (Fig. 3) and redox titrations showed similar results (Table 2) with a high precision that cannot be achieved by the common starch indication method [12]. Practically, the amperometric method is superior to others, since only a few data points are required (in series determinations only one in the region of the linear slope, Fig. 3), and a step by step approach to the actual titration end point is unnecessary [25]. The samples equilibrated with nitrogen were taken after flushing the Winkler bottles with N_2. The nonzero values are partly due to the oxygen dissolved in the Winkler reagents.
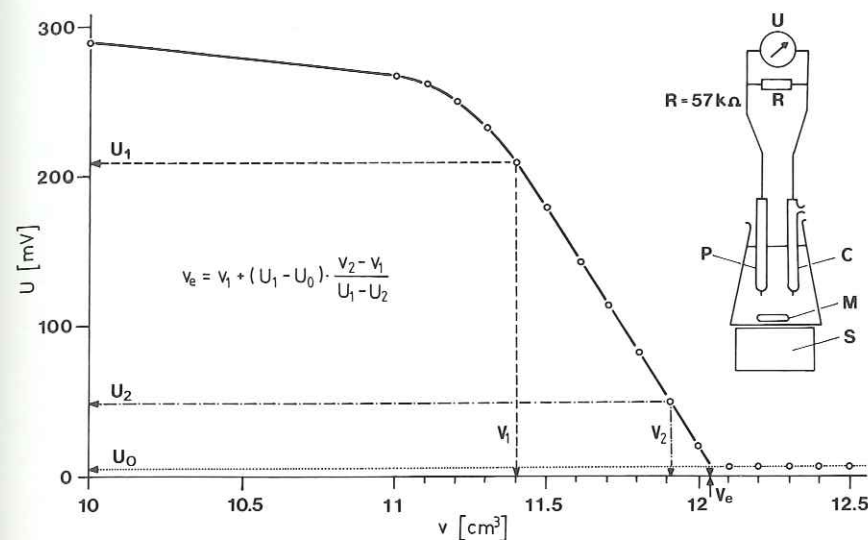
Fig. 3. Amperometric titration. Instrumental setup: C calomel reference electrode, M magnetic follower, P platinum electrode, R electrical resistance, S magnetic stirrer, U high impedance mV-meter. The titrated sample was 114.6 cm^3 air-saturated water, 20.01°C; $_bp$ = 95.2 kPa (= 714 mm Hg); R = 57 kΩ; titrant 0.01 mol $Na_2S_2O_3$ dm^{-3}. The titrant volume at the titration end point, v_e, is calculated according to the equation given in the figure. Since the background potential, U_o, and the slope, $x = (v_2 - v_1)/(U_1 - U_2)$, are sufficiently constant, they need only be determined once. In the following titrations only one titrant volume/mV reading, v and U, in the linear region is required, and the calculation of v_e simplifies to

$$v_e = v + (U - U_o) \times x.$$

The oxygen concentration in the sample, c_s, is then calculated as

$$c_s = \frac{v_e}{V_s} \times TF,$$

where V_s is the sample volume [cm^3] corrected for the volume displaced by adding the Winkler reagents. For a 0.01 mol dm^{-3} thiosulfate solution the thiosulfate factor, TF, equals 2500 μmol O_2 dm^{-3} or 80 mg O_2 dm^{-3}

Table 2. Comparison of the amperometric and redox titration methods in Winkler analysis. The means ± standard deviation of four replicates and the percentage of the theoretical air saturation value (at 20.0°C) are given. The sample volume was 116 cm^3 minus 2 × 1 cm^3 Winkler reagents (App. D). Other amperometric determinations in different years ranged from 99.3% to 100.0% of the expected air saturation value and the precision varied from date to date between ± 0.1% and ± 0.5%

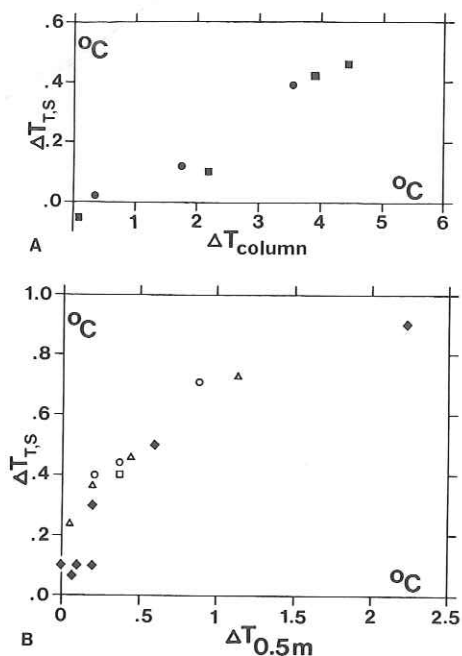|	Amperometric		Redox	
	[μmol O_2 dm^{-3}]	% air	[μmol O_2 dm^{-3}]	% air
Air	261.6 ± 1.06	98.56	263.8 ± 0.75	99.36
Air	264.7 ± 0.31	99.06	256.3 ± 0.28	99.34
N_2 techn.	1.8 ± 0.09	0.67	1.9 ± 0.06	0.71
N_2 pure	1.5 ± 0.19	0.58	1.5 ± 0.16	0.57

