CHALMERS
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Institutionen för vattenförsörjnings- och avloppsteknik

Chalmers University of Technology
Department of Sanitary Engineering

Address:
Department of Sanitary Engineering
Chalmers University of Technology
S-412 96 Göteborg, Sweden

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In-sewer chemical assessment of microbiological processes

Malin Torell

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PREFACE

The Urban Geohydrological Research Group at Chalmers University of Technology is performing studies on sewers. Recent projects have been dealing with sedimentation processes in-sewers, real time flow control and microbiological and chemical processes in-sewer.

This thesis marks a continuation of two decades of research on sewer function and processes. Hans Bäckman looked at infiltration from stormwater to sewers - his ideas have been used by engineers where stormwater leaking from pipes enters the sewer system. Madjid Taghizadeh-Nasser investigated oxygen transfer in a pilot rig of a sewer pipe which leads in to this project which is more applied. Gustavo Perrusquia Gonzales looked at sediment transport in sewers. This study considers biological/chemical aspects during transport. More specifically I will show and evaluate how to characterise the sewage with help of redox potential and traditional parameters such as pH-value, oxygen concentration and conductivity. These parameters have been followed up by determinations of COD, BOD and alkalinity.

ACKNOWLEDGEMENTS

The project was funded by the Swedish Council for Building Research (BFR). The supervisor for the project has been Professor Torsten Hedberg and project leader Docent Gilbert Svensson. Initially a reference group was connected to the project consisting of Research Engineer Evy Axén, Professor Peter Balmér, Professor Torsten Hedberg, Docent Bela Kaffehr, Research Engineer Börje Sjölander, Docent Gilbert Svensson.

This thesis is based on advice from Bela Kaffehr: "Write down what you have done and explain the results you got." I am sorry to say that I have not fulfilled this advice because, then I would be still writing.

In addition to the people mentioned above, I would like to thank: my father for translation of large parts of this thesis from Swedish, to English. Greg Morrison for his advice that has saved a lot of time in my studies and for correcting english in this thesis and all earlier versions that have not been utilized. Lisbeth Teiffel for writing the earlier versions, and Inger Hessel for her final editing of this version.

I would like to thank Lars-Ove Sörman for lighting up my existence in the underground and for giving my instruments a better earth, and Gabriella Kaffehr for helping me with a particularly obstinate analytical instrument.

I would like thank: Inga-Lill Aronsson for trying to answer all my questions, Tibor Nemeth for inspiring me to try to use redox potential measurements for the determination of sewage quality, Doctor Elisabeth Ahlberg who has helped with interpretation of electrochemical measurements, Jan Forsberg who inspired me to use the mathematical model to explain the change in COD.

Furthermore, I would like thank my fellow sisters Chen Wei, Teresia Rd Wengström and Eva Lind Johansson: Chen for telling me to breathe deeply which prevented me from dying during my english spoken performance, and Teresia and Eva, who besides their help, forced me to take a break.

Furthermore, I would like to thank every one that has helped me with this work and a special thanks to those who have encouraged me when I needed it because without their help I would probably not have completed this thesis.

Finally I would like to thank my families for their help and for believing in me.

CONTENTS

SUMMARY

The survey of literature describes processes in sewage during transport from household to the wastewater treatment plant through the sewer net. Sewage consists of suspended material and soluble materials; exchange occurs continuously between the air, the water and the biofilm. The quality of the sewage as well as the type of microorganisms in the sewage is described. This study concentrates on quality changes in the sewage.

A model study demonstrated the connection between oxygen concentration, changes in chemical oxygen demand (COD), biological oxygen demand (BOD) and oxygen uptake. The models have been used in a experimental series where it was stated that oxygen uptake not only depends on the COD value but more on the ability of the materials in the sewage to be adsorbed on solid surfaces. A linear connection between the COD value and the α value in the oxygen transfer coefficient was found.

Besides the oxygen uptake models, two models for determination of COD have been suggested. The models are based on measurements of redox potential, one where the relative potential (the redox potential) is equilibrium controlled and one where the relative potential (the open circuit potential) is kinetically controlled. From this study it appears that the relative potential in sewage is kinetically controlled.

A comparison of the composition between microorganisms and sewage demonstrated that the proportion of phosphorous and nitrogen relative to COD were the same.

Theoretical calculations showed that at least a 50 % reduction of BOD was to be expected in the sewer net leading to regional wastewater treatment plants under aerobic conditions. However, measurements *in situ* gave that the redox condition strongly varied during the day, from aerobic to anaerobic conditions. Finally, in this study a description of the microorganisms development along the sewer or sewer net is proposed.

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A	Contact surface between water and pipe wall.
a	Specific surface.
A_{seg}	Cross-section of water.
b	Arc length.
b_a	The Tafel slope for the anodic reaction.
b_c	The Tafel slope for the cathodic reaction.
BOD_t	Biological Oxygen Demand. The subscript is the time of consumption in days.
C	Concentration.
C_m	Oxygen saturation.
C_0, C_t	Oxygen concentration at time 0 and at time t, respectively.
COD	Chemical Oxygen Demand. Carried out with dichromat unless otherwise specified.
COD_t	COD where the subscript is the time of incubation before determination.
COD_{max}^{ads}	Maximal COD concentration that could be adsorbed on the walls.
E	Relative potential.
E^0, E_0	Redox potential at standard condition.
E_0'	E_0 with one or more coefficients included.
$E_{Ag/AgCl}$	Potential *vs* Ag/AgCl electrode.
E_{eq}	Redox potential at equilibrium.
E_h	Potential *vs* nhe.
Eoc	Open circuit potential.
F	Faraday constant where $F=9.64846 \cdot 10^4$ As mol^{-1}.
f_d	Design factor.
G^0	Gibb's free energy at standard condition.
h	Water depth.
i_0	Exchange current density at the electrode surface.
i_c, i_a	Current density at the electrode surface for the cathodic and anodic reaction, respectively.
i_{lim}	Current density limited by mass transport.
k	A constant.
k^0	Reaction rate at standard condition.
K_La	Oxygen transfer value.
L	Pipe length.
n	Number of electrons.
nhe	Normal hydrogen electrode.
OU_t	Oxygen Uptake. The subscript is the time of uptake in days.
OUR	Oxygen Uptake Rate, the rate at which oxygen is consumed by microorganisms and/or by chemical processes.
P	Probability of a hypothesis.
pe	Population equivalent.
Q	Water flow.
R	Pipe radius.
R	Gas constant where $R=8.3143$ J mol^{-1} K^{-1}.
R_a	Surface load.
S.D.	Standard deviation.

T	Temperature in Kelvin.
t	Time.
t_R	Retention time.
$t(x)$	Statistical t-vale where x is the degree of freedom.
T_x	Lag time.
u	Water flow velocity.
α	Electron transfer coefficient in electrode reactions.
α	The factor that correlates the oxygen transfer value to the value in pure water.
β	The factor that correlates the oxygen saturation to the saturation in pure water.
η	Over potential.
τ, τ_x	Time constants.

1 OBJECTIVES AND SCOPE

Methods are considered here, which allow monitoring of the in-sewer degradation of sewage with the time, thus providing a basis for the determination of the degradability of sewage at an early stage. This will involve an estimation of the amount of oxidizable material, which can be expected to be degraded as well as the probable rate of this degradation at different times. In the future monitoring of the sewage based on real time control, the determination of degradability at different points in the sewer will be of higher importance in designing the sewernet.

This paper will deal with the value of continuous measurements of oxygen and redox potentials in determining the expected course of sewage degradation. The measurements will be made in a simulated sewer. Results from oxygen determinations will be compared with results from simultaneous respirometer measurements and COD determinations. The results of the redox potential measurements will be compared with values calculated from a theoretical model.

The investigation has been approached from the point of view that the most probable factors influencing the biological processes in wastewater during transport are:

* The concentration and state of the energy-yielding nutrients that are available to the microorganisms, i.e. their access to easily decomposable substances[1 2 3].

* The microbiological processing time in the pipe network and the concentration of relevant microorganisms and their lag time. The processing time is related to the time permitting suitable viable conditions for the microorganisms.

* Oxygen concentration and oxygen transfer rate in the wastewater. In lack of oxygen the biological processes will depend on other oxidisers. The redox potential will thus indicate which kind of oxidiser that can limit the rate of degradation and which species or community of microorganisms that will dominate.

In the laboratory experiments described in this paper neither the biofilm nor the activated sludge exist initially. It is only the microorganisms supplied with the sewage that the degradation capacity originated from. The disadvantage of this procedure is a comparatively low degradation rate. On the other hand the procedures will give an advantageous access to a broad abundance of microbiological species.

Theoretically it is possible to have a high degree of degradation already in the sewer[4]. However, *in situ*, the degree of degradation is difficult to determine. In this report the aim is to find a way to estimate the degradation to be expected in-sewer.

Further this report will present a model where the change in redox potential and oxygen concentration will indicate the quality change in the sewage.

To limit the extent of this study the influence of the biofilm which always is present on the pipe walls of the sewer has only been partially considered. Though it is true that the biofilm will influence the quality of the sewage during in-sewer transportation, it is not part of the sewage as long as it still is on the wall. Furthermore, with a biofilm build up the biofilm must be reproducible in the laboratory otherwise the degradation may depend of the quality of the biofilm.

When experiments are performed in simulated sewer pipes, the diversity of microorganisms must be considerably less than under conditions *in situ*, as no biofilm is initially present. However, this may cause a reduction of expected biological processes that can vary, which from an experimental point of view can be advantageous. All microorganisms with long generation time will be negligible.

2 INTRODUCTION

Modern sewage treatment plants effectively remove solids and oxygen-demanding substances before discharge into receiving waters. However, during recent years there has been an increasing emphasis on a more holistic approach to the operation of the sewer pipe system and treatment plant[5]. This is because the sewage treatment process not only depends on the plant process, but also on flow conditions in the sewers; this focuses on a need to consider the whole system.

Sewage treatment plants are sensitive to sporadic high loadings, such as that provided by stormwater in a combined sewer system. Variations in the stormwater volume can be equalised either by changing to a separate system, by constructing retention/detention tanks or local infiltration systems. These measures are mostly physical separations which take no account of the chemical/biological processes occurring in-sewer. Equalisation of flow volume will lead to a change in the in-sewer biological activity, possibly to a more oxygen-limiting environment. At present very little is known about the consequences of changing sewer transport conditions on the functioning of biological treatment in the sewage plant.

There can be no doubt that in-sewer microbiological activity alters wastewater quality and, ultimately, the result of the wastewater treatment[6] [7] [8]. Aquatic microorganisms regulate and modify the chemical composition of their environment through the production and consumption of organic matter, their involvement in nutrient cycling and their scavenging of trace metals and pollutants. Microorganisms also mediate specific reactions through extracelluar, usually enzymatic, reactions. Microorganisms also alter the reactivity and redox state of existing chemical species, change the nature of dissolved organic matter and, in some cases, produce reactive intermediates that can interact with solutes. Aquatic microbes both catalyze thermodynamically favourable reactions and maintain natural waters in a state of chemical disequilibrium[9].

Aerobic respiration in wastewater is mainly due to heterotrophic activity. The result is a rapid utilisation of oxygen which oxidises readily decomposed organic material. Oxygen-rich conditions in a long sewer pipe will therefore lead to a shortage of readily decomposed substances in the wastewater entering the treatment plant. This activity will also lead to a shortage of oxygen and anaerobic conditions. Anaerobic activity leads to the use of nitrate, nitrite and sulphate instead of oxygen and gives an increase in pH. Fermentation may occur in-sewer, although the symbiotic methane-producing bacteria have a long generation time and therefore methane formation is considered unimportant in sewer networks unless the wastewater temperature is high and/or the flow is low. The activity of the microorganisms will increase with increasing temperature as well as the oxygen saturation will decrease. At low flow there will be a thick anaerobic biofilm where the retention time will be long enough for anaerobic activity.

The remaining question is to what extent, and under which conditions, the sewer network alters wastewater quality in either a beneficial or a non beneficial way with respect to traditional sewage treatment.

The ambition of wastewater engineers today is to allow an equalisation of the hydraulic, and consequently the biological, load to the wastewater treatment plant. This is because variations in loading, both hydraulic and in terms of oxygen demanding substances, are considered to be one of the main problems in treatment plants. Equalisation of the hydraulic load can be achieved by regional treatment plants with extensive urban catchment areas. In this case the mean retention time of the wastewater in the sewer is long (more than 6 h). This means that there will be significant microbiological activity in the wastewater during in-sewer transport which in turn will affect subsequent wastewater treatment. Normally there is no attention paid to the microbiological processes in-sewer, largely because the processes are not regulated and no one has really cared if the processes are of importance.

Recently research has pointed out the importance of a correct characterisation of the influent at the wastewater treatment plant. Some of the main parameters are the readily degradable, slowly degradable and inert fractions of the organic content in wastewater[10]. Microorganisms will have a high impact on this distribution. On the other hand, the design of a sewer net will have an important influence on which kind of microorganism that will dominate.

The analysis methods of today for characterisation of sewage are circumstantial, take a lot of time or are incomplete. This thesis is therefore partly devoted to method development where oxygen uptake and redox potential (e.g. open circuit potential) have central positions.

2.1 Wastewater in-sewer

Wastewater is a heterogeneous system containing solid, gas and water phases. The solid phase can be defined[11] as anything from particles upwards of 10^{-9} m (Figure 2.1) to the size that the pipe system allows. This phase is to be found either as layers on the pipe-walls, suspended in the water and in the sediment. The solid phase always contains microorganisms whether it is in the suspended material in the water or fixed in the biofilm. Both biofilm covering the solid surfaces and biofilm eroded from the pipe wall contribute to the suspended materials in the wastewater.

Microorganisms will continuously influence the distribution of various substances between the solid phase and the water phases. It has been shown that a considerable part of this activity can be attributed to the biofilm[6 9 12 13 14] because particles and dissolved compounds such as organic material are adsorbed to solid surfaces. Such local concentrations of nutrients will result in increased microbiological activity thereby increasing the area of the solid surface and as a consequence also presenting a higher adsorptive capacity. On the other hand, with growing thickness, the stability of the biofilm will decrease. This, together with the stress on the biofilm caused by water velocity and turbulence, will result in erosion of the biofilm. The material balances in between the wastewater and the biofilm are demonstrated in Figure 2.2[6]. The oxygen and substrate decrease by uptake from both dispersed cells in the sewage and the biofilm. The number of dispersed cells is balanced on a certain level by growth and by having cells detached from the biofilm and attached to the biofilm. The biofilm and the dispersed cells will convert substrate to biomass, metabolites and products. Finally the biomass will convert to products after death and lysis.

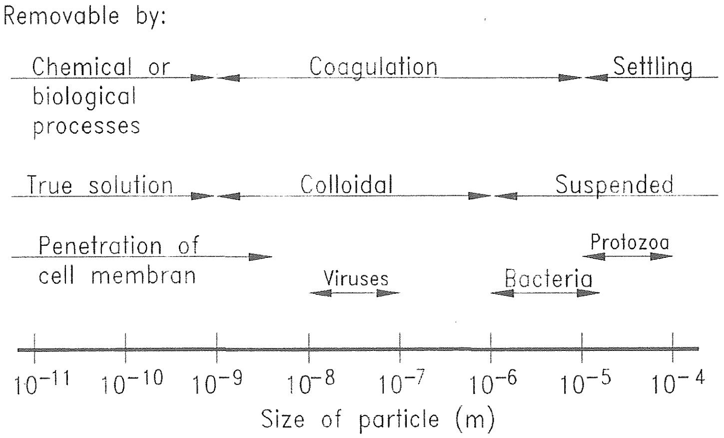

Figure 2.1 Relation between wastewater treatment and physical and microbiological aspects according to the size of particle.

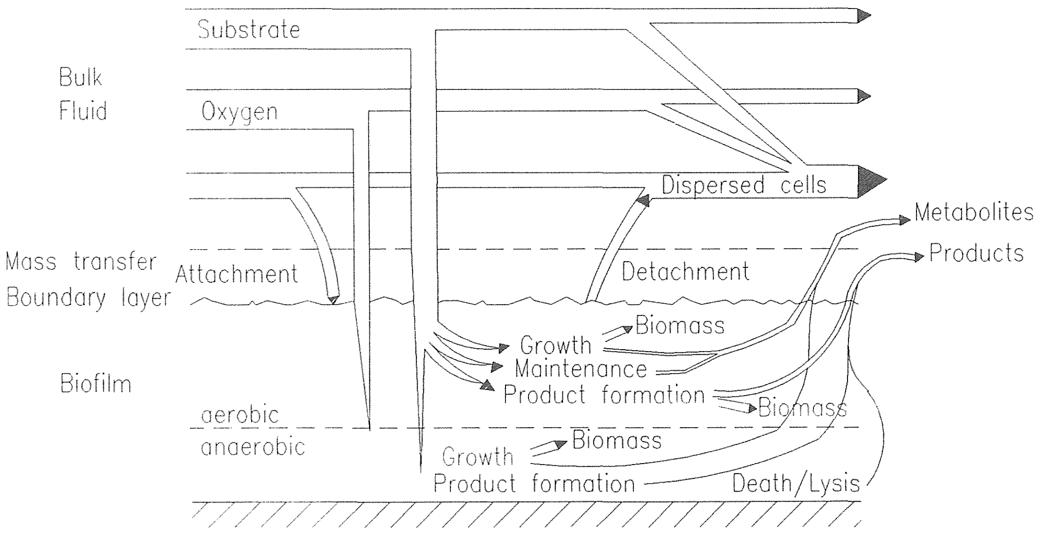

Figure 2.2 A model for biofilm development and exchange with sewage[6].

Wastewater in the sewer system is neither under chemical equilibrium nor steady state condition which results in continuous changes in the configuration of substances and exchange of substances between the phases. The continuous exchange of substances between the solid and water phases involves 1) precipitation/dissolution, 2) adsorption/desorption and 3) microbiological uptake/secretion. In addition, there is also an exchange between water and air, where oxygen is transferred to the wastewater, from which CO_2, NH_3, H_2S, H_2 and CH_4 depending of the condition are emitted. The amount of the various gases emitted varies with the microbiological activity. Transfer between the phases is summarised in Figure 2.3. The various processes will occur whether they are controlled or not, it is only the processing time that will vary.

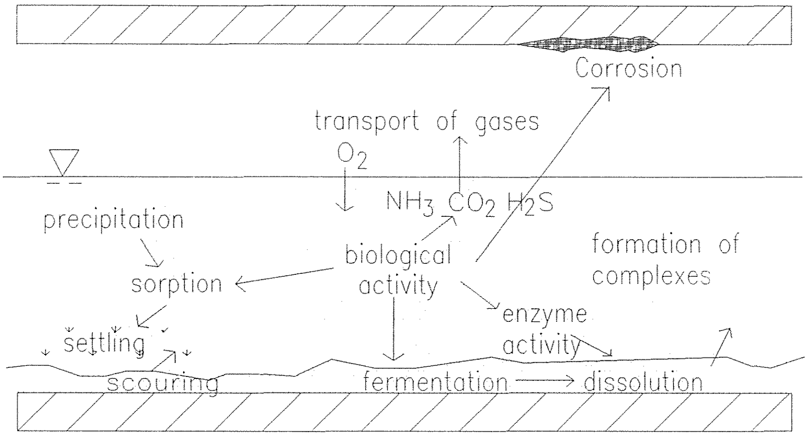

Figure 2.3 In-sewer processes involved in the transfer of matter between phases.

2.2 Municipal wastewater quality

Earlier studies have shown that there is a difference in concentration between the wastewater in the sewer close to the user and influent to the wastewater treatment plant[15]. But how much this depends on infiltration of groundwater or biological activity is hard to say. Furthermore, it can depend on where in the plant the sample of influent is taken. The quality of municipal wastewater within a city varies both temporally and spatially. In general the differences in daily mean concentrations between water sampled close to the user and influent to the plant are far less than the variations during the day[16] in both locations. Table 2.1 shows some typical concentrations of wastewater constituents.

Table 2.2 shows the quality of influent at wastewater treatment plants of different sizes but with similar population and similar geographical density and industrial composition. Differences between the treatment plants are small compared to the variation in Table 2.1, although there is a tendency that the smaller the plant, the more concentrated the sewage will be. Another tendency is that the largest plant has the smallest variation between minimum and maximum concentrations with regard to organic material. A comparison with Table 2.1 classifies the influent (see Table 2.2) as normal to diluted. This is expected as all sewer nets also transport groundwater and stormwater.

Table 2.1 Variations in wastewater quality[17].

