Oxygen Transport in Waterlogged Soils, Part II. Diffusion Coefficients

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INTRODUCTION

As previously outlined several equations are available and have been used for soils and plants. All of them are some form of first Fick’s law as given by

\[ \frac{dQ}{dt} = -DA\frac{dc}{dx} \]  

Equation (1) illustrates some important aspects of aeration in waterlogged soils; first, \( D \) is a property of the medium and the gas, and is affected by temperature \( T \). Likewise, the amount of diffusing substance \( dQ/dt \) is a direct function of the cross-sectional area \( A \) and inversely proportional to the distance \( x \). In fact, increasing the water content of air-dry soil, drastically decreases \( A \) and creates a further resistance for the flow of oxygen through water films around root plants, soil microorganisms and soil aggregates. The solid phase is also limiting the cross-section of surface of the free gaseous diffusion and the length and tortuosity of diffusion path in soil. In most of cases, soil gas porosity and tortuosity of soil voids are expressed in the equations of diffusion as a broad “diffusion coefficient” (apparent coefficient diffusion).

The process of soil respiration is complicated, involves many parameters, and is difficult to realistically quantify. With regard to the oxygen supply, it is convenient to distinguish “macro” and “micromodels” (DeWilligen and Noordwijk, 1984; Obando, 1990), and hence, the flux of oxygen is assumed to have two steps. The first step is related to oxygen diffusion from the atmosphere and the air-filled porosity. The second step is related to the oxygen diffusion through water-films in and around plant roots, soil microorganisms and aggregates. Because of these models we obtain coefficients of macro or microdiffusion, rates of macro or microdiffusion, etc. (Kowalik, 1985). In the macrodiffusion process oxygen is transferred in the soil profile, mainly from the soil surface to a certain depth of the root zone, while microdiffusion deals with the flux over very short distances. Both processes, macro and microdiffusion are highly influenced by soil water content. Of course, if water is added to the soil, the result is that the air-filled porosity decreases and at the same time the thickness of soil water-films around plant roots and aggregates increases. Consequently, both macro and microdiffusion decrease.

Diffusion coefficients in the macromodel process

During the last 40 years, several investigations have been made on diffusion of gas through porous media. Currie (1960) proposed that the oxygen diffusion in soils can be described by

\[ \frac{D_g}{D_0} = b \varepsilon^m \]  

(2)
where \( D_e \) is the diffusion coefficient in soil (cm\(^2\)/min), \( D_0 \) the gas diffusion coefficient in free air (cm\(^2\)/min), \( \varepsilon_g \) the air-filled porosity, \( b \) is a coefficient dependent mainly on the total porosity \( \varepsilon_0 \), and \( m \) a coefficient dependent on the air-filled porosity and the continuity and tortuosity of the flow path. The constant \( m \) has a value which depends on the shape of the soil particles, but generally falls between 1 and 2, for dry materials. The constant \( b \), ranges from 0.5 to 1.0 and depends on the value chosen for \( m \). When water is added to the porous material, the cross section for flow is reduced and the tortuosity of the flow path in increased. As water content approaches saturation, dead-end pores may be formed that contribute to air-filled porosity, but do not aid gas diffusion. Theoretically, the parameter \( m \) should be a function of \( \varepsilon_g \) but in the range of \( 0.1 < \varepsilon_g < 0.4 \), the value of \( m \) is constant for many soils, making it easier to determine \( D_e \) (Sallam et al., 1984).

Commonly proposed macrodiffusion models have been described by several authors (Campbell, 1985; Kowalik, 1985; Sallam et al., 1984; Obando, 1990; Obando, 2003). Some of the values for \( m \) and \( b \) as indicated from the source are given in table 1.

### Table 1. Some examples of the models for diffusion coefficients as a function of air-filled porosity \( \varepsilon_g \).