Fig. 4A,B. Error of temperature measurements in volume samplers, $\Delta T_{T,S}$, as a function of the vertical temperature gradient in the water column. A 2 dm³ Ruttner sampler; ΔT_{column} is the temperature difference in the water column from the surface to the sampling depth. B 5 dm³ Schindler sampler; $\Delta T_{0.5\,m}$ is the temperature difference in the half meter above the sampling depth. *Open symbols* are for vertical series during summer stratification, e.g., for 78-09-18 (Fig. 5). In this case the temperature in the water sampler was always higher than the in situ thermistor measurements serving as the reference for $\Delta T_{T,S}$. *Closed symbols* are for vertical series during inverse winter stratification. In this case the temperature in the water sampler was lower than in situ. The data points are the means of 3 to 10 measurements at every sampling depth (0.3 to 3.8 m) in Kalbelesee. Situations of anomalous temperature stratification (e.g., Fig. 6) were excluded

4 Comparison of Field Measurements in Situ and in Water Samples

4.1 Thermistor Versus Mercury Thermometer

A well-known problem with various volume samplers is the partial displacement of water from upper layers and its mixing with the water at the actual sampling depth. This explains the differences between temperature measurements in situ using the thermistor probe associated with the POS in the stirring chamber and measurements with mercury thermometers built into volume samplers (Fig. 4). The difference was a function of the temperature gradient above the sampling depth. During inverse stratification the temperature in the water sampler was too low, while during summer stratification it was too high with respect to in situ measurements. However, the simple relationship broke down during anomalous temperature stratification (Fig. 6). The two methods corresponded only in situations of temperature homogeneity throughout the

water column. Otherwise differences of 0.5°C were fairly common. The speed of lowering the water sampler to the sampling depth had no influence on the result.

4.2 POS Versus Winkler Method

Whatever the method employed, practical experience is required, not only under favorable laboratory conditions, but also in the adverse environment often experienced by the field ecologist. An investigator with freezing, wet fingers, handles a pipette with reduced precision, and a heavy rain and cold wind may reduce his patience in following the standard procedures required with an electronic instrument. At low subzero temperatures Winkler bottles crack soon after sampling when the water freezes, and air calibration of the POS is unreliable due to ice formation on the membrane. On a hot, sunny day air calibrations may again be difficult since temperature stability of the POS is hard to achieve. Limitations in applying any field method arise in a variety of situations and have to be dealt with individually.
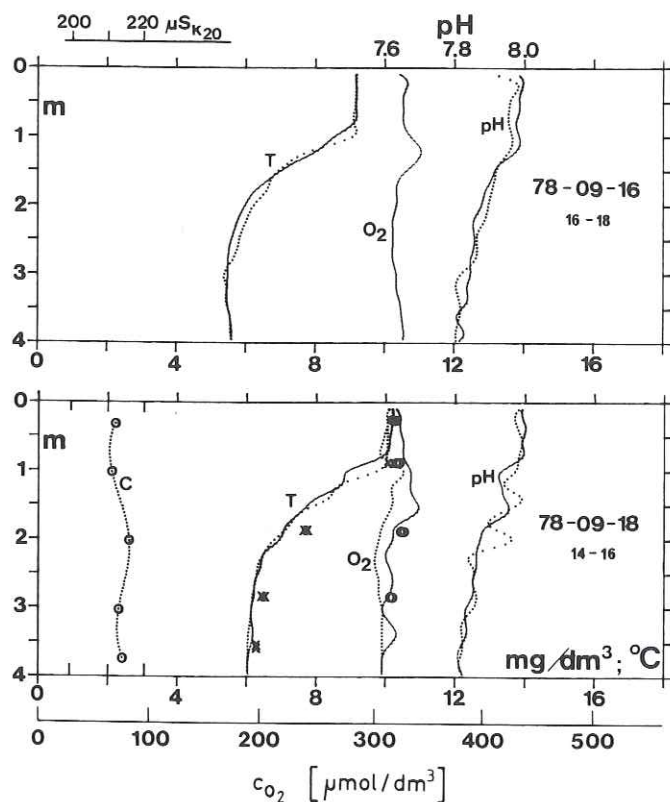
In my experience with different calibration chambers, the quickest and the most reliable procedure was one involving as little handling of the POS as possible. After setting the zero point in an approximately 5% solution of Na_2SO_3 (adding $CoCl_2$ as a catalyst), the sensor was thoroughly rinsed and mounted in the stirring chamber, which was then submersed in surface water for some time. For air calibration the chamber was quickly emptied, taking care to shake water droplets gently off the membrane. Without dismounting the POS, the stirring chamber was left in air and protected from the sun and wind until the temperature and p_{O_2} reading stabilized in the humid atmosphere of the chamber. The 100% air calibration point was then set according to standard equations relating oxygen concentration to temperature and the barometric pressure as corrected for water vapor saturation (App. A). The whole procedure was repeated to test for the expected precision of the calibration method (± 1%, about ± 3 μmol dm⁻³). Zero calibrations in the field agreed with previous calibrations in the laboratory, but this was frequently not the case for air calibrations.

The first measurement in the vertical profile was made after equilibration in water for 5 to 10 min, while the following readings at subsequent depths were taken at 2-min intervals. Most of the time during calibration can be efficiently used for preparing for other measurements, for sampling, etc. The 2-min exposure time required for the oxygen measurement is just sufficient for the registration of simultaneous measurements of temperature, pH and conductivity. Elucidation of the microstructure of vertical profiles was one of the aims in this investigation. For this purpose a stable 3.5 × 3.5 m float allowed positioning of the sensors in situ at precisely 0.05 m intervals in depth. Steps of 0.2 m depth were chosen as the standard for completing descending and ascending vertical series within a reasonable period of time. For plotting and data analysis all values were typed into a computer and interpolated at 0.05 m intervals with a third-degree polynomial spline fitting function. The following plots show the records on descent as dotted lines (one measurement per four dots), those on ascent as full lines.