Constituent	Conc.	Normal	Dilute
BOD$_7$ (mg O_2 l^{-1})	400	290	170
COD$_{Cr}$ (mg O_2 l^{-1})	740	530	320
Nitrogen (total as N) (mg N l^{-1})	80	50	30
Organic nitrogen/free ammonia nitrogen (% of N-total)	60/40		
Phosphorus (total as P) (mg P l^{-1})	23	16	10
Organic phosphorus (% of P-total)	20		
Alkalinity (mg HCO_3^- l^{-1})	183-427		

Table 2.2 Mean values of constituents found in the influent of three wastewater treatment plants during 1990.

Constituent	Rya WWTP		Hammargård WWTP		Lerum WWTP	
	mean	(min, max)	mean	(min, max)	mean	(min,max)
Flow (m^3/d)	350 000		13 300		6 914	
pH	7.2	(6, 8.6)	7.3	(6.8, 7.8)	7.2	(6.6, 8.1)
Cond. (mS/m)	98.2	(-, 185)	-		44	(22, 92)
COD (mg O_2/l)	435	(178, 816)	465	(150, 920)	470	(48, 960)
BOD$_7$ (mg O_2/l)	195	(58, 380)	208	(65, 520)	258	(60, 590)
N (mg N/l)	25.8	(9.2, 35.3)	36	(18, 51)	31	(15, 46)
P (mg P/l)	6.54	(1.8, 16.6)	9.0	(2, 18)	3.6	(1.3, 9.3)
Alk. (mg HCO_3^-/l)	-		-		2.7	(1.2, 4.6)
Persons*	793 000		28 500		15 200	

* The number of persons is based on the yearly BOD-loading.

Despite the fact that the wastewater will be diluted on its way to the treatment plant, theoretically there will always be enough organic matter in the wastewater to support a continuous biological process during transport. The only thing is whether the organic material is readily available for the relevant microorganisms, otherwise the degradation of the material will be preceded by a lag time which will vary depending on the type of microorganisms. There is also a risk in comparing analysis results from treatment plants of different size because the routines of sampling (frequency, type of sampling, etc.) may differ.

2.3 Wastewater disposal system

Sewer systems are primarily designed for the transport of municipal and industrial wastewater and to some extent also stormwater to a treatment plant. The main purpose of the sewer net is simply transport.

Increasing urbanisation in Sweden, starting some 150 years ago, and increasing demands for measures to be taken to avoid the spread of infectious diseases, has led to underground pipe-systems. As the increasing load on receiving waters was gradually found to give lasting effects at and around the outlets, a proper treatment of wastewater was called for. As a consequence at the beginning of this century small plants with mechanical treatment were put into operation[18]. The treatment has increased ever since and by 1965, 30% of the treatment plants were equipped for biological treatment. During the 1970's this number increased to 90% whereof 73% of the plants were also equipped with chemical treatment[19]. However, in most cases, further development was brought about by closure of the local plants and construction of interceptors providing larger and larger systems for the transport of wastewater from extensive urban catchment areas to regional treatment plants. The result has been the development of extended and rather complicated pipe-systems, in which wastewater is often transported up to 20-30 kilometres and consequently has a long retention time. For instance, 20% of the incoming wastewater to the Göteborg regional plant has a retention time in the sewer of 10-16 hours. The retention time in the plant is 8 hours with 2.5 hours in the biological step. Provided degradation of wastewater is looked upon as a purifying process, a completely uncontrolled treatment takes place during the time that the water is contained within the wastewater disposal system. Controlled treatment is at present restricted to the sewage plant.

The example from Göteborg is not unique. Most cities in Sweden and elsewhere are served by a few large wastewater treatment plants. The retention time in the sewer net is therefore often 2-4 times longer than the retention time in the treatment plant.

With regard to the idea of using the sewers for flow equalisation, the retention time in the sewer net will be even longer. However, a utilisation of the sewers to achieve equalisation volumes demands further knowledge of the biological processes in the sewage during transport to the treatment plant. Furthermore, this will be complicated because of the variation in the wastewater quality.

2.4 Control of microbiological processes in-sewer

There are three distinct ways of controlling the microbiological process

* Minimise the process until it can be neglected.

* Maximise the process until complete degradation is achieved.

* Optimise the process to suit the existing treatment plant and sewer net.

Biological processes can be minimised through a short retention time of the wastewater in the sewer net. This can be achieved by placing the final treatment close to the user or by increasing the water velocity. However, this means that the advantage of hydraulic equalisation will be lost. A more extreme procedure is to preserve the wastewater by cooling, adding preservatives or by irradiation. These procedures are unrealistic because of the impact on the subsequent treatment.

To achieve a complete degradation of the wastewater, the retention time and/or the biofilm area has to be increased[20]. Besides, there has to be an increase of the availability of oxidising agents, usually by increasing the oxygen transfer[8] or by the addition of nitrate[21].

The final option is to optimise the processes so that the influent to the treatment plant will have a proper composition and a smooth flow variation. To achieve this the readily biodegradable fraction in the wastewater should be maintained or increased during transport through the sewer until the wastewater reaches the treatment plant. Conceivable ways are to promote aerobic or anaerobic hydrolysis and fermentation (e.g. formation of volatile fatty acids) in the sewer system[22].

The last point may be the most attractive, because in addition to the present ambition to reach a hydraulic equalisation at the treatment plant there will also be a quality equalization. The only problem is to get the proper quality. A prerequisite to achieving this is an understanding and identification of the microbiological processes in the sewer net to be able to more easily describe the ideal sewer system.

2.5 Research domains in-sewer

Depending on the aim of the in-sewer research, the research can be divided into different domains which are illustrated in Figure 2.4. Three of them, sewage, sediment and biofilm are different both physically/chemically and in retention time in-sewer. The sewage contains soluble and particulate organic and inorganic substances, with a retention time of several hours. The sediment is particulate and mainly inorganic with a retention time of weeks or months. The biofilm is mainly organic with different microorganic species and with a retention time that varies from hours to years. Between these systems there is a continuous exchange of materials and this makes the two last research domains, the material exchange between biofilm (sediment) and sewage, and the material exchange between sewage and air phase, of great interest.

2.5.1 Sewage

Some topics of this domain have been thoroughly investigated, both nationally and internationally. For example, the influent to the wastewater treatment plant (see table 2.1 and 2.2) has routinely and continuously been subjected to measuring and sampling. Sampling up-stream in the sewer is less common and has more to do with crises when dealing with how to prevent "bad smell", noxious or explosives gases. Now there is a need to characterise the sewage according to the biological model[10] (see Figure 2.5) were the relation between inert, biomass, slowly degradable, rapidly degradable and directly metabolisable is important for the following wastewater treatment. This relation will change during the sewer net transport but in which proportions is relatively unknown. Halkjaer- Nielsen *et al*[23] have presented a study directed towards this area.

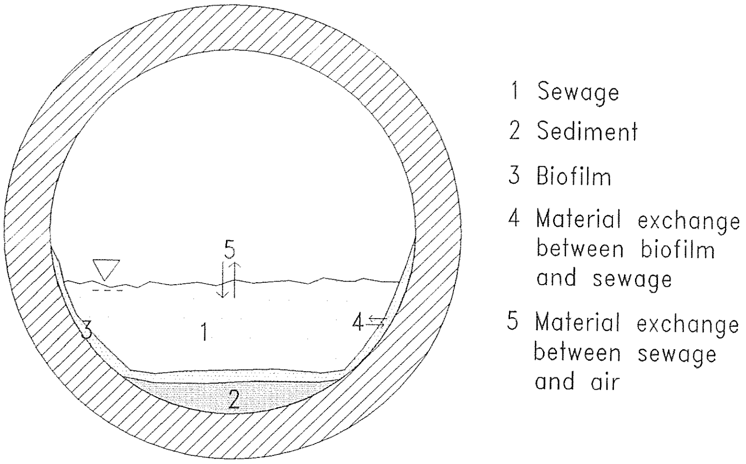

Figure 2.4 Research domain; sewage, sediment and biofilm with their interactions biofilm-sewage and sewage-air.

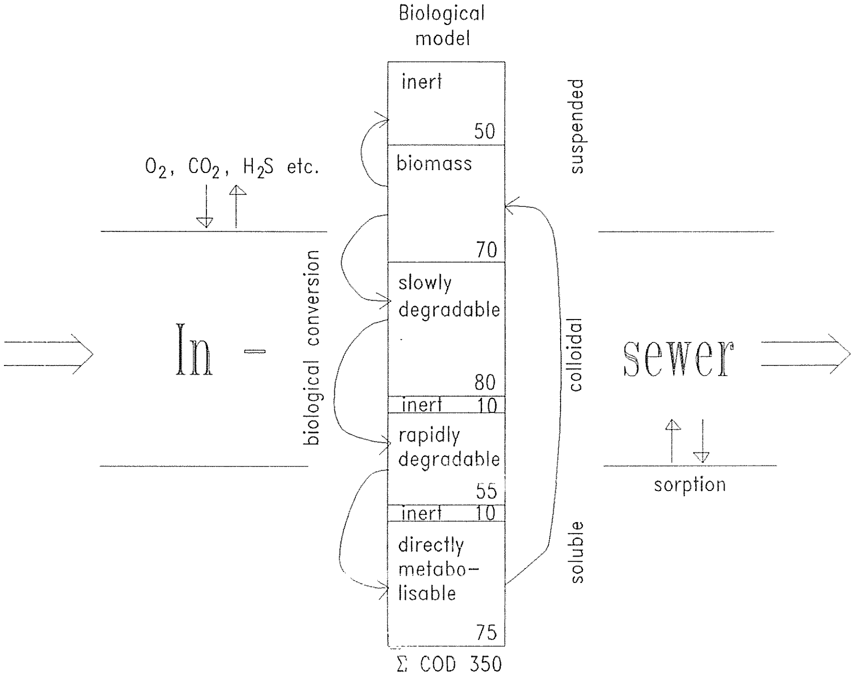

Figure 2.5 In-sewer impact of distribution of components according to the biological model

2.5.2 Sediment

Sewer sediments have been identified as major contributors to the pollution impact of urban stormwater, as they are responsible for the discharge of solids and chemical and biological pollutants into receiving watercourses[24]. Sewers with insufficient gradients suffer from sediment deposition and a reduction of hydraulic capacity due to these deposits contributing to general overloading problems and to the unintended functioning of combined sewer overflows. Because of economic problems, represented by the huge operational costs imposed each year on city managers for the recurrent cleaning-out of sewerage lines and tanks, several experimental studies, intended to solve the problem of deposition and accumulation of sediment in sewers, were undertaken around the world[25]. Various methods have been suggested for the design of self-cleaning sewers.

The origins of sediment and associated pollutants found in sewers are relatively well known. Except wastewater the source of settleable solids are, dust deposits, dirt and organic matters on surface areas and finally from damaged sewer lines[26]. Unfortunely it is not possible to formulate general rules for the rate and nature of surface wash-in to a sewer. The rates of build-up of sediments in sewers vary widely and whilst it is possible to estimate the build-up in small-sized collector sewers, no general rules are yet available to predict the rate of deposition in large sewers[27].

2.5.3 Biofilm

Recently it can be said that more or less all research dealing with wastewater also deals with biofilms. Revsbech et al[28] [29] have successfully measured the profile of pH, oxygen and H_2S with a microelectrode, which gives new possibilities to examine the biofilm. But the major part of biofilm research is made in wastewater treatment plants or in laboratories with the intention of optimising wastewater treatment.

2.5.4 Material exchange between biofilm and sewage

Whether the research domain is biofilm or sewage the exchange between biofilm and sewage cannot be excluded as seen in Figure 2.2. But depending on the domain in view the importance will differ. Typical for a biofilm researcher is that he will notice how the sewage quality influences the biofilm while the sewage researcher notices how the biofilm changes the sewage. The IAWPRC task group has combined experiences from both sides resulting in a general activated sludge model[2].

2.5.5 Material exchange between sewage and air phase

Most of the research to determine oxygen transfer is of an older date. Typically experiments determined the oxygen dependence of the water flow and depth in a conduit. Most of the experiments are carried out in clean water. Compared with sewage this will, in general, give a high transfer rate. More recently research has dealt with sulphide formation[30] and the problems this causes[31].

2.6 Biochemical aspects

It can be assumed that all kinds of microbiological activities are to be found in sewers and that different activities will take place in comparatively limited zones. Normally the zonal distribution is described vertically[32] with the aerobic zone at the top and the anaerobic at the bottom. But in the sewer, distribution is also horizontal[33 34 35 36], as well as vertical. This is because, as the microbiological activity increases through the sewer, the oxygen consumption will reach the limits for the maximal oxygen transfer, resulting in an insignificant aerobic zone. Therefore, in order to understand what is happening in a sewer it is necessary to regard all types of microbiological reactions and consider their consequences.

Microbiological degradation in the sewer can be looked upon as affected by different types of reactions, the type being determined by differences in access to electron acceptors which *per se* constitute the following reaction zones: (I) the aerobic zone in which degradation is affected by aerobic respiration, (II) the anoxic zone by anaerobic respiration with nitrate/nitrite as electron acceptor with facultative microbes, and (III) the anaerobic zone where the disintegration is through fermentation and anaerobic respiration and with strictly anaerobic microbes. A simplified description of the different reaction types is given in the following.

I. *Aerobic respiration.* Oxygen is the final electron acceptor.
Oxidation: organic compound $\rightarrow CO_2 + H_2O + 4e^-$
Reduction: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

II. *Anaerobic respiration.* An inorganic compound, nitrate/nitrite, sulphate or carbonate is the final electron acceptor.
Oxidation: organic compound $\rightarrow CO_2 + H_2O + 4e^-$
Reduction: $NO_3^- + 2H^- + 2e^- \rightarrow NO_2^- + H_2O$

III. *Fermentation.* An organic compound is the final electron acceptor.
Oxidation: organic compound $\rightarrow$ pyruvate $+ 2e^-$
Reduction: pyruvate $+ 2e^- \rightarrow$ lactic acid
(pyruvate is the common reducible intermediate compound)

A fermentable substance must be able to give both oxidizable and reducible intermediate compounds[37].

2.6.1 Aerobic zone and aerobic respiration

Aerobic respiration in wastewater is mainly effected by heterotrophic organisms. They acquire energy from easily decomposed organic material such as soluble organic monomers, acetates, etc., which are oxidized with the aid of oxygen. A consequence of oxygen-rich conditions in long sewer-pipes can be that wastewater when arriving at the treatment plants presents a shortage of easily decomposed substances, which subsequently will lead to a reduced purifying activity in the plants and a dilution of microorganisms in the return-sludge.

In the aerobic zone nitrogen containing organic material is principally decomposed according to the following scheme:

Biomaterial N → organic N → NH_4^+ → NO_2^- → NO_3^-

Consequently, periods of abundant access to oxygen will increase the relation between inorganically and organically bound nitrogen[38]. However, the residence time of wastewater in the sewer under aerobic conditions is too short for the nitrogen oxidizing bacteria to reach important quantities. The generation time, i.e. the time needed for a doubling of their number, is 6 days[39]. Corresponding times for most heterotrophic organisms are 30 minutes to 30 hours[37]. This means that ammonium formed in the sewer by reduction of nitrite and nitrate probably will be negligible throughout the treatment plant.

Sulphur appears in wastewater with different valencies, lowest and highest in sulphide and sulphate, respectively. The oxidation of sulphide to sulphate can occur by both chemical and biological processes. A considerable chemical oxidation of sulphide will take place in the aerobic zone at high ratios of sulphide/sulphate. In wastewater with high oxygen content (30 mg l^{-1}) the concentration of sulphate will amount to 2 per cent of the initial concentration of sulphide after just 1 minute[40].

2.6.2 Anaerobic zone

2.6.2.1 Anaerobic respiration

Anaerobic respiration is from a chemical point of view rather similar to the aerobic. The difference is that instead of oxygen the microorganisms chiefly use nitrite, nitrate and sulphate in the oxidation processes. A deficiency of oxygen leads to biological reductions of nitrite and nitrate to elementary nitrogen, dinitrogen oxide or ammonium, depending on which of the processes is most favourable microbiologically. Reduction to elementary nitrogen from nitrite will occur at comparatively high redox potentials ($E_{h, pH=7}$ = +685 mV). The corresponding redox potential, reduction of nitrite to ammonium is E_h = +340 mV. But thermodynamically elementary nitrogen is more favourable than ammonium above E_h = +150 mV. This means that ammonification is to be expected at low redox potential or/and low ammonium content. In practice Akunna *et al.*[41] have shown, with synthetic wastewater, that a COD/N-NOx ratio >53 will lead to ammonification.

The content of nitrate and nitrite is less than 1 per cent of the total content of nitrogen in wastewater, which means that no substantial denitrification can take place as early as in the sewer. Here the main processes involving nitrogen will be synthesis of new cells and deamination (Figure 2.6).

Nitrite/nitrate reducing microorganisms are facultative anaerobes, i.e. growth also takes place in the presence of oxygen. In contrast to this, reduction of sulphate, which occurs with a shortage of nitrite and nitrate, is an obligate anaerobic process. However, the conditions of the sulphate reducing microorganisms seem to need further examination;

it is known that they can use many different substrates, though the turn-over rate is strongly influenced by the type of substrate available[42].

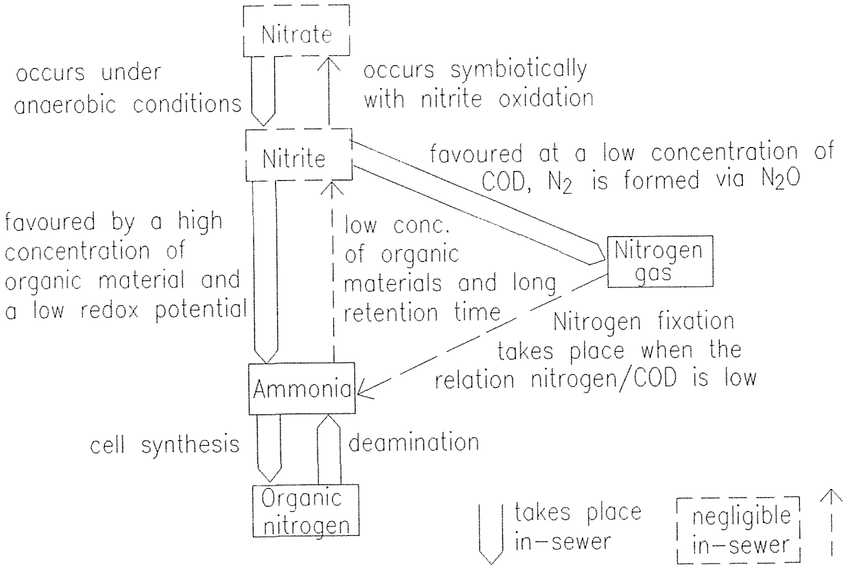

Figure 2.6 Main nitrogen processes in sewer.

2.6.2.2 Fermentation

There exists no distinct border between zones of anaerobic respiration and fermentation. However, in general, fermentation will not start prior to the formation of sulphide[43]. The fermentative processes leading to production of methane proceeds in three steps[44]. The first step is a transformation of complex organic compounds into higher organic acids. Hydrogen gas and acetate are formed in the second step, and methane gas, finally, in the third. As the methane producing bacteria have a considerably long generation time of 6.5 d or more, it is only during warm and/or slow flow conditions that the third fermentative step really can be of importance in the sewage disposal system.

Aerobic and fermentative processes appear to be the most interesting to go into with regard to the sewer and in connection with what is said in earlier sections. Aerobic degradation to consume the soluble degradable substances and fermentation to produce soluble degradable substances. Which one depends of what will suit the treatment plant best. An alternative to aeration could be to dose with nitrate instead. Furthermore, with a preferred fermentation there will also be an undesired sulphide formation and this will be a problem to regulate.

2.6.3 Anoxic zone

Based on biological characteristics the anaerobic zone can be divided into several subzones. When it comes to wastewater it has been found practical to distinguish one particular zone, the anoxic zone. The definition of this zone is that the dominant microorganisms are facultative which means that they can live under both aerobic and anaerobic conditions. In a lack of oxygen they utilise nitrate and nitrite. The respiration has then changed from aerobic to anaerobic.

3 MODELS FOR OXYGEN UPTAKE AND POTENTIAL VALUES.

Models considered in this section will describe the quality changes with time in sewage in a simulated sewer. A simulated sewer where the sewage exchange with the surroundings is only through the gas-liquid surface. This is assumed to correspond to a package of sewage that is transported in the sewer.

3.1 The oxygen uptake in sewage

Changes in the concentration of oxygen indicates changes in the activity of aerobic microorganisms. In cases of known rate of oxygen transfer it is possible to estimate OUR (Oxygen Uptake Rate), the rate at which oxygen is consumed by the microorganisms and/or by chemical processes.