<table>
<thead>
<tr>
<th>Model</th>
<th>( D_e/D_0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Currie</td>
<td>( b\varepsilon_g^m ) (( b \leq 1 )) and ( m ) are functions of the materials investigated.</td>
</tr>
<tr>
<td>Bakker and Hidding</td>
<td>( \varepsilon_g^2 ) for well structured soils</td>
</tr>
<tr>
<td>Bakker and Hidding</td>
<td>( 3\varepsilon_g^3 ) for heavy and puddle soils</td>
</tr>
<tr>
<td>Millington and Quirk</td>
<td>( \varepsilon_g^{3.33} \varepsilon_0^{-2} ) for wet soils (( \varepsilon_0 ) = total porosity).</td>
</tr>
<tr>
<td>Sallam et al.</td>
<td>( \varepsilon_g^{3.1} \varepsilon_0^{-2} ) soils under relatively low air-filled porosity</td>
</tr>
</tbody>
</table>

Most of the models proposed are reliable at air-filled porosities above 0.30. However, below this level there is a great variation among them. When Sallam et al. (1984) determined gas diffusion at low air filled porosity levels (0.05, 0.10, and 0.15), they obtained better agreement between calculated and measured \( D_e \) by reducing the exponent 3.33 in the Millington-Quirk model to 3.1. Therefore, the following formula for soils under relatively low air-filled porosity was proposed: (see table 1).

\[
\frac{D_e}{D_0} = \varepsilon_g^{3.1} \varepsilon_0^{-2}
\]  

(3)
Those models indicate the high influence of soil structure on soil aeration. For example for the Bakker-Hidding models; if one compares the diffusion coefficients for the soils with gas-filled porosity $\varepsilon_g = 0.14$, the puddle soil has $D_\varepsilon$ equal to 0.4 of the aggregated soils, but for the soils with air-filled porosity $\varepsilon_g = 0.70$, the puddle soil has a $D_\varepsilon$ equal to 0.1 of the aggregated soil, indicating the great influence of the soil structure particularly at low values of $\varepsilon_g$. Thus, for every individual soil sample it is necessary to measure the individual relationship between $\varepsilon_g$ and $D_\varepsilon$.

Methods of measurements of values of $D_\varepsilon$ as a function of $\varepsilon_g$ are described in the literature (e.g. Callebaut, 1987).

**Microdiffusion process**

As previously stated, the exchange of oxygen and carbon dioxide through the soil is mainly by molecular diffusion in the gas phase. Gaseous diffusion in soil may be expressed by (Currie, 1961)

$$\frac{\varepsilon C}{\partial t} = D_\varepsilon \frac{\partial^2 C}{\partial z^2} - S_r$$

(4)

or as:

$$\frac{AC}{\partial t} = \frac{D_\varepsilon}{\varepsilon} \frac{\partial^2 C}{\partial z^2} + \frac{S_r}{\varepsilon}$$

(5)

where the term $S_r$ is the apparent average sink or source expressed as moles of gas produced or consumed per unit time and unit soil volume. $S_r$ represents the rate of respiration, positive for carbon dioxide production, negative for oxygen consumption. Equation (5) may be solved for many appropriate boundary conditions. For example, in a uniform soil, active to a depth $L$ at which there is a layer impermeable to gas exchange, the oxygen concentration at depth $0 < z < L$ is

$$C_z = C_0 - S_r \frac{Lz - z^2 / 2}{D_\varepsilon}$$

(6)

This and other solutions have two factors in common: The concentration difference $(C_0 - C_z)$ is a function of depth, and is proportional to the ratio $S_r / D_\varepsilon$. Any increase in $S_r / D_\varepsilon$, whether arising from an increase in $S_r$ or decreased $D_\varepsilon$, increases the likelihood of oxygen concentration reaching some small and critical value below which some or all of the respiration processes would change from an aerobic to a less desirable anaerobic state.
On a large scale equation (6) is fairly realistic since aeration generally changes slowly and both $S_r$ and $D_\text{e}$ often decrease with depth which makes the ratio $S_r/D_\text{e}$ relatively depth invariant (Stolzy et al, 1981). However, if the gas phase is discontinuous somewhere within the soil profile, this assumption of constant $S_r/D_\text{e}$ will not hold for a soil profile, and the meaning of $S_r$ leads to the microsite concept introduced by Currie (1961). They have shown that most structural soils are bimodal with regard to diffusion. They concluded that the crumbs have their own particular relative diffusion coefficients $D_c$, which are mainly affected by the oxygen consumption $S_r$, the spatial distribution of the liquid phase, the pore size distribution and the size of the soil aggregates.