Samples for Winkler determinations were collected by lowering the volume sampler until the middle of the column reached the sampling depth. After raising the sampler,

Table 3. Precision of the Winkler method in studies of oxygen depth profiles during homogeneous (78-09-18) and inhomogeneous (78-03-04) oxygen stratification in Kalbelesee. The means ± standard deviation of two replicates (5 dm³ Schindler sampler) are given
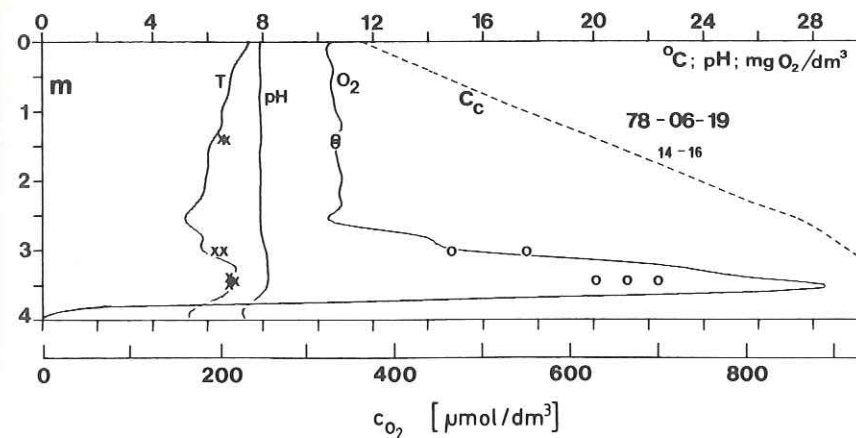
Depth [m]	Homogeneous [μmol O_2 dm^{-3}]	Depth [m]	Inhomogeneous [μmol O_2 dm^{-3}]
0.3	319.4 ± 1.75		
1.0	322.8 ± 1.28	1.3	212.5 ± 30.9
		1.6	179.4 ± 5.19
2.0	326.9 ± 0.97	2.1	80.0 ± 4.47
		2.6	39.4 ± 3.34
3.0	318.1 ± 0.75	3.1	18.75 ± 5.06
		3.6	1.53 ± 2.16

water was continuously siphoned into Winkler bottles until the sampler was half empty. If oxygen stratification was homogeneous, the reproducibility of the Winkler determinations was as good as in the laboratory (± 0.55%; cf. Tables 2 and 3). Even then, however, the in situ method revealed a characteristic microstructure of oxygen (Fig. 5). In the upper meter an interval of 2 h separated the POS (78-09-18) measurements made during descent and ascent. Samples for the Winkler analysis taken in between these registrations corresponded well with the mean values of the air-calibrated POS. However, the remarks on sampling errors in temperature measurements have to be kept in mind when comparing the remaining Winkler dissolved oxygen analyses and in situ POS measurements. Deviations between the two methods do not only originate from the oxygen analysis per se, but are largely due to the variability of oxygen concentration over short intervals of depth and time. Likewise, the high variability of Winkler determinations during clinograde oxygen stratification is due to the sampling method and microstratification, and not to the chemical analyses (Table 3). Therefore only the results for the mixed water layer (the top meter in Figs. 5 and 6) can be used for chemical in situ calibration of the POS.

Another apparent limitation to the comparability of measurements in situ and chemical analyses arises in the case of oxygen supersaturation (Fig. 6). This phenomenon is commonly known as the metalimnetic maximum in lakes with a positive heterograde oxygen distribution [8]. It occurs regularly in eutrophic waters [13, 15, 26], when high photosynthetic production leads to the accumulation of excessive amounts of oxygen, the concentrations of which may increase up to 300% to 500% air saturation. In depths of some meters, however, these supersaturation values do not

Fig. 5. Depth [m] profiles of environmental parameters during summer stratification in Kalbelesee. In situ measurements were taken at 0.2 m intervals moving downward (*dotted lines*) and upward (*full lines*). C conductivity [μS]; O_2 oxygen concentration given as c_{O_2} and ρ_{O_2}, *open circles* show the Winkler determinations; T temperature [°C]; *crosses* show the mercury thermometer readings in the Schindler sampler. The time of measurement is given below the dates

Fig. 6. Depth profiles of oxygen, temperature and pH during "spring stratification" in Kalbelesee. In the zone of homogeneously mixed melt water (78-06-19, 0–2.5 m) the O_2 measurements in situ by POS (*full line*) agreed with Winkler determinations (*circles*). Gassing-out reduced the O_2 content of the three samples from 2.5 m. The absolute saturation concentration, C_c, is shown by the *broken line* ($_b p$ = 81.9 kPa; see App. A, biogenic supersaturation). On the ordinates 0.0 m does not denote the water surface but the standard water mark. Since the actual water surface at 14–16 h on 19 June was 0.3 m above the water mark, C_c for 0.0 m standard depth applies to the actual hydrostatic pressure of a 0.3 m water column. For other explanations see Fig. 5

necessarily exceed the absolute saturation concentration which is a linear function of hydrostatic pressure and the volume fraction of other dissolved gases (App. A). When the hydrostatic pressure is released during hauling of the sample to the surface, gas bubbles form spontaneously and their oxygen content is lost in the Winkler analysis. Gassing out was actually observed in the samples taken from the depth of maximum oxygen concentration (Fig. 6; 3.5 m; 280% air saturation, about 87% absolute saturation), so that the large discrepancy between the two methods could be anticipated.