Under controlled conditions it seems possible to identify the relationship between OUR, oxygen content, BOD and COD in a sewage package with free access to air and removal of gases produced in the system but without any removal of the liquid and solid phases.

Under aerobic conditions the cumulative oxygen transfer and change in oxygen concentration will be the same as the measured biological consumption (BOD).

Theoretically the biologically oxidizable material will be a part of the total amount of chemical oxidizable material (COD). This means that biological oxygen consumption in sewage will lead to a reduction of COD. If the chemical oxidation is negligible which can be assumed in case of aerobic conditions then the COD reduction will be the same as the biological oxygen consumption.

There are fundamental differences in these ways to determine oxygen uptake. In the first two of the cases oxygen uptake is determined by the oxygen consumption and in the last case by the reduction of organic material. This must be considered in the modelling.

Theoretically the oxygen uptake during a certain period can be determined with the aid of COD analyses. Provided, however, that the total COD reduction is affected solely by oxidation monitored by oxygen concentration and further, that no organic material is delivered to the system after the start of the experiment. In practice, it is necessary to consider losses of COD other than those due to oxidation, as by:

1. Sedimentation.This can be prevented by increasing the rate of stirring during the sampling of test aliquots.

2. Surface adsorption. This cannot be avoided. COD reduction caused by surface adsorption can be expected to vary from sewage to sewage. On the other hand, it can be assumed that the reduction of adsorbed organic material will proceed faster than the reduction in the bulk[6]. This means that in the course of time organic material in the biofilm will be consumed whereupon the adsorption of new organic material will keep pace with the consumption. Consequently, in this case losses of organic material measured as COD through adsorption will equal zero.

3. Gas transfer. Transfer of gaseous oxidable substances such as hydrogen, methane and hydrogen sulphide can cause reduction of COD. However, this can probably be neglected even at oxygen content ≈ 0 mg l^{-1} if there is no biofilm at the start of the experiment.

4. Denitrification. This is probably unavoidable at oxygen contents ≈ 0 mg l^{-1} if nitrite/nitrate is present in the sewage. However, in sewage with a high consumption of oxygen there is generally no nitrogen bound as nitrite/nitrate at the start of the experiment but present as ammonia.

5. Nitrogen fixation. This can be neglected as the relation nitrogen/organic material is too great to favour a fixation of nitrogen.

Under these circumstances a change in COD noted for a certain period can be regarded to equal the change in BOD during the same period.

Further with an excess of oxygen the relation between OUR, Oxygen content, BOD and COD can be due to the limits mentioned above, be generalized in the following way:

1 The oxygen uptake rate, OUR, is the sum of the biological and chemical oxygen uptake rate.

2 The change in oxygen concentration in addition to the oxygen transfer rate will correspond to the change in oxygen uptake during time.

3 The change in BOD over time will be the same as the oxygen uptake rate with oxygen excess and if the chemical oxygen uptake is negligible. In practice there is no difference in the registration of chemical oxygen uptake and biological oxygen uptake. In a respirometer they will both be registrered as biological oxygen demand.

4 The change in COD over time will be the same as the oxygen uptake rate.

Figure 3.1 gives an idea of the different methods to determine oxygen uptake. a) shows the oxygen uptake as determined by measurements of the oxygen concentration. This method has the advantage that the uptake can be determined continuously at all oxygen concentrations provided the K_La-value is known. The disadvantage is the difficulty in determining the K_La-value. b) shows the oxygen uptake as determined by measurements in a respirometer. Disadvantages are the limited volume and the cumbersome equipment. c) shows the oxygen uptake as determined by COD-analyses. Disadvantages are the limited number of analyses and the fact that the original sample will be changed by the repeated withdrawal of test aliquots.

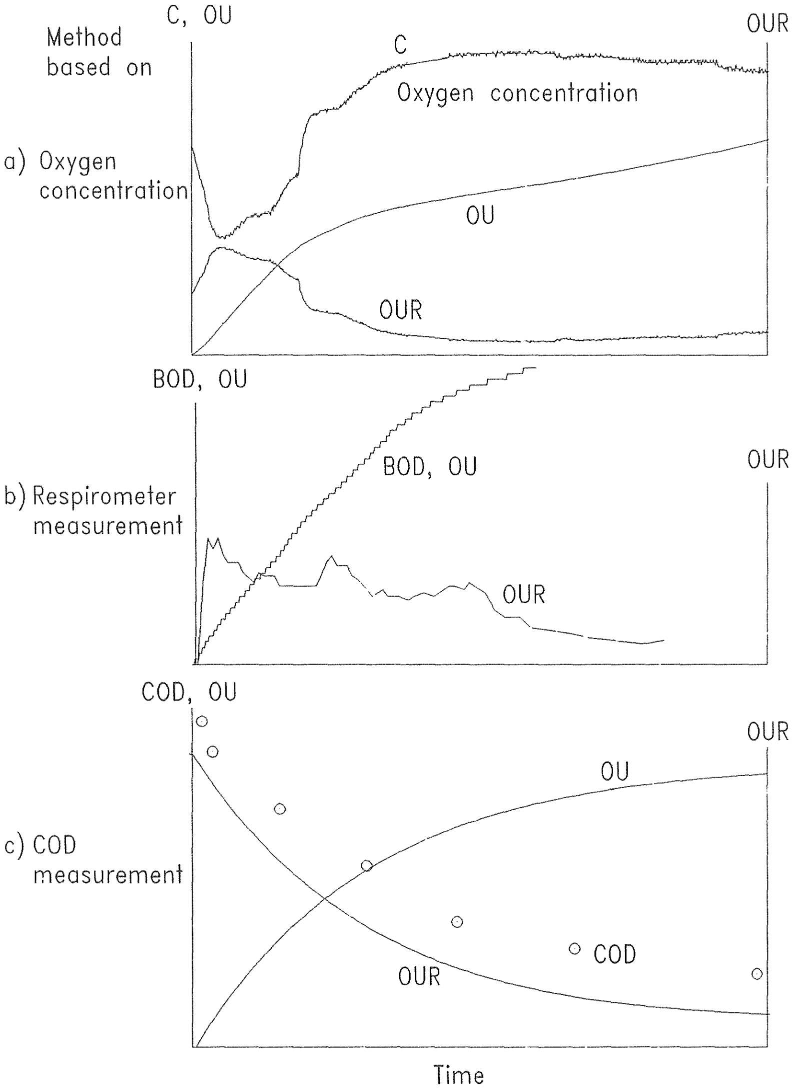

Figure 3.1 Presentation of oxygen uptake in sewage determined by different methods.

3.1.1 Oxygen uptake - the oxygen method

Calculations using determined values of oxygen concentration. Presupposing that the rate of oxygen uptake rate (OUR) equals the rate of oxygen transfer, it is possible to derive OUR from following the general formula for oxygen transfer rate:

$$\frac{dC}{dt} = K_L a(C_m - C) \tag{3.1.1}$$

where
C = oxygen concentration
C_m = oxygen saturation
$K_L a$ = oxygen transfer value

From Equation 3.1.1 the formula for OUR will be as follows:

$$OUR = \frac{dOU}{dt} = K_L a(C_m - C) - \frac{\partial C}{\partial t} \tag{3.1.2}$$

Integration of Equation 3.1.2 will be as follow:

$$OU_t = \int_0^t K_L a(C_m - C)dt - \int_0^{C_t} dC \approx \sum_{k=0}^{t} K_L a(C_m - C_k)\Delta t_k - \Delta C_k \tag{3.1.3}$$

In the experimental part of this work the contribution to the oxygen uptake that depends on the change in oxygen concentration ΔC_k during the time Δt_k will be excluded. The error in oxygen uptake because of this will be C_0 - C_t .

In the case of $C = 0$ mg O_2 l^{-1} from time = t_1 to time = t_2 Equation 3.1.3 will be

$$OU_{t_2 - t_1} = K_L a C_m (t_2 - t_1) \tag{3.1.4}$$

The determination of the $K_L a$ value is achieved by using a non oxygen demanding water, usually pure water. By integration from time t = 0 to t = t Equation 3.1.2 gives after simplifying the following equation:

$$\ln(C_m - C) = k - K_L a\, t \tag{3.1.5}$$

where
k is a coefficient = $\ln(C_m - C_0)$
C_0 is the oxygen concentration at the time $t = 0$.

The $K_L a$ values will be given by the slope showing the relation $\ln(C_m - C)$ *vs* t.

Normally the oxygen transfer value of sewage is related to that of pure water by a factor α and the corresponding values of oxygen saturation by a factor ß. Equation 3.1.3 will then be as follows:

$$OU_t = \sum_{k=0}^{t} \alpha K_L a(\beta C_m - C_k)\Delta t_k - \Delta C_k \qquad (3.1.6)$$

where α is a factor that correlates the oxygen transfer value to the value in pure water
β is a factor that correlates the oxygen saturation to the saturation in pure water

The value ß is usually regarded as equal to 1, whereas the α-values are expected to vary in a range of 0.4-1.1[45]. In the present experiments the K_La values have been calculated from the calculated OU_t values or the slope from oxygen uptake graph. Therefore the K_La values refer to sewage and not to pure water. The value for ß has been supposed to be equal to 1, which explains why tabulated values for oxygen saturation in pure water[46] could be used.

3.1.2 Oxygen uptake - the respirometer method

In a respirometer, unlike the conditions in the simulated sewer, there is no risk that the degradation will be limited by lack of oxygen. The measured values will consequently give an upper limit for the oxygen uptake (OU_t) during aerobic conditions.

$$OU_t = BOD_t - BOD_0 \qquad (3.1.7)$$

The value of BOD_0 is by definition equal to zero. It can be shown that the oxygen uptake can be well enough described by an exponential function as the following equation.

$$OU_t = BOD_\infty (1 - e^{-\frac{t}{\tau}}) \qquad (3.1.8)$$

where τ = time coefficient

By comparing the derivated function of OU(t) according to Equation 3.1.8 and the derivation of the measured BOD(t) it is obvious that Equation 3.1.8 is a simplified model of the true oxygen uptake process (Figure 3.2). The graph in Figure 3.2 based on the measured values shows the fine structure where one microbiological process follows another. This fine structure will be lost in the modelling graph. Despite this discrepancy it can be useful to use the model in comparison with other models.

Determination of oxygen uptake with the respirometer method will give the maximal oxygen uptake because of the excessive oxygen concentration. With other methods it is possible to allow a limited oxygen condition.

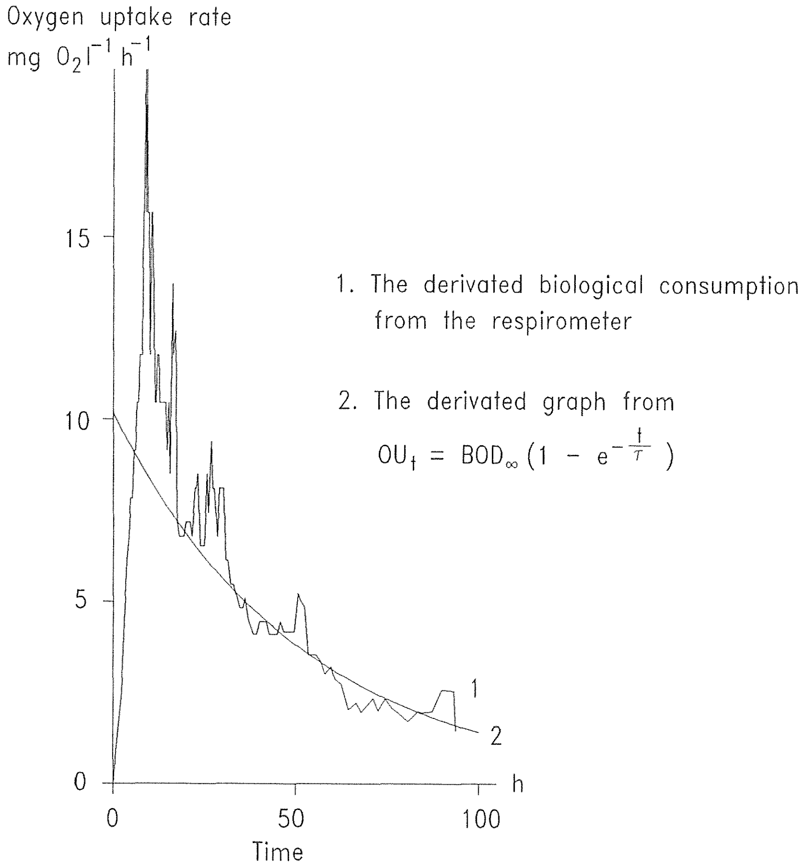

Figure 3.2 Example of a graph from the derivated function OU_t and from the derivated measured BOD_t values.

3.1.3 Oxygen uptake - the COD-method

The OU_t can also be calculated by using determined values of COD, with the following formula:

$$OU_t = COD_0 - COD_t \tag{3.1.9}$$

It is possible to determine the total oxygen uptake at each time by using a similar model as in Equation 3.1.8 but based on COD measurements provided there is an excess of oxygen. In the case of a limited oxygen condition the model will follow the same relation as in Equation 3.1.4. Consequently, the oxygen uptake according to the COD method will be described by two different equations, depending on the condition, as follows:

I. The uptake with an excess of oxygen means that the degradation is substrate limited:

$$OU_t = OU_\infty(1 - e^{-\frac{t}{\tau}}) \qquad (3.1.10)$$

where τ is a time constant
OU_∞ correspond to COD_0 - COD_∞.

II The uptake with an oxygen concentration ≈ 0 means that the degradation is oxygen limited:

$$OU_t = K_L a C_m t \qquad (3.1.11)$$

according to Equation 3.1.4.

In analogy with, for example, the adsorption of protein from a solution[47] it can be expected that the organic material in the sewage will be rapidly adsorbed on to available surfaces and the time required for adsorption will depend of the complexicity of the organic material. This means that the readily degradable material can be expected to be the first material that will be adsorbed on the surface.

Considering the appearance of a comparatively rapid built-up biofilm, that consist of adsorbed degradable substances that are disintegrated in the film. This will initially give a marked COD-reduction, which is then followed by a rather insignificant COD reduction despite a high oxygen uptake in relation to the low oxygen concentration. In this phase the main part of transferred oxygen will oxidise the degradable substances in the biofilm instead of the degradable substances in the bulk. While the organic material in the biofilm will be degradated the oxygen uptake in the film will increase until the total adsorbed COD in the film is the same as the total oxygen uptake in the film. The total oxygen uptake in the bulk will then be the same as the apparent oxygen uptake. This can be described as follows:

$$OU_t^{app} = COD_t^{ads} - OU_t^{film} + OU_t \qquad (3.1.12)$$

where $OU_t^{film} + OU_t^{bulk} = OU_t$
OU_t^{film} is the oxygen uptake in the film
OU_t^{bulk} is the oxygen uptake in the bulk
COD_t^{ads} is the degradable substance adsorbed on the surfaces in the simulated system.

By supposing that OU_t^{film} and COD_t^{ads} follow exponential functions and OU_t a linear function, which can be supposed in the case of oxygen concentration ≈ 0, it is possible to solve the summary equation to give the value of OU_t based on the measured COD value. The equations of COD_t^{ads}, OU_t^{film} and OU_t will be as follows:

$$COD_t^{ads} = COD_{max}^{ads}(1 - e^{-\frac{t}{\tau_1}}) \tag{3.1.13}$$

$$OU_t^{film} = COD_{max}^{ads}(1 - e^{-\frac{t-T_2}{\tau_2}}) \tag{3.1.14}$$

$$OU_t = K_L a C_m (t-T_2) \tag{3.1.15}$$

where	COD_{max}^{ads}	is the maximal concentration of adsorbed COD
	t	is the time
	τ_1	is the time constant for the adsorption to surfaces.
	τ_2	is the time constant for the degradation in the biofilm
	T_2	is the lag time for the degradation in the whole system as well as in the biofilm

By combining Equation 3.1.12 - 15 the apparent OU is derived.

$$OU_t^{app} = COD_{max}^{ads}(1 - e^{-\frac{t}{\tau_1}})e^{-\frac{t-T_2}{\tau_2}} + K_L a C_m (t-T_2) \tag{3.1.16}$$

In the case of an oxygen concentration > 0 Equation 3.1.16 will be replaced with the following equation

$$OU_t = OU_\infty(1 - e^{-\frac{t-T_2}{\tau_3}}) \tag{3.1.17}$$

which will give a little more complicated formula than Equation 3.1.17

$$OU_t^{app} = COD_{max}^{ads}(1 - e^{-\frac{t}{\tau_1}})e^{-\frac{t-T_2}{\tau_2}} + OU_\infty(1 - e^{-\frac{t-T_2}{\tau_3}}) \tag{3.1.18}$$

but still possible to solve.

In the case of sedimentation the apparent oxygen uptake will be

$$OU_t^{app} = COD_t^{sed} - OU_t^{sed} + OU_t \tag{3.1.19}$$

but contrary to the case with the adsorption term, COD_t^{ads} - OU_t^{ads} that tends to go to zero as $t \rightarrow \infty$, the sedimentation term, COD_t^{sed} - OU_t^{sed}, will be > 0 as $t \rightarrow \infty$. Further modelling regarding sedimentation will not be done in this thesis.

3.2 Use of potential measurements to assess biological activity

Determination of the oxygen consumption by measuring the oxygen content gives no indication of the total amount of degradable material; for such information it is necessary to employ other parameters. With this in mind it was thought that the redox potential might be a possible parameter.

Furthermore, determination of the redox potential is of special significance in cases where the rate of oxygen consumption is of the same magnitude as the maximal rate of oxygen transfer (i.e. at an oxygen concentration = 0). Changes in the redox potential will thus indicate changes in the concentration of a redox couple or a shift to a different redox couple. If it is possible to identify the reason for redox potential changes, then it seems possible that the redox potential can function as a measure of the quality of the sewage. This might also be instrumental in providing a theoretically valid explanation of changes in the redox potential.

3.2.1 Oxidation processes and redox potential

The microbiological environment in a sewer will be regulated by oxidisers (electron acceptors) such as O_2, NO_3, NO_2 and SO_4. Conditions can vary from aerobic (O_2 as oxidiser) through anoxic (NO_3 and NO_2) to anaerobic (SO_4). Disproportionation catalysis of organic material (as the electron donor and acceptor) leads to fermentation under all conditions[48]. As organic material is a weak oxidiser, fermentation is unusual in sewer systems with O_2 being used first [1 2 3 49 50].

To a certain degree the type of oxidiser can be identified by simultaneous determinations of the redox potential and the concentration of oxygen. Theoretical values for redox potential can be calculated under equilibrium conditions from Gibb's free energy (Equation 3.2.1) and the Nernst equation (Equation 3.2.1).

$$E^\circ = -\frac{\Delta G^\circ}{nF} \qquad (3.2.1)$$

$$E = E^\circ - \frac{RT}{nF}\ln\left(\frac{red}{ox}\right) \qquad (3.2.2)$$

where
n = number of electrons in the half-cell reaction
F = Faraday constant
T = Temperature
R = Gas constant

Calculated and measured redox potential values for different biochemical processes have been assembled in Table 3.1 and where necessary recalculated to give E_h, the relative potential *vs* the normal hydrogen electrode (nhe). These values are pH dependent and therefore pH is an important parameter to measure in-sewer.

In the aerobic zone heterotrophic oxidation with an optimal E_h of +100 mV is thought to dominate. Nitrification is probably unimportant in-sewer as a generation time of at least 6 h is required. Under anoxic conditions, where reduction of nitrate/nitrite occurs, there will be a tendency towards low E_h values. This is because the thermodynamically favoured end product under high carbon content conditions, NH_3, gives $E_h < -230$ mV [51]. Anaerobic and fermentation products result in E_h values down to -400 mV.

At relative potentials during anaerobic condition in sewer it is thought that the electrode is poisoned[52] [53] and is generally mentioned as a reason for not using redox potential measurements. However, theoretical calculations of redox potential and experimental data have been found to agree well in wastewater[54].

3.2.2 The potential affected by in-sewer common parameters

With section 3.2.1 in mind there is a great temptation to try to use the redox potential to estimate the kind and concentration of oxidiser besides oxygen. According to the Nernst equation redox potential will be affected by oxygen, nitrate and sulphate as shown in 3.2.3 to 3.2.7.