**Diffusion within the soil microstructure (microsite concept)**

The early mathematical treatments of gas diffusion in soil given in Fick’s law equations, deal with soil as a homogeneous porous medium, with a single diffusion coefficient for any set of physical conditions. Currie (1965) pointed out the limitations of this approach. As declared above, he has shown that most structured soils are bimodal with regard to diffusion. “…Most soils show heterogeneity of pore distribution. For example, soil with a highly developed natural ped structure, and cultivate soil with their crumbs and clods, have distinct zones of crumbs pores, separated by more continuous system of intercrumbs pores…measurements of diffusion in packing of soil crumbs show that intercrumbs pores contribute more per unit of their volume to diffusion through the packing than do crumbs pores…Diffusion to depth in heterogeneous soils will thus occur preferentially through intercrumbs pores, but the path to the respiring site will be completed within crumb pores that are partly or even wholly moisture-saturated. Any attempt to describe the aeration pattern in soils possessing such a bimodal pore distribution needs some knowledge of gas diffusion within the crumbs themselves.”

Currie (1961) presented expressions to describe the radial diffusion of oxygen towards the centers of waterlogged soil aggregates, which made it possible to estimate what fraction of a spherical aggregate would be anaerobic, if its radius, the external oxygen concentration, the diffusion coefficient, the solubility of oxygen, and the respiration rate were all known. For any given values for these parameters, there is a critical aggregate radius below which no anaerobic zone exists, and above this critical value the radius of the anaerobic zone rises rapidly with the radius of the aggregate. The relationship between these radii is given by (Smith, 1977)

$$r = r_a - 6D_c \left( \frac{C_w S_r}{S_r} \right)$$  \hspace{1cm} (7)

where $r$ is the radius of the aggregate, $r_a$ the radius of the anaerobic zone at the center of the aggregate, $D_c$ the diffusion coefficient of oxygen within the aggregate, $C_w$ the
concentration of oxygen in water, $S_w$ the solubility coefficient of the gas in water and $S_r$ the rate of uptake of oxygen by the soil. $r_o = 0$ when $r = r_c = (6D_cC_wS_w/S_r)^{1/2}$, which is the radius of the smallest aggregate which can have an anaerobic zone at the centre for a given value of $C_w$. Currie (1961) also made the point that the average respiratory activity of the soil is reduced when there are partially anaerobic aggregates within the profile, so the concentration of oxygen between aggregates at a given depth is higher than if the anaerobic zones were absent, even though aeration of the soil as a whole has deteriorated. In fine textured soils with a well-developed structure, water moves mainly in the relatively large interaggregates pores, so while the drainage of a saturated soil leads to a large increase in the rate of diffusion down the profile (macrodiffusion), it does not initially change the diffusion rate within the aggregates (microdiffusion), and the degree of anaerobiosis in the soil will mainly depend on the size of the aggregates (Smith, 1977). Measurements reported in the literature indicate that the smallest aggregate containing an anaerobic center would have a radius of 9mm, assuming $D_c = 10^{-5}$ cm$^2$.s$^{-1}$ and a respiration rate of $4.31 \times 10^{-7}$ cm$^3$CO$_2$•cm$^{-3}$ soil•s$^{-1}$.

**Diffusion Coefficient in soil aggregates**

Based on published data Smith (1980) showed that values for diffusion coefficient of gases within soil aggregates range from $10^{-2}$ cm$^2$.s$^{-1}$ for very dry aggregates to $10^{-6}$ cm$^2$.s$^{-1}$ for completely water saturated aggregates.

**Rate of oxygen uptake $S_r$**

In the context of soil microstructure, $S_r$ is defined as the rate of oxygen uptake (when uptake is not limited by lack of oxygen) per unit volume of aggregate, including intra-aggregate pore space, i.e. cm$^3$O$_2$•cm$^{-3}$•s$^{-1}$ aggregate. Thus, the rate of uptake per unit volume of soil, including inter-aggregate pores is $S_r(1-\varepsilon_a)$ where $\varepsilon_a$ is the inter-aggregate porosity (Smith, 1980).