The limitations of the chemical method in the field resulting from short-range inhomogeneities of oxygen in natural waters and from formation of gas bubbles have to be taken into account in comparing the two methods and establishing a calibration point for the POS. When measurements were made on homogeneous bodies of water, agreement between the two methods was better than ± 5 μmol O_2 dm^{-3} (1.5%) in most cases, but occasional and unexplained deviations sometimes amounted to 5%. Such measurements with an air-calibrated POS are an order of magnitude less accurate than chemical determinations in unstratified waters. Part of the error of the air calibration value may be due to inadequate water vapor equilibration and to temperature differences between the membrane and compensating thermistor (see also Chap. II.10, gas/liquid factors). Proper chemical calibration, however, ensures high accuracy of the electrochemical in situ method which can then be combined with the unique advantage of the high spatio-temporal resolution of the POS.

5 Case Studies in a Shallow Mountain Lake (Kalbelesee)

The in situ method for measuring oxygen with POS was tested and refined in the course of a 4-year study of the oxygen dynamics in Kalbelesee (Hochtannberg, Vorarlberg, Austria). The calcareous catchment area of about 1.5 km^2 is predominantly characterized by alpine meadows. The lake is 300 m long and divided into a western and a smaller eastern basin. The results discussed here pertain to the western basin (Table 4).

Table 4. Morphometric parameters for the western basin of Kalbelesee (1650 m above sea level, latitude 47°16' N, longitude 10°08' E)

Maximum depth[a]	4.0 m
Mean depth	2.3 m
Relative depth	2.88%
Length	210 m
Maximum breadth	130 m
Area	17.5 × 10^3 m^2
Volume	35.3 × 10^3 m^3
Shore line	660 m
Development of shore line	1.41 m

[a] The water level may change from 3.7 to 4.8 m during the year. All values are for a standard depth of 4.0 m. For explanation of other expressions see [8]

5.1 Oxygen Dynamics During "Spring Stratification"

In winter up to 1 m of the water column above the bottom becomes anoxic, as in many shallow, snow-covered lakes and ponds [1, 3, 5, 7, 16, 18, 19, 23]. By the middle or end of March the winter cover reaches its maximum of 1.7 to 2.7 m. The oxygen
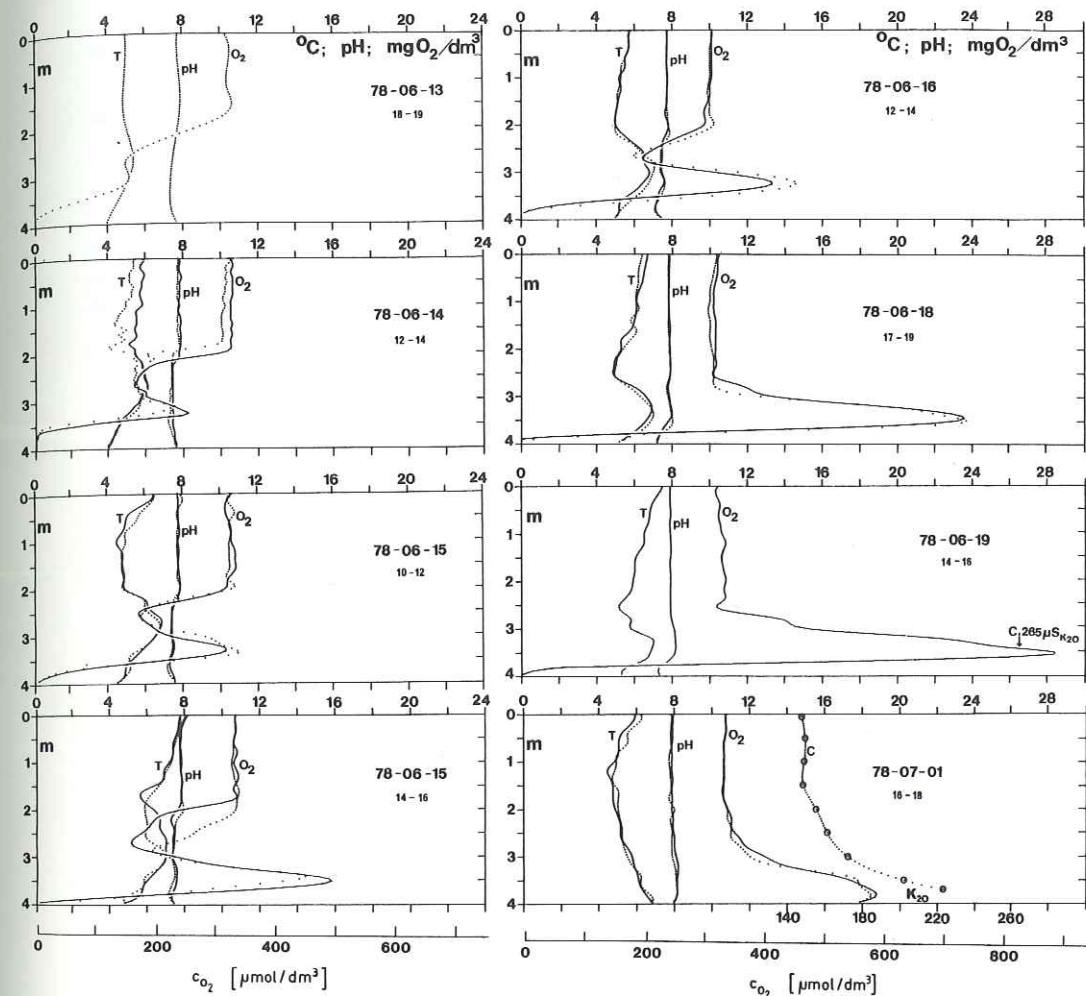