$4e^- + 4H^+ + O_2 \rightarrow 2H_2O$

$$E = E_0 + \frac{RT}{4F}\ln[O_2] + \frac{RT}{F}\ln[H^+] \tag{3.2.3}$$

$5e^- + 6H^+ + NO_3^- \rightarrow \frac{1}{2}N_2 + 3H_2O$

$$E = E_0 + \frac{RT}{5F}\ln\frac{[NO_3^-]}{(P_{N_2})^{\frac{1}{2}}} + \frac{6RT}{5F}\ln[H^+] \tag{3.2.4}$$

when P_N constant equationen can be simplified as follow.

$$E = E_0' + \frac{RT}{5F}\ln[NO_3^-] + \frac{6RT}{5F}\ln[H^+] \tag{3.2.5}$$

Where $E_0' = E_0$ with coefficient included.

Table 3.1 Calculated or measured potential values *vs* nhe for processes occurring in sewage pipes.

Zone	Biochemical process	Reaction	E_h interval (mV)	References
Aerobic	Heterotrophic assimilation	$\frac{1}{4}C + \frac{1}{2}H_2O \rightarrow \frac{1}{4}CO_2 + H^+ + e^-$	-200 - +400 opt. +100	55 56
	Autotrophic assimilation	$\frac{1}{2}NO_2 + \frac{1}{2}H_2O \rightarrow \frac{1}{2}NO_3^- + H^+ + e^-$	> +400	54
		$\frac{1}{6}NH_3 + \frac{1}{3}H_2O \rightarrow \frac{1}{6}NO_2^- + \frac{4}{3}H^+ + e^-$	> +340 $> +250_{pH=7.5}$	56 57
	Chemical oxidation	$\frac{1}{8}HS^- + \frac{1}{2}H_2O \rightarrow \frac{1}{8}SO_4^{2-} + \frac{9}{8}H^+ + e^-$	$> -240_{pH=7}$	54
Anoxic	Reduction of Fe^{3+}	$Fe^{3+} + e^- \rightarrow Fe^{2+}$	< +300	58
	Nitrate/Nitrite reduction	$\frac{1}{2}NO_3^- + H^+ + e^- \rightarrow \frac{1}{2}NO_2 + \frac{1}{2}H_2O$	< +200 $< +420_{pH=7}$	58 51
		$\frac{1}{5}NO_2^- + \frac{6}{5}H^+ + e^- \rightarrow \frac{1}{10}N_2 + \frac{3}{5}H_2O$	+125 - -25 < +450	59 53
		$\frac{1}{6}NO_2^- + \frac{4}{3}H^+ + e^- \rightarrow \frac{1}{6}NH_3 + \frac{1}{3}H_2O$	$< +345_{pH=7}$ $< +330_{pH=7}$ -260	51 60 61
	Nutrient interaction	Phosphorus release uptake	< +150 > 0	59 62 59 62
	Disappearance of microaerophiles and facultative anaerobes.	-	0 - -150 +50 - -100	58 56
Anaerobic	Significant diversity decrease	-	-150 - -350 +50 - -400 +50 - -450	58 55 56
	Sulphide formation	$\frac{1}{8}SO_4^{2-} + \frac{9}{8}H^+ + e^- \rightarrow \frac{1}{8}HS^- + \frac{1}{2}H_2O$	$< -240_{pH=7}$ $< -158_{pH=5.5-6.5}$ -200 - -300 < -100 < 0 < -230 $< -220_{pH=7}$	54 63 63 63 62 64 53 59
	Fermentation	complex organic substans → volatile fatty acid	-256 - -276 -265 - -272	59 62
		complex organic substans → amino acids	-265 - -220	65
	Methane formation	$H^+ + \frac{1}{8}CO_2 + e^- \rightarrow \frac{1}{8}CH_4 + \frac{1}{4}H_2O$	-250 - -310 $-300 - -310_{pH=7.1}$ $-276 - -283_{pH=7.1}$ $< -450_{pH=5-9}$ $-520 - -530_{pH=7.1}$ < -250, opt -330	59 56 62 43 62 53

At high C:N ratio (see section 2.6) the nitrate will mainly be reduced to ammonium.
$8e^- + 10H^+ + NO_3^- \rightarrow NH_4 + 3H_2O$

$$E = E_0 + \frac{RT}{8F}\ln\frac{[NO_3^-]}{[NH_4]} + \frac{5RT}{4F}\ln[H^+] \qquad (3.2.6)$$

$8e^- + 9H^+ + SO_4^{2-} \rightarrow HS^- + 4H_2O$ for pH > 7

$$E = E_0 + \frac{RT}{8F}\ln\frac{[SO_4^{2-}]}{[HS^-]} + \frac{9RT}{8F}\ln[H^+] \qquad (3.2.7)$$

It is well-known that the Nernst formula is only valid at chemical equilibrium and this is not the case with in-sewer wastewater. The resulting redox potential will instead of the equilibrium potential be a mixed potential and not so easy to foresee. If one overlooks kinetics on the electrode surface the mixed potential could be described as in formula 3.2.8.

$$\begin{aligned} E = {} & k + a\cdot\log[O_2] + b\cdot\log[NO_3^-] + c\cdot\log[SO_4^{2-}] - \\ & - d\cdot pH - e\cdot\log[NH_4^+] - f\cdot\log[HS^-] \end{aligned} \qquad (3.2.8)$$

where k and a-f are constants.

At a first look this equation has too many unknown parameters to be attractive. But with knowledge of the concentration of the parameter in the influent at the wastewater treatment plant as seen in chapter 2 the equation could be reduced. The variations in ammonium and sulphate concentration can be assumed to be negligible. The nitrate (and nitrite) is most of the time not detectable in-sewer. This means that the contribution from ammonium and sulphate can be incorporated in the constant k. The formula 3.2.8 can then be rewritten as follows:

$$E = k + a\cdot\log[O_2] - d\cdot pH - f\cdot\log[HS^-] \qquad (3.2.9)$$

After a longer period of an aerobic condition the sulphide will not be detectable which will reduce the formula even more:

$$E = k + a\cdot\log[O_2] - d\cdot pH \qquad (3.2.10)$$

There have been several researchers that have presented an empirically estimated connection between the measured potential and different parameters such as oxygen[65 66], nitrate[65], nitrate/COD[67]. But it has been difficult to find any conformity in their equations. This may be caused by different and vital experimental conditions. For example, Hediut and Thevenot[66] have, in the laboratory, estimated potential dependence of oxygen in activated sludge. The experiments were carried out under two different conditions and they got four different results. The discrepancy can partially be explained by equation 3.2.9. Two tests were carried out after 12 h preliminary aeration with following result:

$$E_h = 0.407 + 0.055\log[O_2] \qquad (3.2.11)$$

$$E_h = 0.412 + 0.060\log[O_2] \qquad (3.2.12)$$

Two other tests were carried out after 12 h anoxic condition and gave the following results:

$$E_h = 0.220 + 0.089\log[O_2] \qquad (3.2.13)$$

$$E_h = 0.321 + 0.077\log[O_2] \qquad (3.2.14)$$

All four results are corrected to pH 7 by the pH relation in Equation 3.2.15

$$E_h = 0.721 - 0.046\mathrm{pH} \qquad (3.2.15)$$

The relationship in Equation 3.2.15 is determined by adding sulphuric acid alternative soda to treated water saturated with dissolved oxygen at 21°C.

Depending on the hydrogen sulphide formation during the anoxic period the initial condition will be totally different. The neglected parameter $f \cdot \log[HS^-]$ will then result in an apparently higher oxygen dependence. As soon as the condition turns to be aerobic the sulphide will be reoxidised in proportion to hydrogen sulphide concentration, oxygen concentration and time[68]. This may explain the discrepancy in the coefficient for oxygen but not the discrepancy in k. If the formula would include the contribution that soluble organic material might have on redox potential an explanation is possible.

With the soluble organic material signed as COD´, where COD´ is an electron donator of four electrons per COD´. Nernst equation can be written for 1) acetate 2), methane, 3) formic acid and 4) sugar as COD´ as follows.

1. Acetate will give

$CH_3COO^- + 2H_2O \rightarrow 2CO_2 + 7H^+ + 8e^-$ (pH-interval 5.5 - 8.5)

CH_3COO^- will then be equal to 2COD´ and the Nernst equation will be written as in equation 3.2.16

$$E = E_0 + \frac{RT}{4F}\ln\frac{[CO_2]}{[COD']} + \frac{7RT}{8F}\ln[H^+] \qquad (3.2.16)$$

with the respect to the carbonic acid equilibrium ($CO_{2,\,air}$ <==> $H_2O + CO_{2,\,aq}$ <==> H_2CO_3 <==> $H^+ + HCO_3^{2-}$) the Equation 3.2.17 can be rewritten as:

$$E = E_0' + \frac{RT}{4F}\ln[HCO_3^-][H^+] + \frac{RT}{F}\ln[H^+] - \frac{7RT}{8F}\ln[COD'] \qquad (3.2.17)$$

2. Methane will give

$CH_4 + 2H_2O \rightarrow CO_2 + 8H^+ + 8e^-$

where CH_4 correspond to 2COD′ and

$$E = E_0' + \frac{RT}{8F}\ln[HCO_3^-][H^+] + \frac{RT}{F}\ln[H^+] - \frac{RT}{4F}\ln[COD'] \qquad (3.2.18)$$

3. Formic acid will give HCOOH = ½COD′ according to

$HCOOH \rightarrow CO_2 + 2H^+ + 2e^-$

$$E = E_0' + \frac{RT}{F}\ln[HCO_3^-][H^+] + \frac{RT}{F}\ln[H^+] - \frac{RT}{2F}\ln[COD'] \qquad (3.2.19)$$

4. Sugar will give $C_6H_{12}O_6$ = 6COD′ according to

$C_6H_{12}O_6 + 6H_2O \rightarrow 6CO_2 + 24H^+ + 24e^-$

$$E = E_0' + \frac{RT}{4F}\ln[HCO_3^-][H^+] + \frac{RT}{F}\ln[H^+] - \frac{RT}{4F}\ln[COD'] \qquad (3.2.20)$$

With the assumption that the potential does not depend on the kind of COD′ only the concentration of the final formula for the redox potential will be;

$$\begin{aligned} E = {} & k + a\cdot\log[O_2] + b\cdot\log[NO_3^-] + c\cdot\log[SO_4^{2-}] + g\cdot\log[HCO_3^-] - \\ & -d\cdot pH - e\cdot\log[NH_4^+] - f\cdot\log[HS^- - h\cdot\log[COD'] \end{aligned} \qquad (3.2.21)$$

The reduced equation in the case of preanoxic conditions will be;

$$E = k + a\cdot\log[O_2] + g\cdot\log[HCO_3^-] - d\cdot pH - f\cdot\log[HS^-] - h\cdot\log[COD'] \qquad (3.2.22)$$

During anoxic condition there can be fermentation and lysis of microorganisms that will increase the concentration of soluble organic material. During short-time oxygen tests the degradation of COD′ will be negligible in respect to the change in redox potential. Consequently there should be estimated a discrepancy in k in the experiments of Heduit and Thevenot[66]. Watanabe *et al*[67] have also found a relationship between COD (e.g. methanol) and redox potential in connection with denitrification. This also the COD′ dependence. The reduced equation in the case of preaerobic condition will be:

$$E = k + a \cdot \log[O_2] + g \cdot \log[HCO_3^-] - d \cdot pH - h \cdot \log[COD'] \qquad (3.2.23)$$

This model presumes that there is equilibrium which means that the coefficient, a, will be RT/4F (e.g. 59 mV at 25°C) according to Equation 3.2.3. The coefficients k, g, d and h will depend on what kind of electron donator that COD' represents. With Equation 3.2.23 it is possible to decide whether there is equilibrium or not. If not, the electrode reactions are irreversible and consequently controlled by kinetics. This leads us to the next step in the theoretical discussion, the open circuit potential which is controlled kinetically and not by equilibrium.

3.3 The open circuit potential in sewage

The potential of sewage is determined by the rates of the reactions at the electrode surface, the anionic oxidation and the cationic reduction. Presumably these originate from different redox couples with a potential of equilibrium differing from the measured potential instrumentally. This means that even if an inert material as platinum or gold is used as electrode during potential measurement the value of the potential will depend on the selection of electrode material. Furthermore, the potential measurement in sewage will be an open circuit potential which means that the anodic and cathodic reaction on the electrode surface will not come from the same redox pair. The reactions can be either electron transfer controlled or mass transport controlled separately. Because of that the transition between activated controlled (e.g. electron transfer control) reactions and mass transport controlled reaction is not distinct there can be a mixture of the two of controls. In this thesis the transition interval will not be discussed.

3.3.1 The open circuit potential electrode dependence

To get an explanation of the phenomenon that the potential value in sewage depends on the material and surface of an inert electrode it is necessary to consider the reactions appearing at the surface of the electrode used to measure the relative potential.

An equilibrium reaction for a substance A written as:

$$A^+ + e^- \rightleftharpoons A$$

covers two opposite reactions:

the cathode reaction $A^+ + e^- \rightarrow A$ giving the current i_c or i_-,
the anode reaction $A \rightarrow A^+ + e^-$ giving the current i_a or i_+.

At equilibrium the following relations are stated:

(I) $i_a = |i_c| = i_0$, where i_0 is the exchange current density

(II) the potential difference follows Nernst´s law as written:

$$E_{eq} = E^{0}_{A/A^{+}} - \frac{RT}{F} \ln \frac{(A)}{(A^{+})} \qquad (3.3.1)$$

where E_{eq} is the potential difference at equilibrium.

By changing the potential difference between the electrode surface (metal) and the solution it is possible to determine the individual currents i_a and i_c, provided the electron transfer constitutes the step controlling the velocity of the reactions:

$$i_a = i_0 e^{\alpha \frac{nF}{RT} \eta} \qquad (3.3.2)$$

$$i_c = - i_0 e^{-(1-\alpha) \frac{nF}{RT} \eta} \qquad (3.3.3)$$

$$\eta = E - E_{eq} \qquad (3.3.4)$$

where η is the forced potential difference, the overpotential (also called the polarisation)
α is known as the transfer coefficient for the reaction, which here can be given as 0.5
n is the number of transferred electrons
F is Faraday´s constant
R is the general gas constant
T is the absolute temperature

The total current is $i = i_a + i_c$ which gives Butler-Volmer´s equation

$$i = i_0 \left(e^{\alpha \frac{nF}{RT} \eta} - e^{-(1-\alpha) \frac{nF}{RT} \eta} \right) \qquad (3.3.5)$$

For large negative and positive values of η Butler-Volmer´s equation can be simplified to the Tafel equation

$$\log i = \log i_0 + b\eta \qquad (3.3.6)$$

where $b = \dfrac{\alpha nF}{RT \ln 10}$ which is called the Tafel slope is for great negative value of η

and $b = \dfrac{(1-\alpha) nF}{RT \ln 10}$ is for great positive value of η.

For reactions involving adsorption on the electrode surface (e.g. electrocatalysis) the value of the exchange current density is determined by the material of the electrode. This means that, depending on this material, the relation between current i and polarisation η will shift parallel of the log(i)-axis (Figure 3.3).

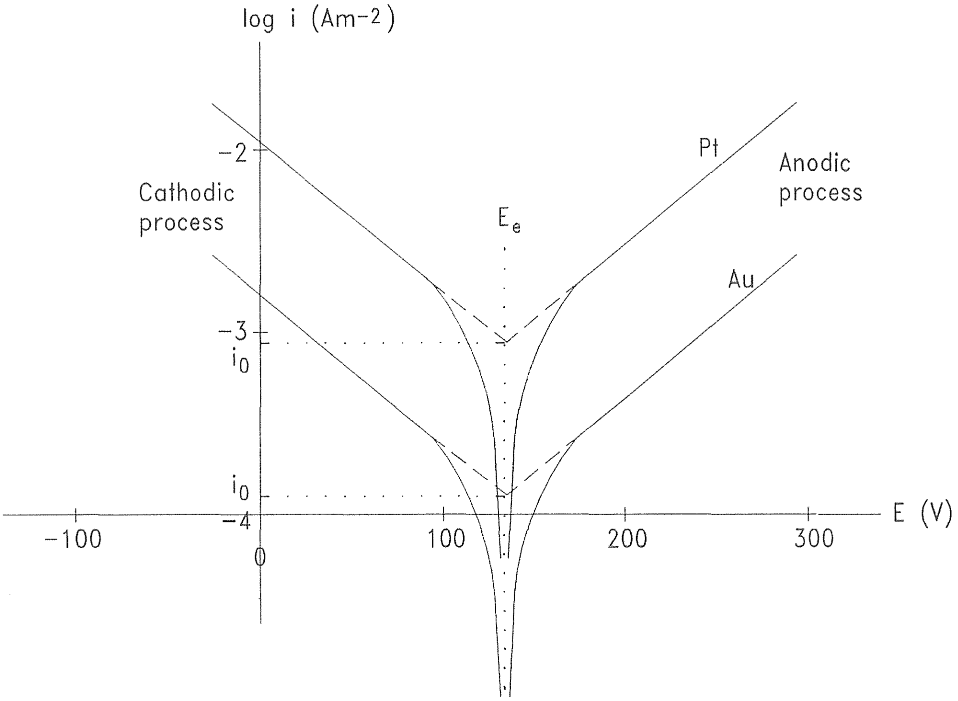

Figure 3.3 Difference in reaction rate of the electron transfer expressed as log | i | on different electrode surfaces and different potential differences.

Even though the exchange current density varies with the material of the electrode the equilibrium potential will not be changed. Chemical equilibrium cannot be expected in sewage which contains a variety of chemical substances. Nevertheless, due to the mixed potential derived from several redox reactions simultaneously taking place on the same electrode surface it is possible to register stable potential differences.

In sewage containing excess of oxygen the potential determining reactions can presume to be as follows:

$$O_2 + 4\ e^- + 4\ H^+ \rightarrow 2H_2O$$

and

$$A \rightarrow A^+ + e^-$$

where A represents an oxidizable organic material. Anodic oxygen reactions occurring in sewage can be neglected. For simplicity this can also be done with the cathodic part reactions of the A-reaction given above. Then the potential determining course will be constituted by the cathodic procedures of the oxygen reaction and the anodic procedures of the A-reaction (Figure 3.4).

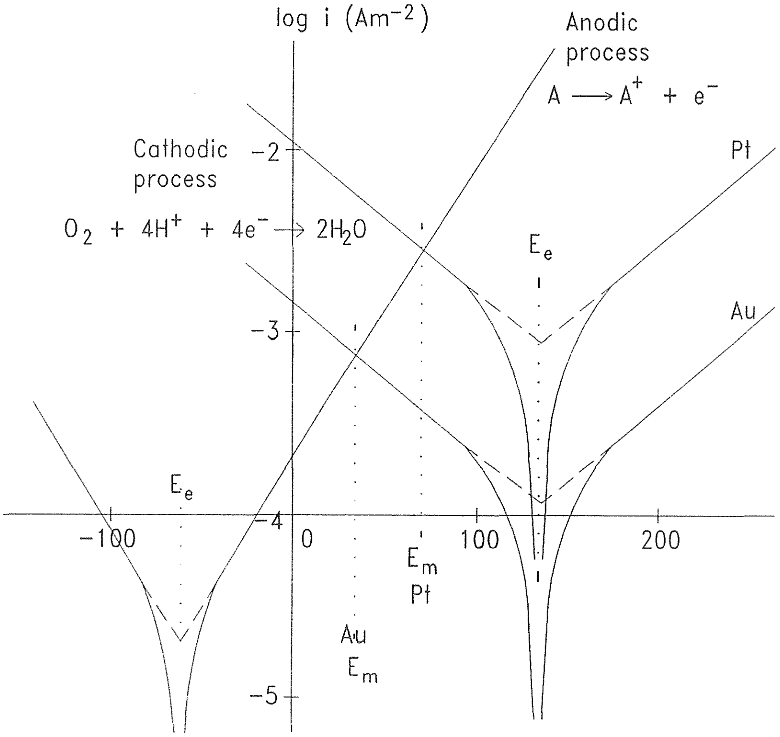

Figure 3.4 The mix potential E_m between two different electrode reactions and on two different electrodes (platinum and gold).

Here, the electrode material will be of considerable significance as the exchange current density is not the same for anodic and cathodic reactions. In some cases this can even imply that the rate determining cathodic reaction (or anodic reaction) will not be the same from one electrode material to the other.

3.3.2 An electron transfer controlled open circuit potential

In an activated controlled open circuit potential Eoc is the potential determined by the total reaction rate of the anodic reactions is equal to the reaction rate of the cathodic reactions. Furthermore, the anodic and cathodic reactions do not come from the same redox pair.

Because of the complexity of the sewage there are lot of possible anodic and cathodic reactions as seen in section 2.6 and 3.2. For simplicity it is assumed that there is only one anodic and one cathodic reactions at a time and the other can be neglected.