Published values for $S_r$ have generally been in the range from $10^{-7}$ to $5 \times 10^{-7}$ cm$^3$O$_2$•cm$^{-3}$•s$^{-1}$ for most of soils (Kowalik, 1985), but the rate of uptake will vary considerably with soil temperature, organic matter content and the presence or absence of living plant roots or fresh crop residues. A reference value has been taken of $2 \times 10^{-7}$ cm$^3$O$_2$•cm$^{-3}$•s$^{-1}$ at 10°C, which may be varied in either direction (Smith, 1980). Certainly, after increasing the temperature from 5 to 10°C, $S_r$ was increased about 11% for every 1°C; for changes from 10 to 20°C it was increased about 6.7% per 1°C, and for changes from 20 to 30°C $S_r$ was increased 3.9 to 6.9% for every 1°C. Values of $S_r$ in the range from $10^{-8}$ up to $10^{-6}$ mg•cm$^{-3}$•s$^{-1}$ are true for most of the arable soils in nature (Kowalik, 1985).
Values of $S_r$ are influenced by other environmental factors such as soil water content and oxygen concentration. The influence of the soil water content $\theta$ on the $S_r$ was very small for higher values of $\theta$ and this range is important in waterlogged soils (Kowalik, 1985). The relation between values of $S_r$ and soil oxygen concentration in the soil air at depth $z$, $C_x$, is a bit more clear. In the range of changes of oxygen concentration from 21 to 10% the respiration was decreased by about 15%. For the values of $C_z$ equal to 5 and 2% the respiration was decreased to 40 and 70%, respectively. That is why some authors suggest that if $C_z$ is below 5%, we do not observe a typical aerobic soil respiration.

**Diffusion through the water-films**

The diffusion of oxygen through the gas phase into the soil profile from the atmosphere can be quick and effective if $\varepsilon_g$ is relatively large. In the liquid phase the diffusion is about $10^4$ times slower than that in the gas phase. It means that resistance to diffusion of 1000mm of the gas phase is the same as the resistance of liquid water-film of depth of 0.1mm. Consequently, thickness of the water-films $d$ create an additional resistance for the flow of oxygen from the gas phase to the surface of plant roots. The value of $d$ is influenced by the soil water content but the quantitative relation between $\theta$ and $d$ is unknown. Thus, the general equation of oxygen transfer in soils is

$$J = -D \frac{dC}{dx}$$

(8)

For oxygen flow through water-films we have (Kowalik, 1985)

$$J = -D' \frac{\Delta C}{\Delta x}$$

(9)

where $D'$ is the “effective” oxygen diffusion coefficient in the liquid phase, taking into account the tortuosity of soil pores and effective cross-section for diffusion. $\Delta C$ is the difference of oxygen concentration on the surface with contact with the gas phase and on the surface with contact with the root surface. $\Delta x$ is the thickness of water film $d$. For waterlogged soils, and taking into consideration the influence of soil tortuosity and effective cross-section of soil porosity, we have

$$J = -D' \frac{\Delta C}{d}$$

(10)

For waterlogged soils, Bolt (cited by Kowalik, 1985) reported a value for $D'$ equal to $2.5 \times 10^{-5} \text{cm}^2 \cdot \text{s}^{-1}$. 

Measurement of Oxygen Diffusion Rate

The polarographic method

Theory

The polarographic determination of oxygen diffusion rate is based on the characteristic of the current-voltage ($I_d$-$V$) curve obtained when oxygen in aqueous solution is electrochemically reduced in a cell in which one electrode, the cathode, consists of a sleeve-insulated thermo-pure platinum wire, while the other is some standard half-cell (e.g. saturated Ag/AgCl reference electrode) the oxygen being replaced by the flow from the surrounding soil. The term polarography was introduced by Herovsky and Shicata in 1925 who developed an apparatus to obtain the graphical representation of the voltage-current curves (Stolzy and Letey, 1964). The curves were called polarograms and the apparatus the polarograph. At present, polarography is a highly developed electrochemical method of analysis. The polarogram shows a step for each reducible species present in solution. This step is the characteristic potential and the height proportional to the concentration of the component. In favorable cases several components may be detected and determined quantitatively from the polarogram. To avoid the residual current due to the dissolved oxygen it is necessary to remove it by bubbling an inert gas (nitrogen or hydrogen) through the solution before the actual measurements. Thus, the limiting current is fixed only by the rate at which the element of interest can reach the electrode surface. It is from this practical principle that the platinum electrode technique was conceived. Oxygen dissolved in electrolytic solutions is easily reduced at both dropping-mercury electrode and platinum electrode and produces a polarogram of two waves of approximately equal height and extending over a considerable range. It has been stated that the first wave is due to the reduction of oxygen to hydrogen peroxide, and the second wave is ascribed to the reduction of hydrogen peroxide either to hydroxyl ion or to water. Thus, the following reactions take place at the surface of the electrodes:

a) In neutral or alkaline solution:

\[
\begin{align*}
O_2 + 2H_2O + 2e^- & \rightarrow H_2O_2 + 2OH^- \\
H_2O_2 + 2e^- & \rightarrow 2OH-
\end{align*}
\]

b) In acid solution:

\[
\begin{align*}
O_2 + 2H^+ + 2e^- & \rightarrow H_2O_2 \\
H_2O_2 + 2H^+ + 2e^- & \rightarrow 2H_2O
\end{align*}
\]
The limiting current $I$

There are two main mechanisms by which an electroactive substance reaches the surface of an electrode: migration of a charged species caused by the potential difference existing between the electrode surface and the solution, and diffusion of a substance from a region of high concentration to one of lower concentration. Successful polarographic measurements demand that the electroactive species reach the surface of the micro-electrode by diffusion, this being the only process amenable to straightforward mathematical treatment (Dennis et al., 1974).

In principle, limiting current (total current) that flows in a cell includes contributions from several different processes. It includes the residual current, the migration current and the diffusion current. The current that would flow in the absence of the substance of interest is the residual current; the migration current is the difference between the limiting current actually obtained and the limiting current that would be obtained in the absence of any electrostatic force, and the diffusion current reflects the rate at which the ions or molecules of the substance reach the electrode surface. In practice, the current that actually matters is the difference between the total current and the residual current, which is due to the presence of the substance of interest. This current is the so-called “wave height” (See fig. 1). The total current flowing will in fact be equal to the current carried by the ions undergoing normal electrolytic migration, plus the current due to diffusion of ions

$$I = I_d + I_m$$  \hspace{1cm} (11)

where $I$ is the total current, $I_d$ the diffusion current, and $I_m$ the migration current. In practical polarographic work the migration current is eliminated by adding an indifferent electrolyte to the system (e.g. KCl) in concentration so large that its ions carry essentially all the current but does not react with the material under investigation, nor at the electrodes within the potential range studied. Under these conditions the solution is maintained at a low, constant resistance, whilst the migration current of the species under investigation virtually disappears. The residual current is subtracted automatically from the total observed current.

In the determination of oxygen flux in soils the residual current due to impurities is too small to require correction (Lemon, 1962) and as declared earlier, the migration current is controlled by making the reference electrode large in comparison with the small area of the platinum electrode. Under these conditions equation (11) becomes

$$I = I_d$$ \hspace{1cm} (12)

The rate of diffusion of the oxygen to the electrode surface is given by Fick’s second law equation and the potential of the electrode is controlled by the Nerst equation (Stolzy and Fluhler, 1978) which also applies for the potentiometric method of measurement oxygen in soils. However, this method is out of reach from this
lecture; readers are recommended to review this subject in basic books of soil chemistry, e.g. Bohn et al. (1985).

![Diagram of Oxygen polarographic plateau in a soil suspension.](image)

**Fig. 1 Typical Oxygen polarographic plateau in a soil suspension.**

**The diffusion current $I_d$**

Of particular interest in polarography is the diffusion layer, a film of solution perhaps 0.05mm in thickness at the surface of the electrode (Dennis et al, 1974). By referring to the reduction of oxygen in a soil suspension, let us see what happens at the surface of the platinum electrode as its potential is varied (fig. 1). From A to B, at approximately –0.1V versus Ag-AgCl reference electrode, little, if any, oxygen is reduced and the current flow is negligible. At B, where the potential of the platinum electrode is equal to the decomposition potential of the oxygen ions (about –0.2V) the current suddenly commences to increase and the platinum electrode becomes depolarized by the oxygen ions which form H$_2$O$_2$, consequently a rapid increase in the current flowing through the cell will be observed. At the point C the current no longer increase linearly with applied potential but approaches a steady limited value at the point D. No increase in current is observed at higher cathode potentials unless a second compound, such as hydrogen depolarize the microelectrode.