Fig. 7. Depth profiles of oxygen, temperature and pH during "spring stratification" after icebreak in Kalbelesee. Measurements were taken at depth intervals of 0.5 m (78-06-13), 0.1 m (78-06-14), and 0.2 m (all others) and plotted using a spline fit interpolation. Much detail of the actual depth profile remains elusive with 0.5 m depth intervals. However, a high confidence in the interpolations of 0.2 m intervals is justified on the basis of comparison with the profiles taking 0.1 m intervals. Note the close correspondence of downward (*dotted line*) and upward traces (*full line*), especially in the region of the O_2 peak and the first and second O_2 minimum. The fact that O_2, temperature and pH changed simultaneously in 2 to 3 m in the downward and upward profile in one case (78-06-15, 14−16 h) indicates a short term displacement of the whole water body in this region
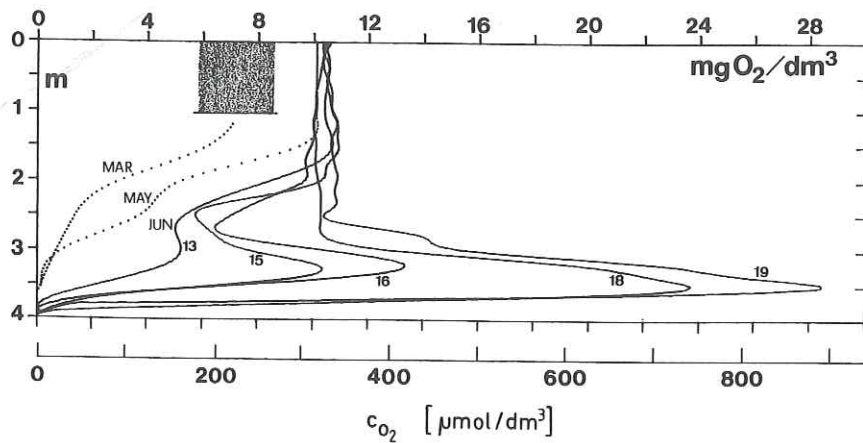
Fig. 8. Dynamics of dissolved oxygen before and after icebreak during "spring stratification" in Kalbelesee. In March and May (*dotted profiles*) the winter cover extended to about 1 m depth as indicated by the dark area. Icebreak occurred on the 11th of June. The *numbers* are the dates in June for the corresponding profiles (*full lines*, plots from Fig. 7)

conditions then become severe, occasionally causing winter fish kill [1]. With the onset of thaw, melt water passes the lake below the ice and forms a layer of water with low conductivity and increasing oxygen concentration. In 1978 icebreak occurred on the 11th of June. Two days later the surface temperature had risen above 4°C, but, due to chemical stratification, there was no immediate spring overturn in spite of homeothermy. After icebrak, a peak of oxygen concentration increased from day to day in 3.5 m depth (Fig. 7), where the conspicuous concentration of algae (mainly *Gymnodinium* sp.) set a sharp limit to the Secchi disk transparency. Isolated from atmospheric oxygen the stagnant, previously anoxic water became gradually supersaturated with oxygen. The photosynthetic source of oxygen and the mud, acting as an oxygen sink, maintained an extremely steep oxygen gradient in the free water column. The period of oxygen increase is summarized in Fig. 8. This illustrates the striking similarity of the development of the oxygen distribution in this shallow lake with that observed in the top millimeters of mud in the marine littoral (Chap. III.2). Surprisingly, however, oxygen concentrations decreased only negligibly during the night.

The same pattern of oxygen stratification evolved after icebreak in all years of observation. Even though this is usually restricted to 2 to 4 weeks, the occurrence of the "spring stratification" exerts a profound influence on the limnology of the lake. The high nutrient levels in the stagnant water layer in combination with high light intensities after icebreak support an efficient fixation of nutrients in algal biomass and secondary production. While the spring flood passes over the lake without mixing, the chemical stratification disappears gradually with the decreasing supply of melt water to the mixolimnion and with the photosynthetic reduction of bicarbonate concentration in the stagnant water layer. The chemical destabilization in the presence of anomalous temperature stratification (Fig. 7) leads to a delayed spring overturn. As a consequence of the previous spring stratification, the lake enters the summer stagnation period in a much more eutrophic state than in the case of an immediate spring over-
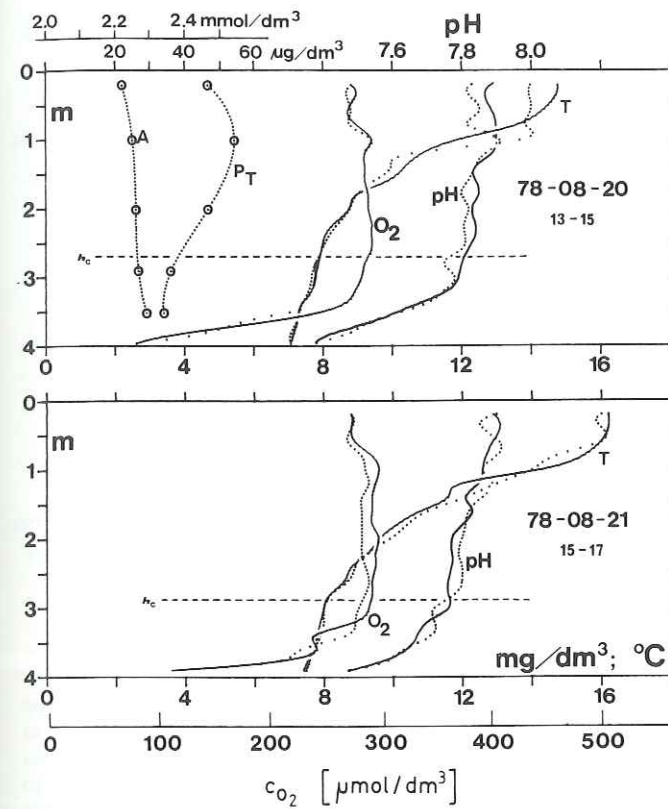
Fig. 9. Depth profiles of environmental parameters during summer stratification in Kalbelesee. *A* alkalinity (mmol dm^{-3}), P_T total phosphorus (μg dm^{-3}). The *horizontal line* indicates the critical depth, h_c, separating two ecotopes on the basis of different correlations between ecological parameters (cf. Fig. 11)