In this case the anodic reaction can be described as in Equation 3.3.7

$$Ox_1 + n_1e^- \overset{k^{01}}{\rightleftharpoons} Red_1 \qquad (3.3.7)$$

where k^{01} is the rate constant at standard condition ($Ox_1 = Red_1$)
n_1 is the number of electrons involved in the anodic reaction.

The Nernst equation will be as follows:

$$E_{eq} = E^{01} + \frac{RT}{n_1F} \ln \frac{[Ox_1]}{[Red_1]} \qquad (3.3.8)$$

where E_{eq} is the potential under equilibrium
E^{01} is the standard potential.

The anodic current density will, from a kinetic description, be written as:

$$\frac{i_a}{n_1F} = k^{01}[Red_1]\, e^{(1-\alpha)\frac{n_1F}{RT}(E-E^{01})} \qquad (3.3.9)$$

The same for the cathodic reaction will be as follows:

$$Ox_2 + n_2e^- \overset{k^{02}}{\rightleftharpoons} Red_2 \qquad (3.3.10)$$

where k^{02} is the standard rate constant ($Ox_2 = Red_2$)
n_2 is the number of involved electrons in the cathodic reaction.

The Nernst equation for the cathodic reaction will be:

$$E_{eq} = E^{02} + \frac{RT}{n_2F} \ln \frac{[Ox_2]}{[Red_2]} \qquad (3.3.11)$$

Finally the kinetic description of the cathodic reaction:

$$-\frac{i_c}{n_2F} = k^{02}[Ox_2]\, e^{-\alpha\frac{n_2F}{RT}(E-E^{02})} \qquad (3.3.12)$$

When $| i_a | = | i_c |$ then E = Eoc, combining Equations 3..3.9 and 3..3.12 gives

$$n_1F\, k^{01}[Red_1]\, e^{(1-\alpha)\frac{n_1F}{RT}(E-E^{01})} = n_2F\, k^{02}[Ox_2]\, e^{-\alpha\frac{n_2F}{RT}(E-E^{02})} \qquad (3.3.13)$$

After logarithming and sustituting the anodic Tafel slope ($RT\ln 10/(1-\alpha)n_1F$) with b_a and using b_c instead of the cathodic Tafel slope ($RT\ln 10/\alpha n_2F$) Equation 3.3.13 will be:

$$\log n_1Fk^{01}[Red_1] + \frac{1}{b_a}(Eoc-E^{01}) = \log n_2Fk^{02}[Ox_2] - \frac{1}{b_c}(Eoc-E^{02}) \qquad (3.3.14)$$

After reorganisation of Equation 3.3.14 the equation for the open circuit potential in sewage for activated controlled electrode reaction will be as follows:

$$Eoc = \frac{b_ab_c}{b_a+b_c}\{\log(n_2Fk^{02}[Ox_2]) - \log(n_1Fk^{01}[Red_1])\} + \frac{E^{01}b_c}{b_a+b_c} + \frac{E^{02}b_a}{b_a+b_c} \qquad (3.3.15)$$

By further reorganisation of Equation 3.3.15, the equation will show three terms of different character

$$Eoc = \frac{b_ab_c}{b_a+b_c}(\log[Ox_2] - \log[Red_1]) + \frac{b_ab_c}{b_a+b_c}\log\frac{n_2Fk^{02}}{n_1Fk^{01}} + \frac{E^{01}b_c + E^{02}b_a}{b_a+b_c} \qquad (3.3.16)$$

where the first term is concentration dependent, the second electrode (e.g. material and surface) dependent and the last equilibrium dependent.

Comparing this with Equation 3.2.23, where no account has been taken to the kinetics on the electrode surface, the influence of the reduced form in the cathodic reaction and the oxidised form in the anodic reaction is neglected. Instead the Equation 3.3.16 contains the standard rate constants which vary with the choice of electrode surface. This also means that if the electrode surface is changed during the measurement the standard rate constant will probably change.

Under aerobic conditions it can be assumed that $[Ox_2]$ is equivalent to a function either of the concentrations of oxygen and hydrogen ions or solely of the oxygen concentration; the alternative depending on which step of the reaction that is the rate determining step. With the same reasoning as in Section 3.2 that $[Red_1] = [COD']$ the following expression will be obtained:

$$Eoc = \frac{b_ab_c}{b_a+b_c}(\log[O_2] - pH - \log[COD']) + \frac{b_ab_c}{b_a+b_c}\log\frac{n_2Fk^{02}}{n_1Fk^{01}} + \frac{E^{01}b_c + E^{02}b_a}{b_a+b_c} \qquad (3.3.17)$$

The partial derivative of Eoc with respect to pH will thus be:

$$\frac{\partial Eoc}{\partial pH} = -\frac{b_a b_c}{b_a + b_c} \quad \text{alternative} \quad \frac{\partial Eoc}{\partial pH} = 0 \tag{3.3.18}$$

provided that $[COD^-]$ is not dependent on pH too. Also the partial derivative of Eoc with respect to $\log[O_2]$ will have the same absolute value.

$$\frac{\partial Eoc}{\partial \log[O_2]} = \frac{b_a b_c}{b_a + b_c} \tag{3.3.19}$$

However, one of the reactions on the electrode surface can be expected to be mass transport controlled.

3.3.3 The mass transport controlled open circuit potential

If either the anodic or the cathodic reaction is mass transport controlled the open circuit potential will be quite different from the activated controlled case. Let, for instance, the cathodic reaction be mass transport controlled then $i_c = i_{lim}$ and consequently independent of the potential but the water velocity and the bulk concentration.

At $|\, i_a \,| = |\, i_c \,|$ the relation will be:

$$n_1 F k^{01} [Red_1] e^{(1-\alpha)\frac{n_1 F}{RT}(E-E^{01})} = i_{lim} \tag{3.3.20}$$

where $i_{lim} = f\,([O_2],\ \text{water velocity}\,)$

After logarithming and putting in b_a for the anodic Tafel slope the relation will be:

$$\log n_1 F k^{01} [Red_1] + \frac{1}{b_a}(Eoc - E^{01}) = \log i_{lim} \tag{3.3.21}$$

By reorganizing equation 3.3.2, the equation for the open circuit potential for a mass transport controlled electrod reaction will be as follows:

$$Eoc = E^{01} + b_a\{\log i_{lim} - \log(n_1 F k^{01} [Red_1])\} \tag{3.3.22}$$

Or if the anodic reaction is mass transport controlled:

$$Eoc = E^{02} + b_c\{\log i_{lim} - \log(n_2 F k^{02} [Ox_2])\} \tag{3.3.23}$$

By deriving Equation 3.3.22 the open circuit potential with respect to log i_{lim} it can be shown that variations in the concentration of $[Ox_2]$ and/or variation in water velocity will vary as the Tafel slope for the anodic process:

$$\frac{\partial Eoc}{\partial \log i_{lim}} = b_a \qquad (3.3.24)$$

On condition that equation (3.3.23) concerns a reaction of the first order a deriving with respect to pH will give:

$$\frac{\partial Eoc}{\partial pH} = -b_c \qquad (3.3.25)$$

3.4 Evaluation

The models that have been described in this section have had the aim of determing continoues quality and quality change in sewage *in situ*. The weakness with the oxygen uptake model is the difficulty to determine the α value for the oxygen transfer in sewage in situ. However, the oxygen uptake models can be used as a valuable tool to gain further knowledge and understanding of the chemical and biological processes in sewage during laboratory experiments.

The models based on potential measurement are partly in the development stage. The equilibrium model should give the same value regardless the type of electrode that is used. This is, however, not the case as have been reported by several researchers[69]. If the kinetic model is valid then the electrode surface will be a critical point, because without a stable surface it will be impossible to get reproducable results.

However, apart from what kind of model that is valid the models show that it is possible to measure changes in the concentration of both oxidizable and reducible compounds.

4 THEORETICAL CONSIDERATIONS OF LITERATURE DATA.

4.1 Open circuit potential

The experiments of Heduit and Thevenot[66] mentioned in section 3.2.2 gave the value of $\frac{\partial Eoc}{\partial pH} = -46\,mV$ which implies the following Tafel slopes in case of that Eoc is electron transfer controlled

1.	$b_a = 75$ mV	if	$b_c = 120$ mV
2.	$b_a = 197$ mV	if	$b_c = 60$ mV

where the last result indicates that the number of electrons in the anodic rate determining step is less than one which of course is impossible. Hitherto the electron transfer coefficient α has been assumed to be 0.5. In the case of a partly blocked electrode surface or if the electron transfer occurs through a film the value of α will decrease and the Tafel slope can exceed 120 mV.[70] For b_a= 75 mV the α value will be 0.4 and b_a = 197 mV will give an α value of 0.3. With oxygen as the cathodic reaction and platinum as the electrode material the probably alternative would be option 2. This result indicates that the anodic reaction may be pH-dependent.

In pretreated sewage Heduit and Thevenot[66] also determined the redox potential as a function of $\log[O_2]$. In their four experiments the values for the expression

$$\frac{\partial Eoc}{\partial \log[O_2]} = \frac{b_c\, b_a}{b_c + b_a}$$

were found to be 55, 60, 89 and 77 mV, respectively.

In electron transfer controlled reactions the two values first mentioned will give $b_c = b_a$ = 120 mV, but they will also agree fairly well with the expected result under a condition of equilibrium. The two last mentioned values will give preposterous results unless the electrode surface in these cases was partly blocked.

However, supposing that the reactions are controlled by mass transport the results will appear quite different. If in the first place, the anode reaction is controlled by mass transport this would imply that equation 3.3.24 will be valid with the partial derivative $\frac{\partial Eoc}{\partial \log[O_2]} = b_c$. Consequently, b_c in the four experiments will be 55,60, 89 and 77 mV, respectively. The two values first mentioned will give Tafel slopes around 60 mV, which is to be expected with oxygen reduction taking place on a platinum electrode. In contrast to the conditions presented in these first two experiments the sewage in the last two was kept anoxic for 12 h before the measurements of the open circuit potential were made, a condition which might have affected sulphide formation. If sulphide has a proportionately higher exchange current density on platinum than oxygen it seems reasonable to visualize a shift from an anode reaction controlled by mass transport to a mass transport controlled cathode reaction. In an intermediate state of mixed control an increase of the slope is to be expected.

This discussion illustrates that it seems to be impossible to present a generally valid expression for the pH-dependence of the open circuit potential in sewage. In cases where it can be stated that the cathode reaction is an oxygen reduction, the pH dependence cannot be determined because the anodic reactions pH-dependence is unknown Because of the complexity of sewage more applied research is needed in this area.

The calculations that have been done hitherto have been based on the assumption that the value of an open circuit potential only has been derived from one cathode and one anode reaction. It seems however probable that at succesive decreasing oxygen concentration other cathodic reaction than the oxygen reduction will be dominant (for instance $SO_4^{2-} \rightarrow HS^-$). A corresponding relation ought to exist for the anode reaction too, constituted by one or several irreversible reactions, the dominating role of which will be determined by the progress of the degradation. Here the conditions discussed in Section 2.6 can be considered, as pyruvate is usually formed as an intermediate compound in fermentation. Thus with a suitable electrode pyruvate may play a dominating role in cathode reactions.

4.2 Chemical aspects from a microbiological point of view

The extent of microbiological activity is dependent on the concentration of active microorganisms and the substrate. The amount of microorganisms in the wastewater depends on the retention time in the sewer-net and the erosion of biofilm from the wall, access to substrate and time of generation, which in turn depends on the quality of the substrate. The activity and type of microorganism in the biofilm is not dependent on the length of the sewer, but the water velocity, the quality of the sewage and the durability of a unitary type of electron acceptor. Many microorganisms can utilise several different compounds as energy sources. However, some compounds can give generation times that are 10 times greater or smaller than those given by other sources. This means that the energy source will govern the type of dominant microorganism.

As a substrate for microorganisms the sewage is seen to be rather poor because of the low substrate concentration. Fortunately the relation between different nutrients compared to the carbon content in wastewater have only moderate variations as seen in Figure 4.1 (processing data from Göteborg, Kungsbacka and Lerum treatment plants and from the sewer net in Göteborg[71]). The same is valid for the nutritive requirements of different microorganisms[37 43 58]. Also this is visualised in Figure 4.1, where the organic content is estimated as COD. Because of the similarity in the composition between wastewater and bacteria, the wastewater can be seen as a liquid consisting of viable bacteria and products from bacteriolysis. Then it appears that nutrients will be in excess compared to the organic content. This is because organic substance is also required as an energy source for cell synthesis. The same situation arises if the microorganisms are seen as an adaptation to the wastewater, still the energy source is needed.

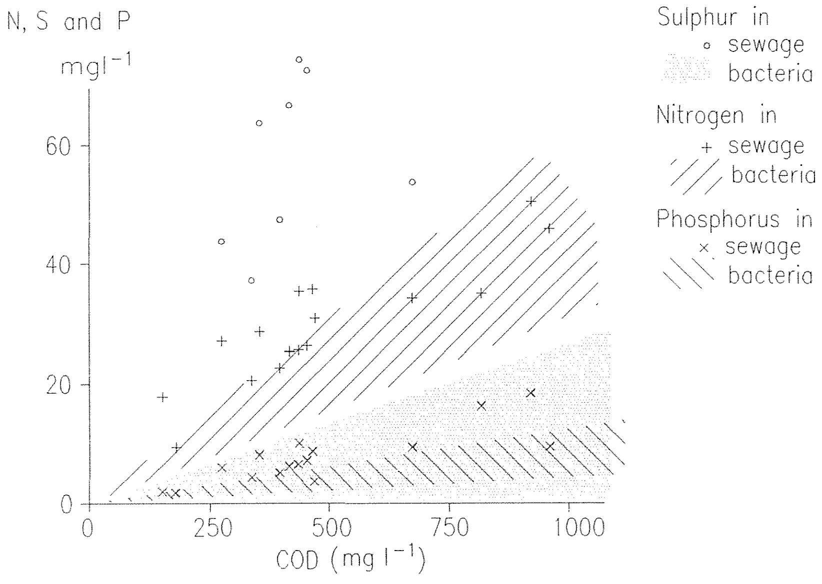

Figure 4.1 Comparisons of the concentrations of nitrogen, phosphorus, and sulphur in wastewater and microorganisms, respectively related to COD.

The nutritional requirements of a wide range of different microorganisms are similar; according to Speece[43] the essential elements are in order of quantity: C, N, S, P, Fe; furthermore the trace elements Co, Ni, Mo, Se, riboflavin and vitamin B_{12} are required. Norén[37] and Characklis[6] have given practically the same order, though they have ranked phosphorus before sulphur. In addition, manganese, copper, and zinc have often been described as essential elements. The relation C:N varies for different microorganisms, the range being 6:1 - 12:1[58]. Other reported relations are:

N:S:P = 5:0.07:1 [37] and = 6:2.5:0.85 [43]

The adaptability of microorganisms is considerable, not at least because of that the microorganisms live collectively and in symbiosis with each other. Nitrogen is taken up as both nitrate/nitrite and ammonium, sulphur as both sulphate and sulphide. Thus, nutrients can be obtained from anaerobic as well as aerobic origin. Ammonium constitutes 60% of the nitrogen content of wastewater, which corresponds well with the monthly mean results from the influent at the Rya wastewater treatment plant[72] (Figure 4.2). Polyphosphates, being the most common source of phosphorus, represent 55% of the total phosphorus content of wastewater[8].

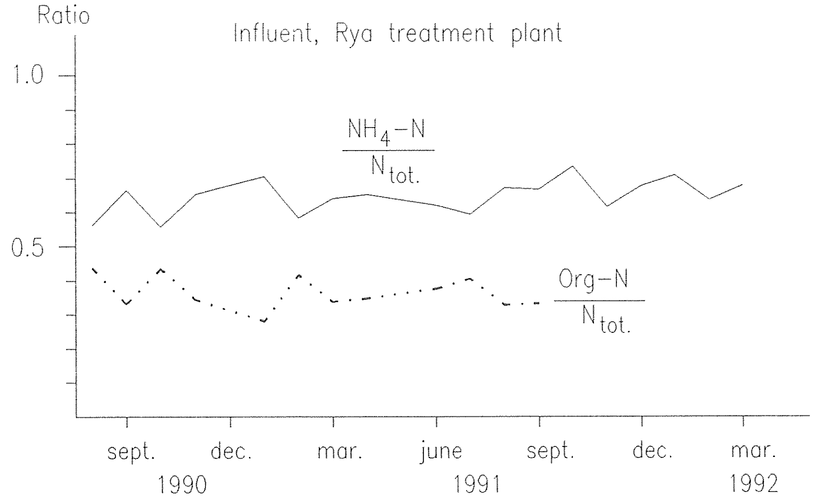

Figure 4.2 The monthly ammonium mean value from the influent at Rya wastewater treatment plant

Figure 4.1 shows that if nitrogen and phosphorus in sewage isconsumed by the microorganisms then the COD-content in sewage whould have to be available for the microorganisms as carbon. But in reality only a part of the COD-content consists of biological degradable matter[72] which is illustrated in Figure 4.3. Normally the BOD_5/COD ratio varies between 0.4 - 0.8[11]. The monthly mean value from the Rya wastewater treatment plant is about 0.4 and this value seems to be independent of both flow and season.

According to Figure 4.1 the COD/N_{total} ratio is between 10-20 but as Figure 4.2 shows the nitrogen exists mainly as ammonium and organic nitrogen, which means that the $COD/N\text{-}NO_x$ ratio could be much greater than the break point at 53 for ammonification mentioned in section 2.6.2.1. This will lead to ammonification of the remaining nitrate/nitrite in sewer (see section 2.6.2.1) which if not normally expected. However, there is no proof that this will be the case.

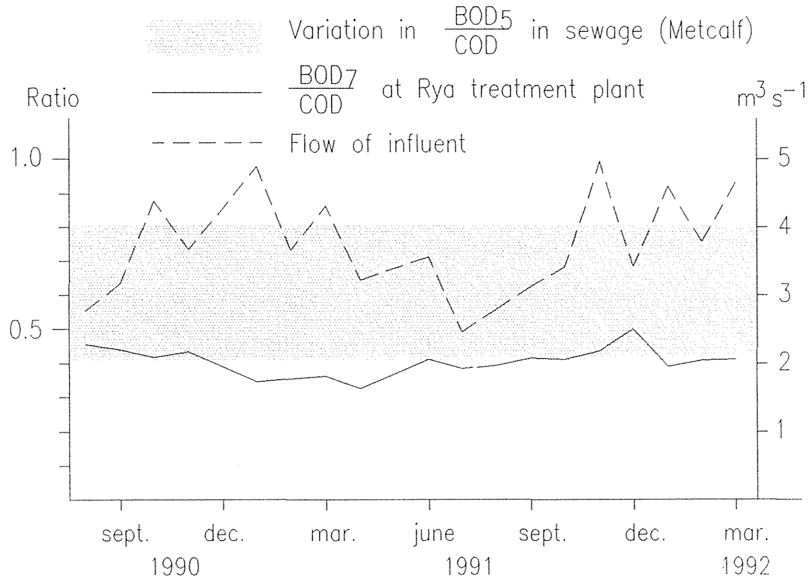

Figure 4.3 BOD_7 /COD ratio from the influent at Rya wastewater treatment plant compared with literature values.

It can be concluded that it does not matter what kind of microorganism that is available the activityisl not nutrient limited. Furthermore the nutrient andbiodegradable organic material content seems to be rather constant relative to COD. Compared with the normal relationship between BOD and COD the value at the Rya wastewater treatment plant is low. The reason for this may be the microbiological activity in the sewer.

4.3 Calculations of oxygen availability in sewer

Oxygen concentration in-sewer depends on the oxygen transfer and the oxygen consumption. Oxygen consumption is a function of the number of active microorganisms during non-limiting oxygen and substrate conditions. The upper limit of activity presumed to be comparable with the activity in a bioreactor (e.g. rotating disc reactor with a complete biofilm). The lower limit presumed to be comparable with respirometer measurements with initially no biofilm at all. In the following section a simplified sewer network will be tested as a bioreactor and compared with respirometer measurement. Furthermore this consumption will be related to the estimated oxygen transfer.

4.3.1 A simplified sewer network

For the further discussion of this paper a simplified sewer network is outlined in Figure 4.4. All real sewer nets have a tree structure with the smallest diameters towards the upstream end of each branch. The smallest diameter used is due to practical reasons often around 200 mm. With normal slopes of 0.005 to 0.010, gravity sewers with a diameter of 200 mm will carry between 0.03 m^3 s^{-1} and 0.05 m^3 s^{-1}. This means, that sewer diameters larger than the minimum diameter are not required until several thousands of persons are connected. Table 4.1 gives the wastewater load on the main sewer of the simplified network.