At any point on the surface as a result of migration and diffusion from the main bulk of the solution always exceeds the number of oxygen ions which react and are deposited upon the electrode. At the point C the rate of supply of the oxygen ions from the main bulk of the solution to the microelectrode has become equal to the rate of their deposition. Hence at potentials more negative than point D, the concentration of undischarged oxygen ions at the microelectrode surface is negligibly small relative to the oxygen-ion concentration in the bulk of the solution. No further increase in
current passing through the electrolytic cell can be expected, since the limiting current is now fixed by the rate at which oxygen ions can reach the electrode surface. As a consequence of this electrolysis, a concentration gradient is established, causing oxygen to diffuse from the bulk of the solution toward the surface of the electrode. If oxygen did not diffuse toward the electrode, the current would fall to zero almost instantaneously because the surface concentration of oxygen would drop to the value governed by the electrode potential and would change no more (Dennis et al., 1974). Nevertheless, the current is sustained by diffusion of additional oxygen toward the electrode under the influence of the concentration gradient. We are now in a position to appreciate the significance of the salient features of a typical current-applied voltage curve with reference to the reduction of oxygen. The minus sign to applied potential signifies that the platinum electrode is made the negative electrode (cathode).

The polarographic principle of platinum electrode

According to the simplest model for a diffusion-controlled process, the observed current is directly related to the difference between the concentration of the oxygen in the bulk of the solution $C$ and at the surface of the electrode $C_e$. Thus, we may write.

$$ I = D(C - C_e) $$  \hspace{1cm} (13)

where $I$ is the current and $D$ the diffusion coefficient of oxygen in the porous medium. Fundamentally, it is the potential of the platinum electrode that fixes the surface concentration $C_e$ of the oxygen. At potentials more negative than 0.7V versus Ag-AgCl for the reduction of oxygen, essentially all of the oxygen reaching the electrode surface is immediately reduced. Thus, the surface concentration is so small compared to the bulk concentration that the term $(C - C_e)$ becomes virtually equal to $C$, and the current attains a limiting value called oxygen diffusion current, which has been denoted by the symbol $I_d$. Hence,

$$ I_d = D \cdot C $$  \hspace{1cm} (14)

Analytical applications of polarography to soil oxygen evaluation rely upon the direct proportionality between the diffusion current and the bulk concentration of the oxygen in the liquid and gas phase. For diffusion of an electroactive substance to a stationary platinum electrode under polarographic conditions, in which all the diffusing ions or molecules move in the same direction, the current at an instant $t$ seconds after the electrolysis is begun is given by

$$ I_d = nFADt(dC/dx)_0 $$  \hspace{1cm} (15)
where \( n \) is the number of electrons consumed by each ion or molecule of the electroactive substance (\( n = 4 \) for oxygen), \( F \) the number of coulombs per faraday, \( A \) the area of the electrode and \( \frac{dC}{dx} \) is the concentration gradient normal to the electrode surface at time \( t \). Both \( I_d \) and \( n \) are taken to be positive for cathodic processes and negative for anodic ones, in accordance with the accepted sign convention for the platinum electrode. The factor measured is actually the electric current, which is related to the flux by

\[
I_d = nFAF_x
\]  

Here \( F_x \) is the oxygen diffusion rate to the surface of the platinum electrode in soil in \( \text{mol/cm}^2/\text{sec} \). Therefore,

\[
F_x = \frac{I_d}{nFA}
\]

In order to express results in minutes and grams rather than moles and seconds, the factor 60 and 32 are included, and instead of \( F_x \) the symbol ODR can be applied (Letey and Stolzy, 1964). Thus, equation (17) becomes

\[
ODR = 32 \cdot 60 \left( \frac{I_d}{nFA} \right)
\]

And finally ODR is calculated by

\[
ODR = \frac{32 \cdot 60I_d}{4 \cdot 96500A} \quad (\text{g} \cdot \text{m}^{-2} \cdot \text{min}^{-1})
\]

where \( I_d \) is in amperes.