turn, which together with the flood of melt water would effect an efficient washout of nutrients. For similarly limited "meromictic behavior" of lakes compare [5, 22].

5.2 Continuous Measurement of Oxygen, Oscillations, and Correlations with pH and Temperature

Continuous recording of oxygen adds another dimension to the measurement of oxygen profiles in lakes. An example from the summer stagnation is presented here, showing the typical increase in oxygen at the level of the thermocline and a sharp decrease near the bottom, which is an exception for Kalbelesee during summer (Fig. 9). On calm, cloudless days the diurnal variation of surface temperature amounted to about 4°C with minimum temperatures at 0600 to 0700 h, and a maximum at 1800 h (Fig. 10). The temperature increase at 1 m depth was delayed until 1000 h and was connected with the onset of a slight breeze. At 1 m the oxygen concentration remained above the air-saturation value at surface temperature throughout the night. Even near
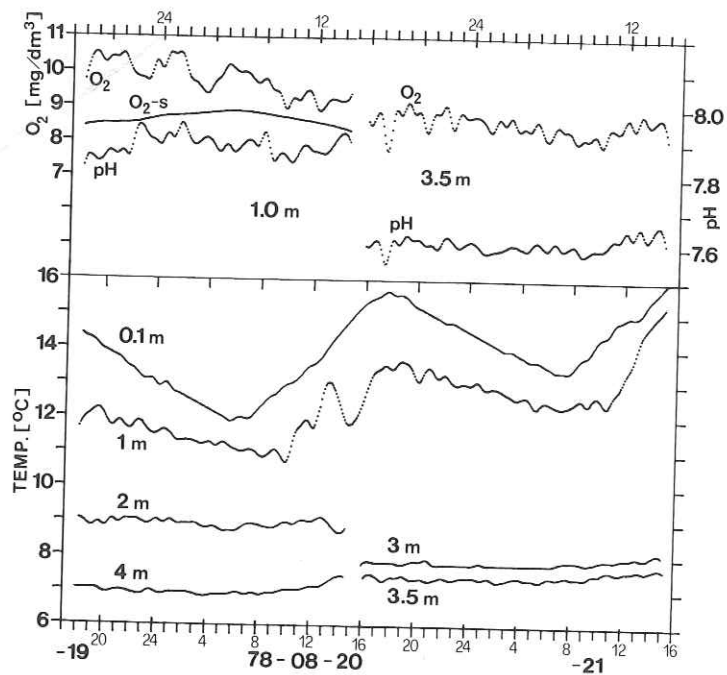
Fig. 10. Continuous records of oxygen, pH, and temperature at different depths in Kalbelesee. The corresponding vertical profiles are shown in Fig. 9. Two thermistors were continuously exposed at 0.1 and 1 m depth; two were changed from 1 and 4 m to 3 and 3.5 m respectively. During the first period (19/20 August) the POS and pH electrode were exposed at 1.0 m and then transferred to 3.5 m depth (20/21 August). O_2-s is the saturation concentration corresponding to equilibration with air at the surface temperature
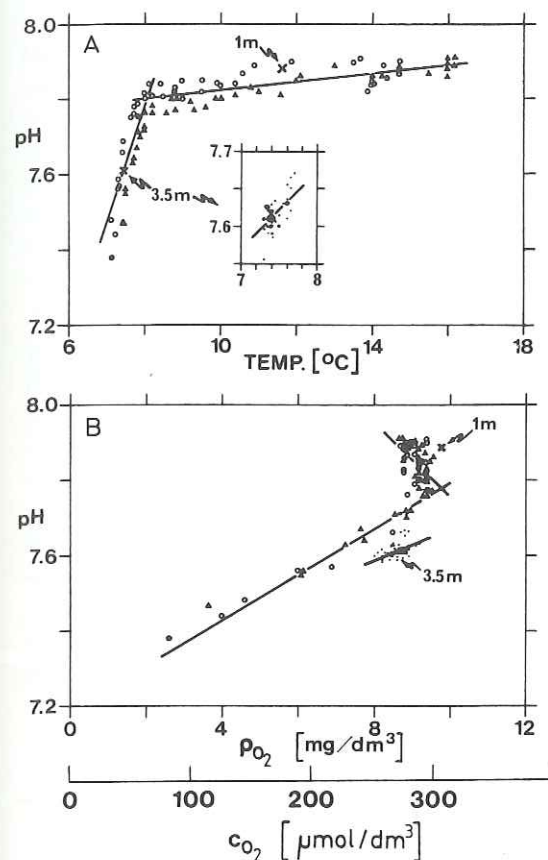