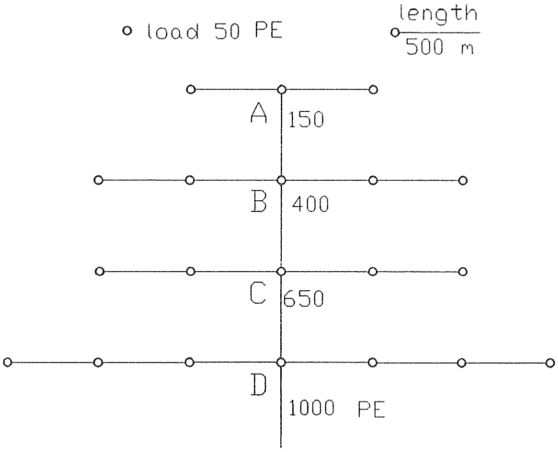

Figure 4.4 A simplified sewer network.

Table 4.1 Typical data in a sewer network with 0.2 $m^3pe^{-1}d^{-1}$, contributing areas with a load of 50 pe and infiltration of 0.1 $ls^{-1}km^{-1}$ of pipe length. The equivalence of a person is expressed as pe and the pipe length per pe is assumed to be 10 m.

		Sewer section			
		A	B	C	D
Persons, total	(pe)	150	400	650	1000
Sewage flow (q_s)	(ls^{-1})	0.35	0.93	1.50	2.30
Infiltration flow (q_i)	(ls^{-1})	0.15	0.40	0.65	1.0
Flow, main sewer (q)	(ls^{-1})	5.00	1.33	2.15	3.30
Main sewer (ϕ)	(mm)	225	225	225	225
Water depth (h)	(m)	0.02	0.03	0.04	0.05

The calculated average water depth in Table 4.1 is true for the 24 hours average flow and can be regarded as the part of the sewer cross-section that is always in contact with wastewater. Usually it is assumed that each person produces: 70 g BOD_7 per day, 13.5 g N_{tot} per day and 2.7 g P_{tot} per day. This allows the calculation of average concentrations for the 1000 pe of the simplified network. The concentrations will be: 350 g BOD_7 m^{-3}, 67.5 g Nm^{-3} and 13.5 g Pm^{-3}, which corresponds well with the figures of Table 2.1 and Table 2.2.

The wastewater retention time, t_R, for the simplified network varies naturally with the distance from the outlet. However, an estimate of the average retention time can be done based on the figures given in Table 4.1. A velocity of around 0.2 m s^{-1} gives an average retention time, t_R = 1.8 h.

A retention time of 1.8 h means that the wastewater from 1000 pe, on an average, is in contact with the pipe walls for 1.8 h and that the biological process time will be 1.8 h.

4.3.2 The sewer as a pipe reactor

By regarding the sewer as a bioreactor, in which the main degradation occurs at a biofilm present on the pipe-walls it is possible to calculate the surface-load R_a (g BOD $m^{-2}d^{-1}$) with the following formula:

$$R_a = \frac{QC}{A} \tag{4.1}$$

where Q is the wastewater flow (m^3 s^{-1})
C is the substrate concentration (g BOD m^{-3})
A is the contact surface (m^2)

In the following Figure 4.5 the geometrical properties of the pipe reactor are defined

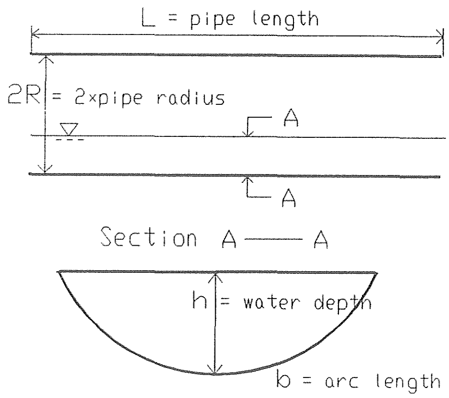

Figure 4.5 Cross-section of pipe partly filled with water.

where L is the length of the pipe (m)
b is the arc length (m)
R is the pipe radius (m)
h is the water depth (m)
A_{seg} the cross-section of water (m^2)
A is the contact surface ($A = b \cdot L$) (m^2)

The flow of the water can be calculated by the following formula:

$$Q = u \cdot A_{seg} \tag{4.2}$$

where u is the water flow velocity ($m\ s^{-1}$).

The cross-section of the water can be calculated as follows

$$A_{seg} = R^2 \arccos(1-\frac{h}{R}) - (R-h)\sqrt{2Rh-h^2} \tag{4.3}$$

and the arc length as follows:

$$b = 2R \arccos(1-\frac{h}{R}) \tag{4.4}$$

By combining Equation 4.1 - Equation 4..4 the surface load is derived:

$$R_a = \frac{CuR}{2L}\left[1 - (1-\frac{h}{R})\frac{\sqrt{2\frac{h}{R} - \left(\frac{h}{R}\right)^2}}{\arccos(1-\frac{h}{R})}\right] \tag{4.5}$$

This Equation 4.5 may be simplified by linear regression for $h < R$ as follows:

$$R_a \approx \frac{Cuh}{2L}(1.363 - 0.363\frac{h}{R}) \tag{4.6}$$

Introducing a design factor f_d, which varies with different cross-sections, circular and rectangular, gives the following expressions for a circular channel:

$$f_d = \frac{1}{2}(1.363 - 0.363\frac{h}{R}) \tag{4.7}$$

and a rectangular channel:

$$f_d = \left(\frac{2h}{\text{width}}+1\right)^{-1} \tag{4.8}$$

With the design factor, f_d, Equation 4.1 will become

$$R_a = f_d C\frac{uh}{L} = f_d C\frac{h}{t_R} \tag{4.9}$$

where t_R is the retention time of water in channel.

Figure 4.6 shows the design factor versus the water depth relative to the radius for the circular channel and the width for the rectangular channel. A circular channel with sediment on the bottom will give a design factor more close to the rectangular channel, but on the other hand, the water depth will decrease which favours oxygen transfer.

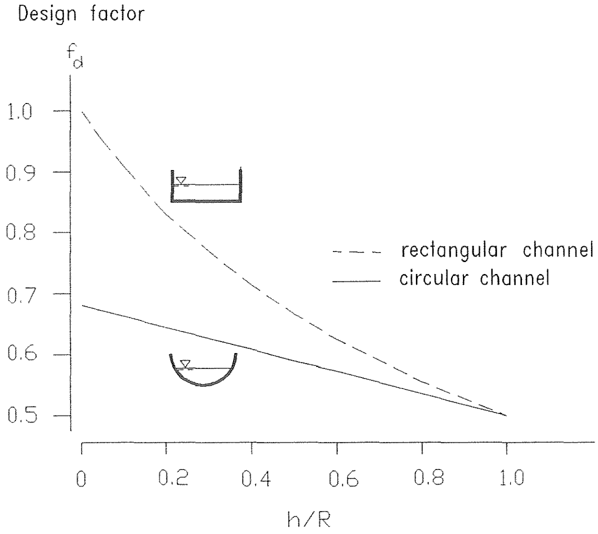

Figure 4.6 The design factor (f_d) for a circular and a rectangular channel.

The relation between surface load and the reduction in BOD has been experimentally studied with a rotating disc filter (a bioreactor where the oxygen is non-limiting). Barnes and Wilson[73] have presented design criteria for a rotating filter and some of the results are given in Table 2. These results need to be corrected depending on the number of stages. The correction factor for more than 4 stages is 0.85. Provided the sewer net can be seen as a rotating filter it will be a filter with more than 4 stages. In the case of sewers the surface load in Table 4.1 should be multiplied by 0.85.

Table 4.2 Surface load *vs* reduction in BOD, for rotating disc filters, at an inlet BOD concentration of 300 mg l^{-1}.

Surface load (g BOD $m^{-2}d^{-1}$)	144	45	25	14
Reduction in BOD (%)	50	80	90	95

With the aid of Equation 4.9 and Table 4.2 it is possible to calculate the theoretical conditions for the achievement of 80% BOD-reduction in wastewater, i.e. the sewer length and the retention time of water in the sewer. A calculation with Equation 4.9 for the simplified sewer network in Figure 4.4 gives for an average depth of 0.03 m a retention time $t_R = 4.1$ h. A 50% BOD reduction gives a retention time $t_R = 1.3$ h. The average retention time of the simplified network is 1.8 h, which means that a BOD reduction of at least 50% would be expected.

4.3.3 Oxygen balance in wastewater

Access to oxygen in a sewer depends on the relation between oxygen transfer on one hand and the consumption of oxygen on the other. The transfer of oxygen is promoted by a large area of contact with air, while consumption is promoted by a large area of contact with solid material.

Oxygen transfer from air to water is determined by the concentration of oxygen at saturation, the current oxygen concentration in the water, the factor of oxygen transfer and the specific surface. Mathematically the rate of oxygen transfer can be expressed by the formula mention in section 3.1.1:

$$\frac{dC}{dt} = K_L a(C_m - C) \tag{4.10}$$

where
C = The current concentration of oxygen in the water ($g \cdot m^{-3}$)
C_m = The saturation value of oxygen ($g \cdot m^{-3}$)
K_L = Oxygen transfer constant ($m\ h^{-1}$)
a = Specific surface (m^{-1})

The oxygen transfer constant and the specific surface are directly related to the design of the sewer. The oxygen transfer constant increases with increasing slope of the sewer and with decreasing dimension of the pipes. The specific surface on the other hand increases with increasing pipe-dimensions.

Oxygen consumption in a sewer can be expected to vary considerably with variations of the chemical and biological content of the wastewater. In-sewer, at steady state, the oxygen consumption can be followed by the balance with the oxygen concentration.

At steady state the following relation is valid;

$$|Oxygen\ transfer\ rate| - |Oxygen\ consumption\ rate| = 0 \qquad (4.11)$$

The concentration of oxygen will be determined by a balance of equal amounts of consumed and transferred oxygen. With a known value of K_La and saturation the determination of the oxygen concentration enables a calculation of the consumption of oxygen. Taghizadeh-Nasser[45] determined K_La-values experimentally for sewers, in the range of 4-8 h^{-1} depending on the water depth with lower values for high water depths. However, clean water was used in this experiments. Consequently the in-sewer K_La value is probably even lower.

The results from the calculations for the simplified sewer net showed higher results. The potential degradation of organic matters for the sewer net was calculated to 50%, which corresponds to an oxygen consumption of 175 mg O_2 l^{-1} during a retention time of 1.8 h, which means a rate of about 100 mg O_2 l^{-1} h^{-1}. To meet this potential oxygen consumption rate a K_La-value of 10 h^{-1} is required.

The conclusion is that, at least in primary wastewater pipes, oxygen transfer will be the limiting factor for the biological processes in several occasions.

The theoretical calculation shows that it would be possible to obtain a 50% purification of the wastewater before reaching the sewage plant (section 4.3.2). However, whether this is the case has to be discussed further.

To increase the oxygen transfer, different measures can be done. One of the simplest ways of increasing the K_La-value is to keep the water depth low. This can be done by minimising inleakage of groundwater and local disposal of stormwater.

On the other hand, using the sewers for flow equalisation leads to an increase in water depth resulting in anaerobic processes. However, even anaerobic processes are capable of degrading organic material but gases like dihydrogen sulphide and methane which are formed may be difficult to handle.

Further studies on degradation in wastewater should be done. To use the sewers for flow equalisation one has to be able to predict the oxygen content in order to eventually take measures against unwanted anaerobic processes. But at the same time it is also interesting to study how complete the anaerobic bioreactions are in gravity sewers.

5 EXPERIMENTAL

The chemical conditions present in sewage during the transport through the sewage system have been studied by measurements both *in situ* and under simulated sewer conditions. This chapter details the analyses, measurements and experimental setups, both in the laboratory and field, used to monitor changes in sewage quality.

5.1 Materials and methods

5.1.1 Physical and chemical analyses

Variations in **the open circuit potential** were measured with combined electrodes (Figure 5.1), an Ingold gold ring electrode with a Ag/AgCl reference electrode and a Satron platinum ring electrode with a Ag/AgCl reference electrode. The electrode was connected to a signal amplifier of Satron PH200 or a Intab data logger with an impedance for the signal of 100 MΩ. For measurements at the Rya wastewater treatment plant an Inventron platinum wire electrode with a Ag/AgCl gel reference electrode was used.

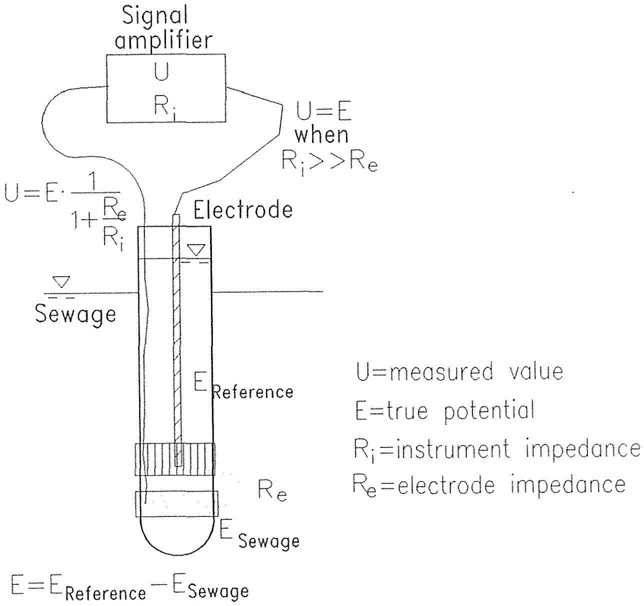

Figure 5.1 Schematic of a redox electrode.

pH was measured with two different electrodes (Ingold) one conventional with a KCl solution electrolyte and one with a KCl gel electrolyte.

Conductivity was measured with different equipment. In laboratory studies it was difficult to carry out the conductivity measurements in the same container as other electrode measurements due to potential leakage and interference with other results. At first this problem was solved by the use of a through-flow electrode (Inventron) combined with a hose pump. Then by galvanic separation of the different signal amplifiers. The separation was performed with an isolating amplifier to every signal amplifier. Finally the measurements was performed simply by manual recording.

Dissolved Oxygen Concentration was measured with a Clark-cell electrode Satron type 153 connected with a Satron POT 12. Reliable results demand a water velocity of at least 0.5 m s^{-1}. This was achieved by stirring with a propeller

Chemical Oxygen Demand (COD) was determined by a commercial sealed tube method (D Lange cuvette LACK 114) with a measuring range of 150-1000 mg O_2 l^{-1}. Samples of 2 ml were added to the prepared oxidation mixture (96% H_{S4}, 2% $HgSO_4$ and dichromat indicator), heated in a LASA heater and measured in a LASA pocket photometer.

Total Organic Carbon (TOC) was determined in a total carbon/total organic carbon analyzer (Astro 1850). The samples were treated with ultrasound before the analysis. The principal scheme in the analysis was as follows. The sample is pumped into the analyzer by a peristaltic pump. Most of the sample is bypassed to a drain. Part of this flow is transferred to the Inorganic Carbon scrubber assembly. Phosphoric acid solution is added to this stream before it reaches the CO_2 scrubber. The acid addition drives the inorganic carbon into CO_2 which is then scrubbed out of the solution. The sample is then mixed with persulphate solution and delivered to the reactor module, where carbon in the sample is converted to CO_2. The vapour is analyzed for CO_2 in an infrared analyzer, Astro 5800.

Biological Oxygen Demand (BOD) was determined in a respirometer (Sapromat A6, J.M.Voith A.G., Heidenheim). The sample size is 250 m. The sample is stored in a closed system where produced CO_2 is absorbed in soda lime. The fall in pressure is compensated by electrolytically produced oxygen, the amount of which is then registered as consumed oxygen. In one sample the nitrification was hindered by addition of 1 m ATC solution (200 m Allyl-Thio-Carbamide to 100 m) to 1000 m distilled water.

Alkalinity was determined according to the appropriate Swedish standard (SIS 02881 39). Samples (50 m or 100 m) were titrated with 0.02 M HCl to pH 5.4 during air bubbling. A mixed indicator (0.1% of 3 parts bromcresol green and 2 parts methyl red in ethanol) was used to indicate pH 5.4.

5.1.2 Laboratory measurements

Saturated oxygen condition: Respiration measurements in samples of 250 m were carried out in a closed system (Sapromat A6, J.M.Voith A.G., Heidenheim). The same instrument was used in the BOD measurements.

Simulated sewer conditions, ranging from aerobic to anaerobic: The main parts of the equipment comprised two beakers of 6 l for storage of sewage, and plates of plexiglass on which electrodes for redox potential, pH and oxygen measuring were mounted. The plexiglass plate was fitted to the upper areas of the beakers (Figure 5.2, Figure 5.3). During the experiments the beakers were immersed in a waterbath with a temperature of 20°C.

One of the beakers was filled with sewage and stirred with a propeller (width 100 mm) at a rate of between 50 to 200 revolutions per minute in order to get a suitable range of O_2 concentration and/or redox potential and also to simulate different water velocities. In the first experiments a fixed rate of 160 revolutions per minute was settled by a revolution regulator and controlled with the aid of a stroboscope. During the experiment test aliquots to be submitted to different analyses, were drawn off from the beaker with the aid of a pipette the tip of which had been broken to minimize a filtration of the sewage. Later on the test aliquots were portioned by decanting. Also with the intention of getting representative aliquots the revolution rate was temporarily increased (to more than 200 rpm) during sampling.

Anaerobic storage was accomplished simply by keeping sewage in the other beaker without stirring (Figure 5.2, Figure 5.3). This kind of storage is not strictly anaerobic as it allows a diffusion of oxygen into the sewage. However, it seems to correspond well to the actual situation in the sewer net, except for pressure pipes. In some of the experiments the concentration of oxygen in the sewage has been regulated by diffused aeration in the bottom of the beaker, and under anaerobic conditions, nitrogen or carbon dioxide. In order to prevent a re-entry of oxygen into the sewage when nitrogen or carbon dioxide was used, the plexiglass plate holding the electrodes was lowered into the surface of water. Thereby the area of water open to air will be negligible.

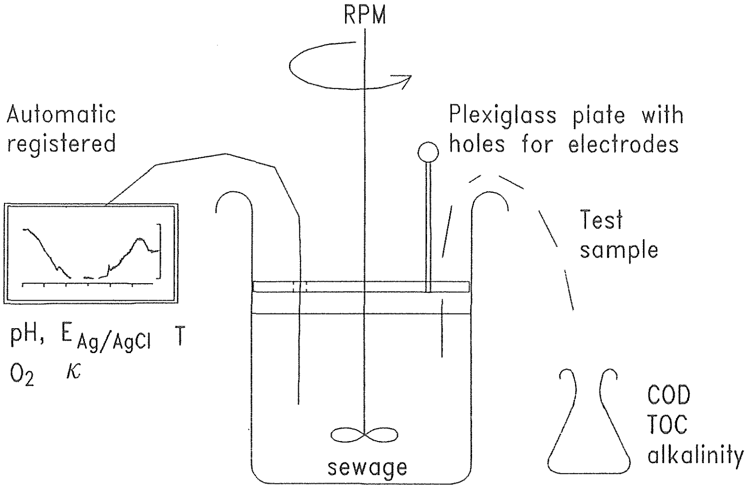

Figure 5.2 Scheme over the laboratory experiments.

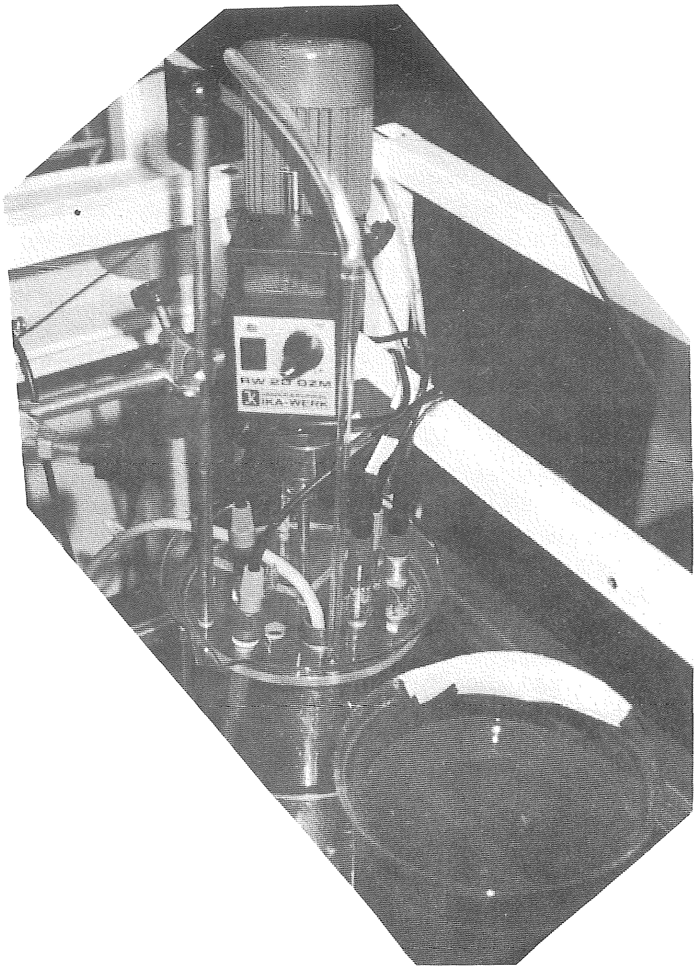

Figure 5.3 Equipment for determinations under aerobic as well as anaerobic conditions. with the plexiglass plate holding the electrodes.