**The physical principle of ODR**

Calculating the diffusive resistance offered by the liquid shell (water film of thickness \( d \)) surrounding the electrode, it will be shown that at equilibrium, the boundary conditions of the water-film/electrode diffusion-system are those of the simple case for steady-state conditions using cylindrical coordinates. It follows that diffusion must conform with the following equation

\[
\frac{Q}{t} = 2\pi hD_z \left[ \frac{C_0 - C_1}{r \ln(b/a)} \right]
\]
Concentration at the electrode surface $C_1$ is equal to zero and from what can be seen in fig. 2 it follows that the diffusion rate to the platinum electrode can be expressed by

$$\frac{Q}{At} = D' \frac{C_b}{a \ln(b/a)}$$  \hspace{1cm} (21)$$

where $Q/t$ is the diffusion rate in g·sec$^{-1}$, $D'$ the coefficient of oxygen diffusion through water films in cm$^2$·s$^{-1}$, $A$ the area of the platinum electrode in cm$^2$, $C_b$ the concentration of oxygen in the soil liquid phase on the border with the gas phase in mg·cm$^{-3}$, $A$ the radius of the cylindrical platinum electrode in cm, and $b$ the radius of the outside surface of water-film on the platinum electrode (platinum electrodes plus thickness of water-film $d$) in cm.

Fig. 2  Simplified model to show the geometry of a platinum electrode in relation to the distribution of oxygen in the soil profile and the microdiffusion calculations i.e. diffusion through the water films.

In equation (20) the resistance of the liquid path $d$ between the border with gas phase and the electrode surface is expressed by the term $a \cdot \ln(b/a)/(D' \cdot A)$. The liquid shell between electrode and the border with the gas phase may be considered as a lateral extension of the diffusion path in the soil profile (diffusion in the $z$ direction). Under normal conditions the direction of oxygen diffusion is from the soil
atmosphere into and through the water-films. This potential gradient can be very strong and have a great effect on $C_b$ (Raats, 1989). For the final segment of the diffusion path to the roots we have

$$J_x = D' \frac{C_b}{R_r \ln(R_w / R_r)}$$

(22)

From

$$F_x = \frac{I_d}{nFA} = ODR,$$

(23)

we have

$$ODR = 60 \cdot 10^{-3} \cdot D' \frac{C_p / R_r}{\ln(1 + d / R_r)}$$

(24)

Equation (24) quantifies the resistance of the water-film thickness $d$ relative to transport in the gas phase of the soil profile, and makes allowance for the fall in oxygen concentration which occurs across the water-film. For polarographical measurements the general equation of oxygen transfer in soil (first Fick’s law) can be expressed as

$$J_x = D' \frac{dC}{dx}$$

(25)

For oxygen flow through water films we have (Kowalik, 1985)

$$J_x = D' \frac{(C_b - C_a)}{(a - b)} = D' \frac{\Delta C}{\Delta x}$$

(26)

where $D'$ is the “effective” oxygen diffusion coefficient in the liquid phase, $\Delta C$ the difference of oxygen concentration on the surface in contact with the gas phase and on the surface in contact with the root surface, and $\Delta x$ the thickness of the path ($b - a$).

Substituting ($b - a$) by the thickness of water film $d$, we have

$$J_x = D' \frac{\Delta C}{d} \quad \text{mg cm}^{-2} \text{ sec}^{-1}$$

(27)

Taking a physical unit of rate of flow in g cm$^{-2}$ min$^{-1}$ it was proposed by Letey and Stolzy (1964) to introduce a symbol ODR (oxygen diffusion rate) where for one dimensional flow

$$ODR = 60 \cdot 10^{-3} J_x = -60 \cdot 10^{-3} D' \frac{\Delta C}{d} \quad \text{g cm}^{-2} \text{ min}^{-1}$$

(28)
Making the assumption that
\[ \Delta C = C - C_e = C_p - C_e \]  
(29)
and taking \( C_e = 0 \) for one-dimensional diffusion we obtain

\[ ODR = 60 \cdot 10^{-3} D' \frac{C_p}{d} \]  
(30)

From this notation, it is clear that the measurement of ODR is related at the same time to the measurement of the potential oxygen concentration in soil \( C_p \), the soil water regime related to the thickness of the soil water films \( d \), and the soil structure influencing the coefficient \( D' \) (Kowalik, 1985).

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