Fig. 11. Correlations of oxygen concentration, pH, and temperature in the vertical profiles shown in Fig. 9, and in the continuous registrations shown in Fig. 10. *Circles* and *triangles* are for the vertical profiles of August 20 and 21 respectively. The *crosses* show the mean values of the continuous registrations at 1 and 3.5 m depth as indicated by *arrows*. The inset shows the pH-temperature relationship in the continuous registration at 3.5 m with an enlarged temperature scale. The intercepts of the pH-temperature and pH-oxygen regressions are at 7.80 and 7.79 pH and at 8.08°C and 308 μmol O_2 dm^{-3} (9.87 mg O_2 dm^{-3}) respectively. Inserting these values in the vertical profiles (Fig. 9) gives the critical depth separating two ecotopes

the bottom, in the region of the steep oxygen gradient, the concentration fell only very slowly during the night (Fig. 10). This contrasts with the conspicuous diurnal oxygen minima characteristic for eutrophic ponds [13, 24, 26].

Short-term oscillations of the physicochemical parameters at fixed depths are superimposed on their daily fluctuations. The amplitude of these oscillations (Fig. 10) is related to the vertical gradient of the respective parameter at the depth of measurement (Fig. 9). Oxygen concentration, pH, and temperature were correlated both in the vertical profiles and in the continuous registration at 3.5 m (Fig. 11). This correlation at a depth where oscillations predominate over daily fluctuations supports the interpretation of these rapid changes in terms of internal seiches and excludes the possibility of simple noise in the registration. The amplitude of the seiches can be estimated by comparison of the amplitudes and vertical gradients of the parameters; values between 0.1 and 0.2 m were independently deduced from the oxygen, temperature, and pH measurements at the depth of 3.5 m (Figs. 9 and 10). For the interpretation of vertical profiles measured on descent and ascent, the rapid, oscillatory displacement of different bodies of water may be even more important than the relatively slow changes in dissolved oxygen within a body of water (for an extreme case of the former type see Fig. 7, 78-06-15, 14—16 h; note the simultaneous changes in oxygen, pH, and temperarature).

Various ecological parameters in aquatic biotopes are correlated [6, 14, 29] and the study of these physicochemical relationships is substantially facilitated by the simultaneous in situ measurement of these parameters. For example, the temperature-pH relationship of a shaded and an unshaded sediment surface is not constant [6]. A comparable change in the temperature-pH and the oxygen-pH relationship was observed between the well-irradiated water column and the water column near the sediment in the lake (Figs. 9 and 11). The intercepts of the regression lines define a critical depth separating the water column into different ecotopes (Fig. 9). The point of inflection in the oxygen profile provides a definition of the critical depth in static terms (concentrations). However, changes in the correlations of ecological parameters indicate that

different mechanisms prevail in each ecotope. This paves the way toward a better understanding of the dynamics and regulatory interactions in ecosystems and may have a bearing on the functional interpretation of algal distribution, critical light intensities, community respiration and other processes.

6 Discussion

In this study I have investigated some of the pitfalls and limitations of discrete sampling of the water column for the measurement of oxygen stratification by the Winkler method that result from high spatio-temporal resolution. In situ measurement by POS gives an undistorted picture of the oxygen dynamics in time and space. The need for continuous or semicontinuous profiling of physicochemical parameters was recognized long ago [17, 27, 28]. The determination of microstratifications of temperature and salinity revealed an unexpected complexity and heterogeneity of the water column in the oceans, and the application of in situ profilers equipped with additional physicochemical sensors, namely POS, stimulated a revolutionary development of various disciplines in oceanology.

With this in mind, it is hard to conceive why the in situ measurement with POS is not more generally and rigorously applied in limnological surveys and for routine monitoring of aquatic systems. The reasons may be economic. Most chemical and biological analyses require some kind of sampling procedure combined with determinations after transport to the laboratory. In a purely sampling-type study, relatively little time is saved by using POS, and the comparability of measurements in situ and in samples may possibly be restricted. Apart from methodological objections to discrete sampling, however, the economic rationale shifts if additional parameters such as depth, temperature, pH, conductivity or light intensity and transmission are transmitted by in situ sensors. In semicontinuous profiling simple registration is possible by reading from the electronic instruments. A continuous record of the water column requires automatic recording of the signals on an X-Y recorder, high currents on fast-reacting POS or mathematical correction for time delays [11, 27]. Continuous profiling is the method of choice for investigations in deep lakes and oceans, but imposes technical and economic difficulties in studies of shallow aquatic systems.

Apart from the problems associated with volume samplers, there are probably equally as many sources of error in chemical and electrochemical methods of dissolved oxygen analysis. Interference has to be expected for both methods, especially in natural low-oxygen environments and anoxic waters. In the presence of hydrogen sulfide a special modification of the Winkler method with the simultaneous measurement of H_2S should be applied [9]. An ordinary POS will also produce erroneous results, and should be replaced by an H_2S-insensitive sensor (Chap. I.6). Just as a short description of chemical oxygen analysis (App. D) cannot provide a general guideline for every kind of field situation, the instructions provided by manufacturers of POS merely constitute an aid to users, but are not a guarantee for precision in the frequently cited range of ± 1% (see Chap. I.2). A few unsatisfactory encounters with POS may elicit aversion to the apparently fallible electrochemical method and motivate a return to the reassur-

ing safety of the traditional Winkler titration method. The chemically trained limnologist may find it easier to judge the reliability of his Winkler dissolved oxygen analysis than to estimate confidence limits of electrochemical in situ measurements. In fact, theoretical and practical guidelines for the Winkler analysis are exhaustively reviewed in many text books, while field applications of POS are treated with an apparent restriction to some theoretical aspects. Thus it seems that tradition and prejudice may be responsible for the continued preference shown by many laboratories for the chemical analysis of dissolved oxygen despite the various advantages of POS in routine measurements in situ.