Only domestic sewage has been used in all experiments. The sewage (in-sewer) age was usually less than 10 minutes. After collection it was thoroughly shaken or stirred and then passed through a strainer (size 1 x 1 mm) as pretreatment.

5.1.3 Field measurements

Analyses (COD, alkalinity, oxygen concentration, temperature, conductivity, pH and redox potential) were carried out in the inlet to a sewage tunnel at Partille, later on at Slamby in the same tunnel and finally at the wastewater treatment plant of Göteborg (Ryaverket). Figure 5.4 presents a schematic map of the major sewer network in the Göteborg region.The sewage (in-sewer) age at the Partille point was 0-2 h. When arriving at the Slamby sampling point the sewage has travelled 4 h in a large tunnel. The in-sewer age of the sewage at Slamby will thus be up to 6 h and at the treatment plant it will be up to 17 h as the time lag between Slamby and the treatment plant is 10 h.

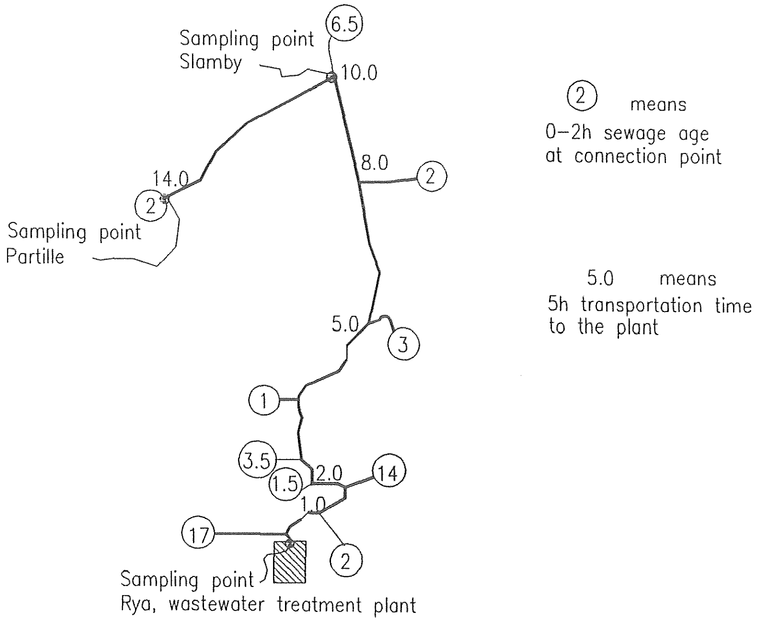

Figure 5.4 View of a part of a sewage system with tunnel and sampling stations.

In the first experiment in the tunnel the electrodes were fixed into a sampling channel located in a small wagon. Sewage was pumped through the channel which rendered electrode measurements possible. After passage through the wagon, samples of the sewage were collected for analyses of COD and alkalinity. However, as the pump pipe often got filled with mud and had to be cleared after about 1 to 2 hours, continuous supervision was necessary. Therefore, a new equipment that eliminated the risk of obstruction in the pump and pipes had to be designed. Here, the electrodes were carried by a small vessel floating in the sewage stream and connected with an instrument box (Figure 5.5 a and b). This set up was found to function decidedly better than that primarily used.

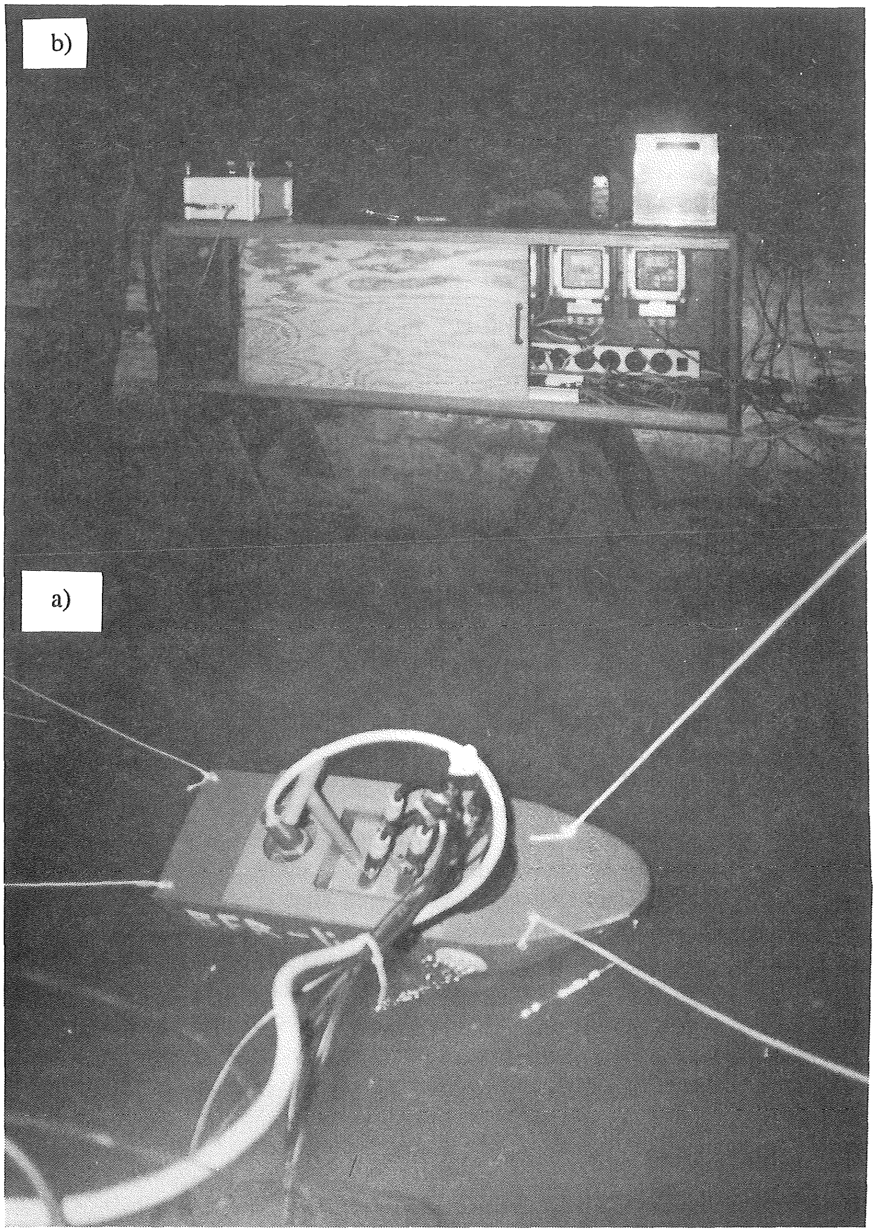

Figure 5.5 Equipment for field measurement, (a) vessel carrying electrodes, (b) box with logger, computer and signal amplifiers.

6 RESULTS AND DISCUSSION

The aim of the experiments reported below has been to facilitate the possibility to identify, follow and estimate the significance of different changes occurring in the wastewater during the transport through the sewer net. Due to a subdivision of the aim the experiments are reported in three different sections.

The purpose of section 6.1 was to examine if conserved wastewater can be used as a reference water in future studies to compare different methods. To examine if preservation by freezing of wastewater gives samples which are identical to the original water even after thawing after different storage times in the freezer.

In section 6.2 the investigations dealt with how closely changes in wastewater in a simulated sewer can be followed and/or predicted by measurements of pH, redox potential, oxygen concentration and conductivity together with analyses of COD, TOC and alkalinity. The aim was to study methods by which the in-sewer degradation of sewage can be continuously followed over time, and especially methods which will utilize equipment available at most sewage plants. Up to now such methods have not come into use. Of special interest is dissolved oxygen concentration related to the oxygen demand of sewage. Furthermore the information that the open circuit potential might add about the sewage quality.

The aim of section 6.3 was to recognise changes *in situ* due to microbiological activity in the wastewater by measurements at two points of the sewer. The experiment was performed to investigate if degradation in sewage can lead to significant differences between values achieved in analyses of samples taken at two different points of the sewer net.

6.1 Preserving of wastewater by freezing

6.1.1 Experimental design

As the main part of the changes in the sewer net originate from biological activity it was considered to be sufficient to compare results obtained in a respirometer with on one hand fresh wastewater and on the other the same water which had been frozen for varying periods. In the experiments the total consumption of oxygen was registered automatically every 10 minutes. As a safety measurement, the oxygen consumption was also registered manually. The rate of the registrations was settled in daytime with regard taken to the consumption of oxygen. For the whole experimental series 10 l of fresh sewage (not older than 10 minutes in the sewer) was shaken and passed through a strainer (size 1 x 1 mm). Six samples of 250 m were immediately put into the respirometer, the rest was frozen in portions of 300 m. After three weeks three of these portions were thawed in hand warm water (ca 40°C) and put into the respirometer and after another week a further three samples were treated in same way. The values achieved with the first six samples were registered manually. In the other series automatically registered respiration values have been reported.

6.1.2 Experimental results

Figure 6.1 to Figure 6.3 present in separate graphs the results of 5 days continuous measurement of the oxygen consumption in all aliquots pertaining to the fresh sewage as well as to the sewage stored frozen for 3 and 4 weeks, respectively. Table 6.1 gives the BOD_5 values determined in all aliquots after 5 days incubation. It gives also the median values and mean values ± standard deviation (S.D.) in fresh sewage, in sewage frozen for 3 weeks and in sewage frozen for 4 weeks.

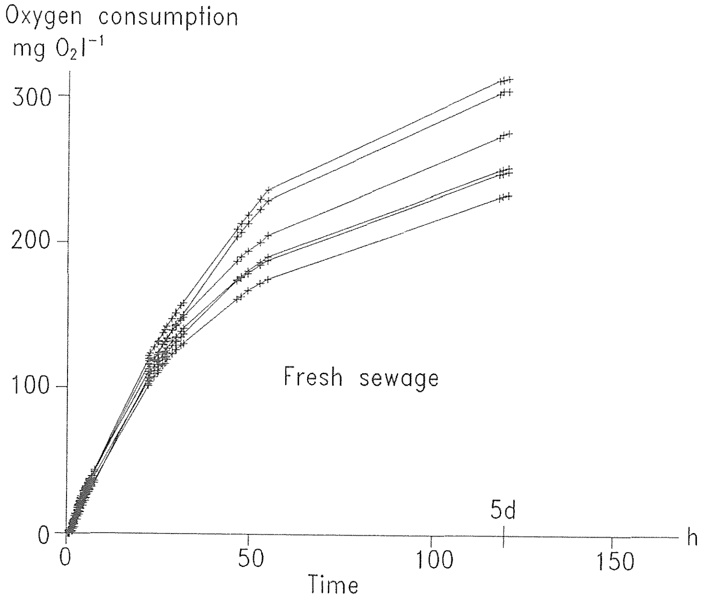

Figure 6.1 Respiration measurement in fresh municipal sewage. Manual registration.

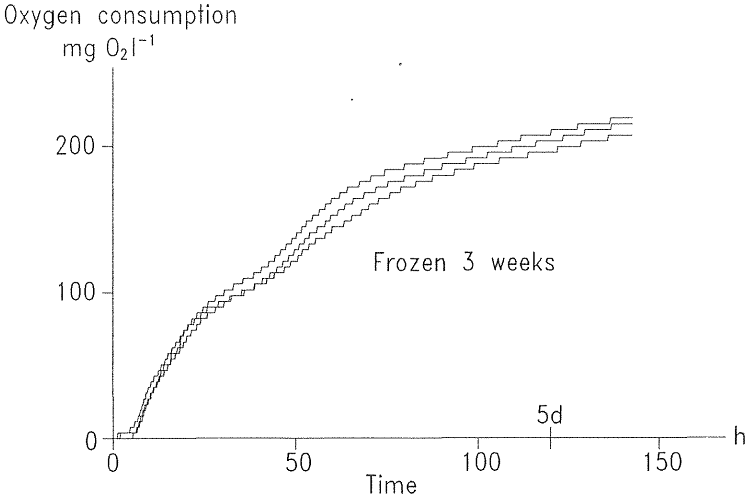

Figure 6.1 Respiration measurement in thawed sewage. Registration every 10 minutes.

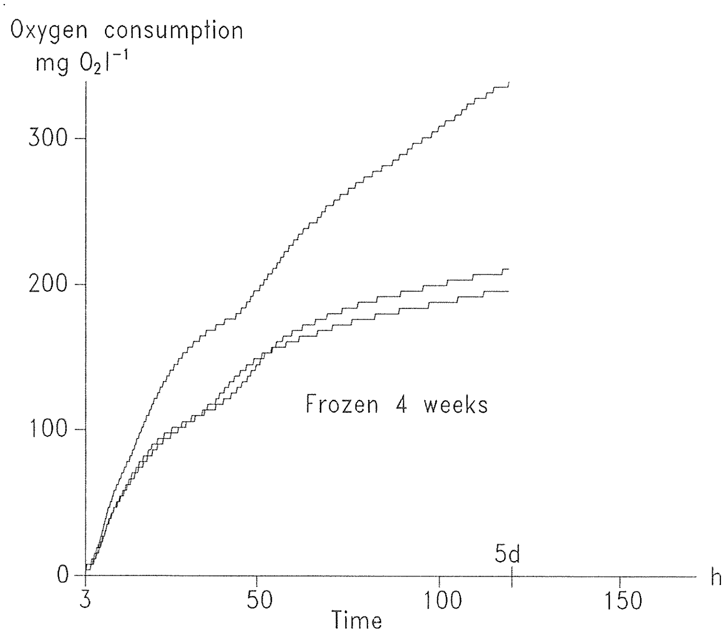

Figure 6.3 Respiration measurement in thawed sewage. Registration every 10 minutes.

Table 6.1 BOD_5 in fresh and thawed samples

Sample	BOD_5, mg O_2 l^{-1}						Median value	Mean value	S.D.
	Sample aliqout								
Fresh	252	234	305	314	250	276	264	272	32
Frozen 3 weeks	221	197	204				204	207	12
Frozen 4 weeks	211	197	342				211	250	80

Remarks to the results. It was clearly seen that the colour of the highly differing aliquot sample from sewage frozen for 4 weeks was much darker than all other aliquot samples. Moreover, the lag time of biologically activity varied notably. For sewage frozen for 3 weeks the lag time of the three aliquot samples was 1.1, 1.8 and 5.3 hours, respectively while the lag time of the six aliquot samples from fresh sewage only varied 0.5 to 1 hours. In addition, lag times for both fresh sewage and sewage frozen for 3 weeks can not be directly compared with those from sewage frozen for 4 weeks, as here 3 hours elapsed after the start of the respirometer before the automatical registration started.

6.1.3 Evaluation of fresh and frozen sewage

The graphs of the oxygen consumption over time in the aliquots of the three principal groups are somewhat dissimilar. To get a more surveyable picture the measurements have been summarized in Figure 6.4 to give a graphic presentation of the median values registered in these groups. Median values were chosen to eliminate the extreme values that are often obtained with biologically materials. It shows that the graphs of the frozen samples, are nearly identical apart from the longer lag time needed in the series of sewage frozen for three weeks. This lag time may be due to a later start of the respirometer in the relation to the moment of thawing or to differences in the temperature of the water employed for the thawing. During the first day the graph of the fresh sewage was almost identical with the other two graphs, thereafter the graphs of the frozen portions displayed a gradual decrease of the rate of the oxygen consumption.

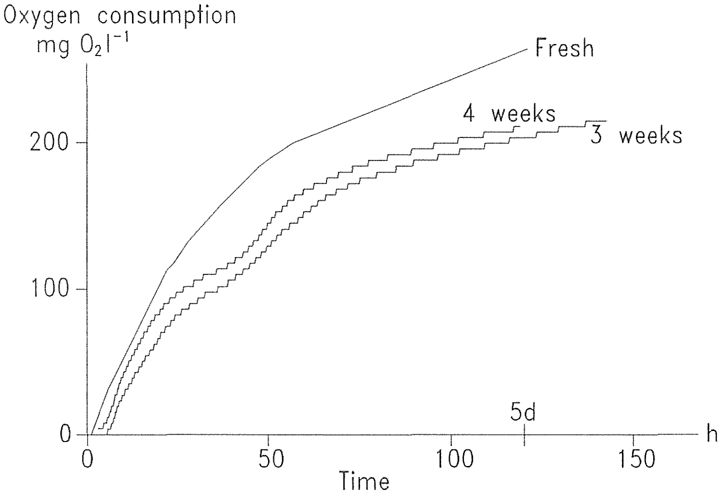

Figure 6.4 Respiration measurements over time in wastewater taken fresh or stored frozen for 3 and 4 weeks, respectively. The diagram presents median values.

The difference between the graphs was examined with the aid of values determined after 5 days (Table 6.1). A statistical calculation using the method of pooled variance estimate (Statgraphics by Statistical Graphics Corporation) gave the following t-values for the differences between the groups.

Fresh sewage *vs* frozen 3w:	t(7) = 3.25,	P = 0.014
Fresh sewage *vs* frozen 4w:	t(7) = 0.61,	P = 0.56
Fresh sewage *vs* frozen 3 and 4w:	t(10) = 1.63,	P = 0.13

The P-values given above show a significant difference between fresh sewage and sewage frozen for 3 weeks. It is true that a pooling of all determinations of the frozen samples (3 and 4w) gave an insignificant difference *vs* fresh sewage, but the P-value indicates a dissimilarity in about 9 cases of 10. With regards taken to the statistical evaluation and the highly differing values observed (Figure 6.1 to Figure 6.3 and Table 6.1) it does not seem possible to preserve a reference sewage for future experiments by keeping it frozen under the conditions of the present experiments. It might be argued that an increased number of series should have been used as this possibly could have given more defined results. However, the figures reported here, indicate that this would have required much more material, which from a practical point of view would have been impossible to handle.

In the design of experiments factors were considered which might affect the homogeneity of sewage portions. For instance how vulnerable are the microorganisms during the time needed for freezing and thawing. A number of microorganisms in the sewage may be killed by the crystallization and the recrystallization during these periods. It is known that up to 90% of exponentially growing microorganisms may die by cold shock[74]. Clearly the microorganisms will be affected by freeze/thawing, but the organic material will probably not be affected. Of course, if the freeze/thawing procedure is long there will be an opportunity for degradation in the sewage. This means that the same experiment but with inoculated samples would probably have given similar results between fresh and frozen sewage as the (available) organic material are still there. In order to reduce the time used for freezing and thawing, sewage to be frozen was divided into comparatively small portions of 300 m and frozen in plastic bottles of 400 m. However, the use of small containers means a comparatively large contact area between sewage and walls and thus a risk of loss of degradable materials by adsorption to walls. The risk of getting such losses from fresh sewage is less if the portions were brought directly into the respirometer. A difficulty affecting both fresh and frozen sewage is how to divide the original sewage into portions of homogeneous composition with regard to nutrients and microorganisms. Even though the sewage of this experiment had been shaken and passed through a strainer, conglomerates of microorganisms and/or nutrients may have been unevenly distributed. For example, the highly deviating BOD_6 value of 342 mg O_2 l^{-1} (see Figure 6.3) determined in the aliquot frozen for 4 weeks points to this possibility.

Conclusion: The factors discussed above give additional weight to the previous conclusion that freezing should not be used as preservation of sewage.

6.2 Degradation in sewage in a simulated sewer.

6.2.1 The experimental design

In the experiment that follows the equipment described in section 5.1.2 was used. For a study of continuing degradation it seems necessary to choose parameters suitable for the determination of conditions which can indicate different stages of the degradation processes. Though no system has been elaborated for such a study, the personnel of comparatively big sewage treatment plants have for many years followed changes in the influent quality partly through sample analysis and partly through continuous monitoring. With respect to the continuous measuring their usual parameters have been pH, temperature and conductivity. In addition oxygen concentration and redox potential (e.g. the open circuit potential) have been commonly determined and with the aid of automatic analysis often also TOC and COD. Less used is equipment for the continuous determination of sulphide, ammonium etc. With regards taken to the facts mentioned above and with considerations to expected possible results the following parameters were chosen for an experimental series on continuing degradation.