References

1. Amann E, Gnaiger E (1979) Jahreszeitliche Abhängigkeit der Nahrungszusammensetzung von Regenbogenforellen (*Salmo gairdneri*) im Kalbelesee (Hochtannberg, Vorarlberg). Oesterr Fisch 32:32–39
2. Atwood DK, Kinard WF, Barcelona MJ, Johnson EC (1977) Comparison of polarographic electrode and Winkler titration determinations of dissolved oxygen in oceanographic samples. Deep-Sea Res 24:311–314
3. Barica J, Mathias JA (1979) Oxygen depletion and winterkill risk in small prairie lakes under extended ice cover. J Fish Res Board Can 36:980–986
4. Boyd CE, Romaire RP, Johnston E (1978) Predicting early morning dissolved oxygen concentration in channel catfish ponds. Trans Am Fish Soc 107:484–492
5. Elgmork K (1959) Seasonal occurrence of *Cyclops strenuus strenuus*. Folia Limnol Scand 11: 1–196
6. Gnaiger E, Gluth G, Wieser W (1978) pH fluctuation in an intertidal beach in Bermuda. Limnol Oceanogr 23:851–857
7. Greenbank JT (1945) Limnological conditions in ice-covered lakes, especially as related to winter-kill of fish. Ecol Monogr 15:343–349
8. Hutchinson GE (1957) A treatise on limnology. I. Geography, physics, and chemistry. John Wiley and Sons, New York, pp 1015
9. Ingvorsen K, Jørgensen BB (1979) Combined measurement of oxygen and sulfide in water samples. Limnol Oceanogr 24:390–393
10. Kanwisher JW, Lawson KD, McCloskey LR (1974) An improved, self-contained polarographic dissolved oxygen probe. Limnol Oceanogr 19:700–704
11. Kersting K (1978) Automatic continuous oxygen- and temperature-profile measurements. Verh Int Ver Limnol 20:1216–1220
12. Knowles G, Lowden GF (1953) Methods for detecting the end-point in the titration of iodine with thiosulfate. Analyst 78:159–164
13. Kushland JA (1979) Temperature and oxygen in an Everglades alligator pond. Hydrobiologia 67:267–271
14. Lair N, Restituite F (1976) Projoect alpin O.C.D.E. pour la lutte contre l'eutrophisation. Lacs du massif central francais. II. Le Lac de Tazenat, interrelation entre paramètres. Ann Stn Biol Besse Chandesse 10:100–144
15. Lingeman R, Flik BJG, Ringelberg J (1975) Stability of the oxygen stratification in a eutrophic lake. Verh Int Ver Limnol 19:1193–1201

16. Mathias JA, Barica J (1980) Factors controlling oxygen depletion in ice-covered lakes. Can J Fish Aquat Sci 37:185–194
17. Mortimer CH (1974) Lake hydrodynamics. Mitt Int Ver Limnol 20:124–197
18. Nagell B, Brittain JE (1977) Winter anoxia. General feature of ponds in cold temperature regions. Int Rev Gesamten Hydrobiol 62:821–824
19. Pennak RW (1968) Field and experimental winter limnology of three Colorado mountain lakes. Ecology 49:505–520
20. Poole R, Morrow J (1977) Improved galvanic oxygen sensor for activated sludge. J Water Pollut Contrib Fed March 1977:422–428
21. Reynolds JF (1969) Comparison studies of Winkler vs. oxygen sensor. J Water Pollut Contrib Fed, Washington, Dec 1969, pp 2002–2009
22. Ruttner F (1955) Über die Entstehung meromiktischer Zustände in einem kaum drei Meter tiefen Quellsee. Mem Ist Ital Idrobiol 8:265–280
23. Schindler DW, Comita GW (1972) The dependence of primary production upon physical and chemical factors in a small, senescing lake, including the effects of complete winter ogygen depletion. Arch Hydrobiol 69:413–451
24. Seki H, Takahashi M, Hara Y, Ichmura S (1980) Dynamics of dissolved oxygen during algal bloom in Lake Kasumigaura. Jpn Water Res 14:179–183
25. Talling JF (1973) The application of some electrochemical methods to the measurement of photosynthesis and respiration in fresh waters. Freshwater Biol 3:335–362
26. Uhlmann D (1966) Produktion und Atmung im hypertrophen Teich. Verh Int Ver Limnol 16: 934–941
27. Landinham Van JW, Greene MW (1971) An in situ molecular oxygen profiler. A quantitative evaluation of performance. Mar Technol Soc J 4:11–23
28. Westerberg H (1972) A free falling polarographic oxygen sensor. Medd Havsfiskelab Lysekil 126:1–25
29. Webb KL, D'Elia CF (1980) Nutrient and oxygen redistribution during a spring neap tidal cycle in a temperature esturay. Science 207:983–985
30. Wilcock RJ, Stevenson CD, Roberts CA (1981) An interlaboratory study of dissolved oxygen in water. Water Res 15:321–325