Oxygen. Changes in the concentration of oxygen indicate changes in the activity of aerobic microorganisms. In cases of known rate of oxygen transfer it is possible to estimate OUR (Oxygen Uptake Rate), the rate at which oxygen is consumed by the microorganisms and/or by chemical processe. On the contrary, if the oxygen uptake rate is known it is possible to estimate the oxygen transfer constant. In the experiments the OU measured in the respirometer and the simulated system will be compared and the oxygen transfer constant in the sewage will be estimated.

Open circuit potential. Determination of the potential is of special significance in cases where the rate of oxygen consumption is of the same magnitude as the maximal rate of oxygen transfer (i.e. at an oxygen concentration = 0). Changes in the redox potential will thus indicate changes in the concentration of the redox couple or a change to a different redox couple. If it is possible to identify the reason for redox potential changes then it seems possible that the redox potential can function as a measure of the quality of the sewage. It is also the aim to give a theoretically valid explanation to the changes in redox potential.

pH - value. Microbiological activities will liberate and/or bind H^+, thus influencing the pH of the sewage. To this must be added that most of the redox couples which govern the reactions in the sewage are of a pH dependent nature, which makes the pH an indispensable parameter to be determined.

Conductivity. Microbiological degradation will also result in mineralisation (i.e. organic + O_2 --> H_O + inorganic) and therefore lead to an increased conductivity, the value of which can be recorded by conductivity measurements. It is also known that the ionic strength will influence the measured value of redox potential due to the liquid junction potential as well as the chemical activities. This influence was regarded as negligible during the evaluation of the results. In the regulation of the instruments it was found that simultaneous measurements with a conductivity electrode and other electrodes could give rise to disturbances. However, this was solved in the first experiment by using a flow-through conductivity electrode. In the last experiments it was possible to separate the conventional conductivity electrode galvanically from other electrodes with an isolating signal amplifier.

In addition to the continuous determinations of oxygen, redox potential, pH and conductivity further information was obtained from test aliquots taken at different occasions from the experimental samples in which the degradation was followed. The test aliquots were submitted to determinations of COD, TOC and alkalinity. All of these parameters can be seen as quality parameters. The relation between COD and TOC can give a conception of the possible part of readily degradable material. Furthermore COD will in these experiments be used in the estimation of the oxygen transfer coefficient (section 3.1.3). It was regarded to be of interest to examine alkalinity during the degradation process as alkalinity is considered to decrease during aerobic degradation. Alkalinity is also reported to be a limiting factor in low alkalinity wastewaster in nitrification. Therefore if the alkalinity is changing during sewer transport then this may have an influence on the following wastewater treatment.

In the experimental series the equipment described in section 5.1.2 and presented in Figure 5.2, Figure 5.3 was used. The experiment contains a series of three experiments, A, B and C carried out in slightly different ways.

In common for experiments (A - B) were repeated COD determination, continuous measurements of pH, oxygen concentration and redox potential and manual measurement of temperature. Respirometer measurements which are described later were performed parallel with the measurements mentioned above. Manual recording was performed parallel with the automatic recording in case of malfunction of the datalogger.

Conductivity was measured in experiments A and B but not in C. In experiment C a potential measurement with two different electrodes (Au and Pt) was preferred.

In experiment A it was decided that alkalinity only should be determined at start and termination. As an unexpectedly great difference was found between the two measured alkalinity values it was decided that repeated determinations should be made in the two other series. In this case the revolution rate during the sampling was not changed. As indicator in case of sedimentation the samples was analyzed on total Fe.

In experiments B and C repeated alkalinity determinations and repeated TOC determinations were added. Furthermore the routines for test sampling were changed after experiment A. Because, the results of this experiment indicated that the revolution rate during the sampling was too low to prevent sedimentation. In later experiments, therefore, more representative samples were achieved by a considerable increase of the revolution rate in connection with the sampling.

To get more information of the sewage quality three of the six available beakers in the respirometer were used for samples which had been diluted 1:1 with distilled water. The intention was to facilitate the detection of a possible threshold of the noxious effect exerted by the content in the sewage. In this way it seemed possible to procure knowledge of the frequency of such threshold values at a range of dilution up to 1→2. The rest of the places were used for unmodified sewage but with one exception. In experiment A nitrification was suppressed with ATC in one of the respirometer samples. However, as no difference, that could be related to nitrification,was found between the aliquot sample with ATC and the other, it was decided to refrain from the suppressing of nitrification in the following experiments for the favour that the sewage would not be modified at all. The respirometer measurements were carried out at 20°C

The experiments A and B were carried out at room temperature (20.5°C) and experiment C at 16 to 17°C.

Owing to the fact that a great deal of the redox reactions in sewage are pH dependent, this series was added with three new experiments in which pH and redox potential were determined during titration of 100 m sewage with 0.02 M HCl. In the first titration the sample was an aliquot from the sewage used in experiment B, the second sample was a mixture 1:1 of the first sample and distilled water. The third sample was taken at the same sewer point as the first sample but at a different time.

Finally, using the simulated system (Figure 5.2, Figure 5.3) the transfer rate of oxygen into pure water was measured at 20°C and 16.5°C, respectively. The determinations were made at a water depth of 230 mm and a propeller velocity of 160 RPM. Zero oxygen concentration was achieved by bubbling nitrogen gas through the water while keeping the plexiglass plate lowered to the water surface to prevent reentrance of oxygen and to keep the propeller velocity at high level (about 500 RPM) to spread the nitrogen bubbles more efficiently. When the oxygen concentration had reached zero or was close to zero the stirring was reduced to 160 RPM and the plexiglass plate raised to admit free access of the air.

6.2.2 Experimental results

The results of the different analyses are presented in Table 6.2 - Table 6.5 and Figure 6.5 - 6.13.

Figure 6.5 - Figure 6.7 present the automatic registrations of pH, oxygen concentration, redox potential and conductivity performed in the simulated sewer. During the occasions when aliquots were taken for analyses of alkalinity, COD and TOC were also measured. As seen in Figure 6.5 there are uncompleted short breaks in the automatic registrations of sample experiment A. A longer break appeared in experiment B, here the automatic registration was completed by manually registered data. This is indicated by short lines in the middle of the graphs (Figure 6.6). Finally at the treatment of the sample experiment C the conductivity electrode was changed for a redox potential platinum electrode. Figure 6.7, therefore, gives graphs for two different measurements of the redox potential, one with the previously used Au-electrode and one with the Pt-electrode, but both with a Ag/AgCl reference electrode.The electrodes were controlled against the chinhydrone electrode.

Table 6.2 gives the results of the determinations of alkalinity, COD and TOC in the aliquots taken at different times from the sewage in the simulated sewers. Values achieved with filtered aliquots are within brackets. The table also gives the automatically registered values of pH, oxygen concentration and redox potential, read off when the aliquots were taken from the simulated sewers.

Figure 6.8 - Figure 6.10 give graphs of the cumulative oxygen consumption over time in sewage during incubation in the respirometer. Diluted sewage samples are denominated with 1:1.

Table 6.3 gives the results of the determinations of alkalinity, COD and TOC in sewage both before and after the respirometer measurements. After the respirometer measurement the sample obtained by pooling aliquots with the same dilution grade.

Figure 4.14 - 4.15 show three different graphs of the pH and redox potential titration with 0.02 mol l^{-1} HCl in 100 m sewage saturated with oxygen.

Figure 6.13 shows graphs of oxygen transfer in the simulated system at a water depth of 230 mm and at 16.5°C and 20°C, respectively.

Table 6.2 Results from experiment A, B and C during simulated sewer condition.

Sample	Time h	Alkalinity mg HCO_3^- l^{-1}	COD mg O_2 l^{-1}	TOC mg C l^{-1}	pH	Oxygen mg $O_2 l^{-1}$	$E_{Ag/AgCl}$ mV Au	
A*	0	112	244 (96)	-	7.8	5.60	151	
	2.67	-	227	-	7.8	4.69	87	
	5.67	-	206	-	7.6	3.24	72	
	24	-	167	-	7.5	4.08	60	
	47.7	-	128	-	7.9	7.18	66	
	167	60	54	-	7.6	7.48	101	
B	0	175	500 (210)	109 (76)	8.4	6.18	20	
	3.5	225	480	94	8.1	0.14	-40	
	6.25	234	490	104	8.2	0.12	-71	
	24	239	380	76	7.5	0.67	-58	
	48	246	350	73	7.4	0.0	-45	
	127	271	260 (65)	46 (26)	7.6	5.30	35	
C	0	159	590 (300)	134 (96)	8.0	7.53	6 Au	-141 Pt
	3	151	520	126	8.1	5.18	-27	-110
	6	166	500	127	8.0	1.47	-29	-106
	23	161	490	126	7.0	0.0	-131	-180
	95	210	400	91	7.4	0.0	-282	<-300
	143	212	300 (99)	69 (31)	7.4	0.0	-151	-224
	148.3	-	-	-	7.4	0.06	-145	-192

( )Value of the filtered sample.
*The stirring rate was not increased during sampling resulting in an incomplete suspension of solids in the beaker.

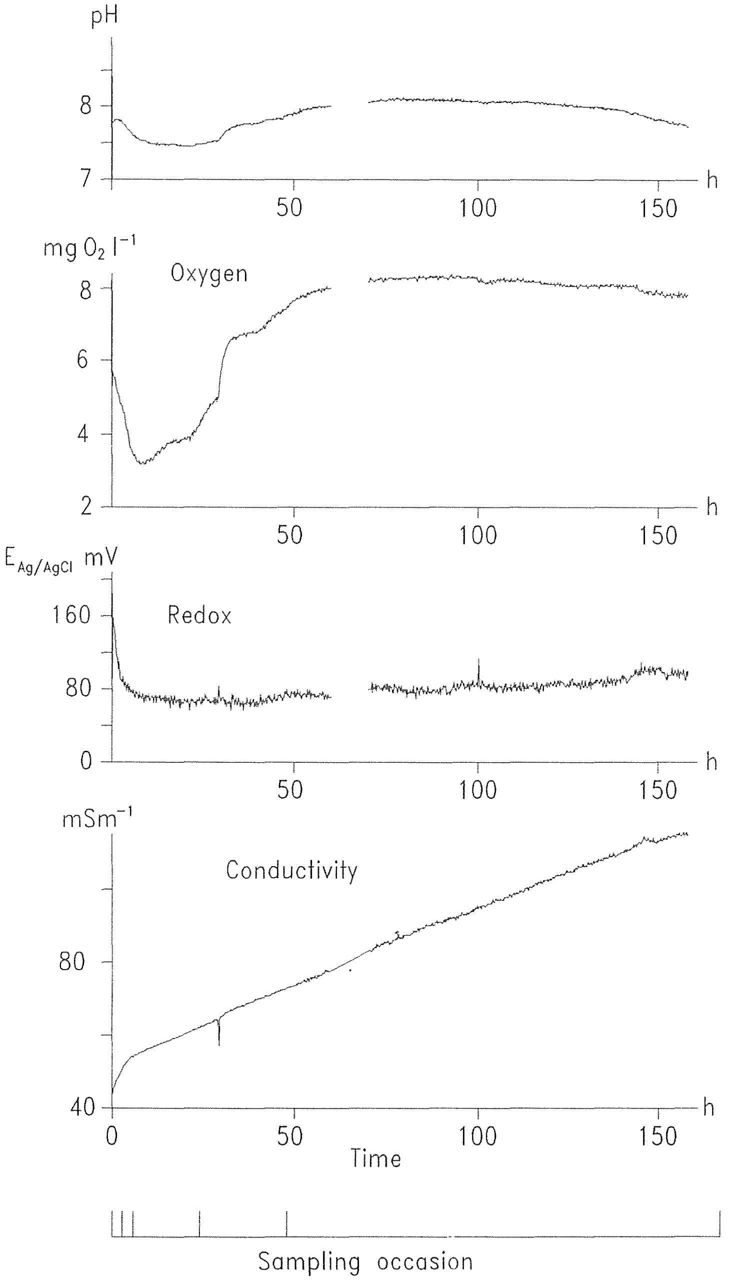

Figure 6.5 Experiment A. pH, oxygen concentration, open circuit potential and conductivity measurements during simulated sewer condition. The time for separate analysis is marked as sampling occasion.

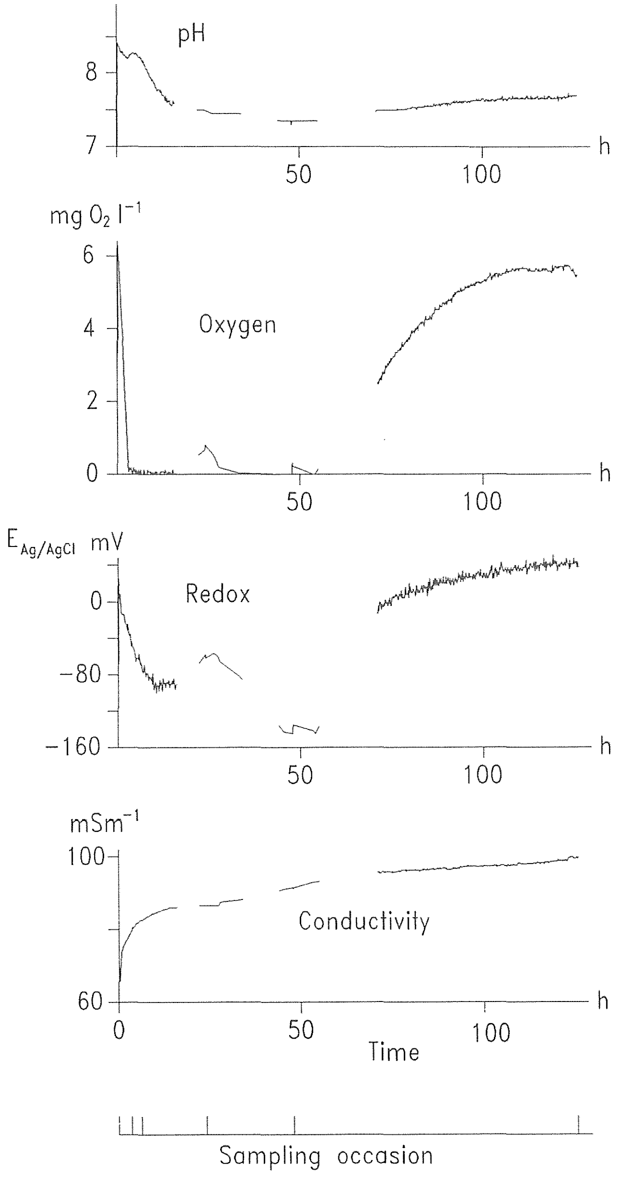

Figure 6.6 Experiment B. pH, oxygen concentration, open circuit potential and conductivity measurements during simulated sewer condition. The time for separate analysis is marked as sampling occasion.

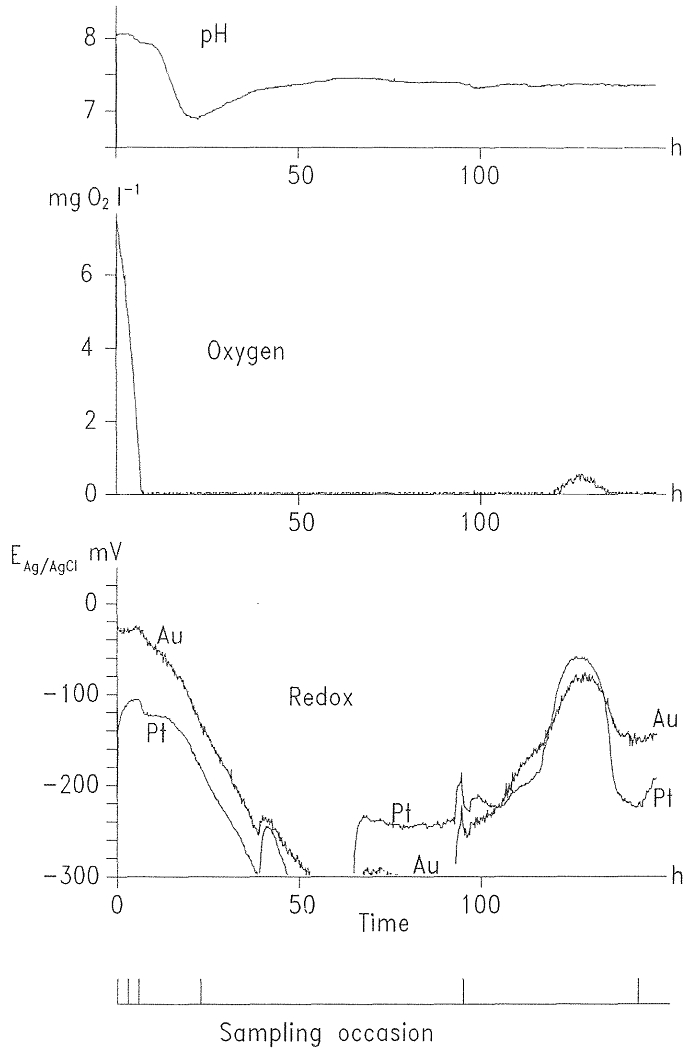

Figure 6.7 Experiment C. Measurements of pH, oxygen concentration and open circuit potential measurements during simulated sewer condition with both gold and platinum electrodes. The time for analysis is marked as sampling occasion.

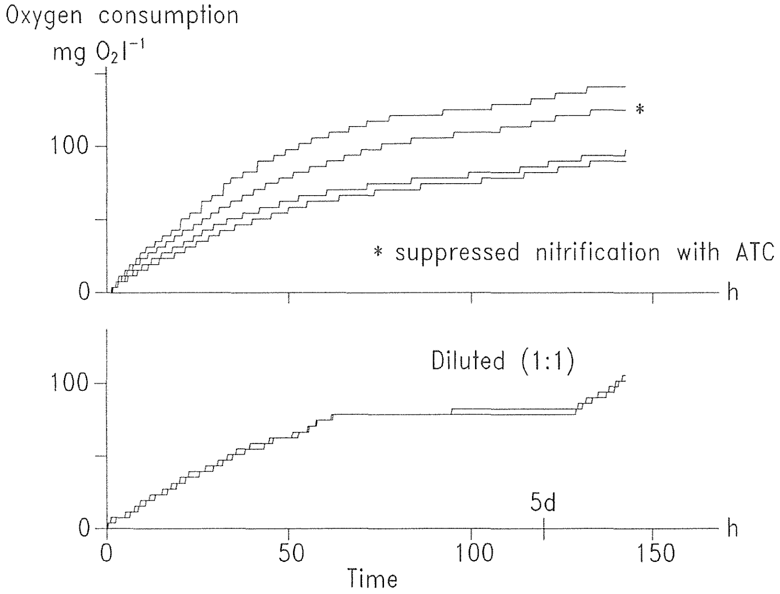

Figure 6.8 Experiment A. Respirometer measurement in sewage with sewer age of 10 minutes.

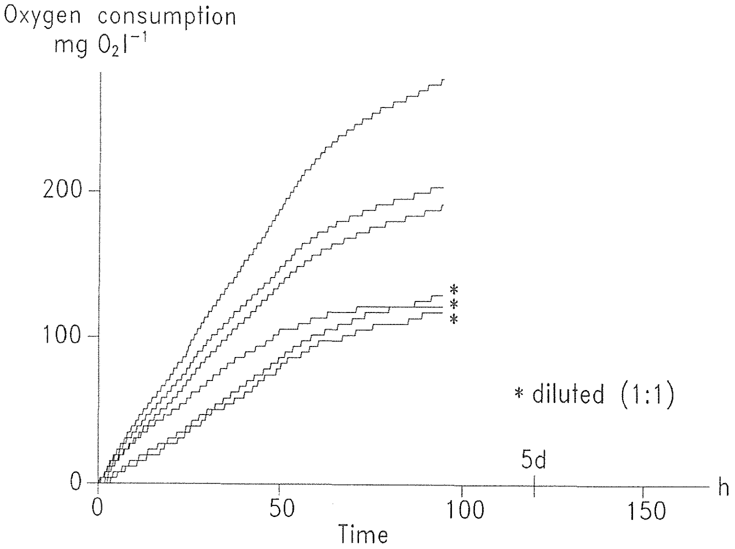

Figure 6.9 Experiment B. Respirometer measurements in sewage with sewer age of 10 minutes.

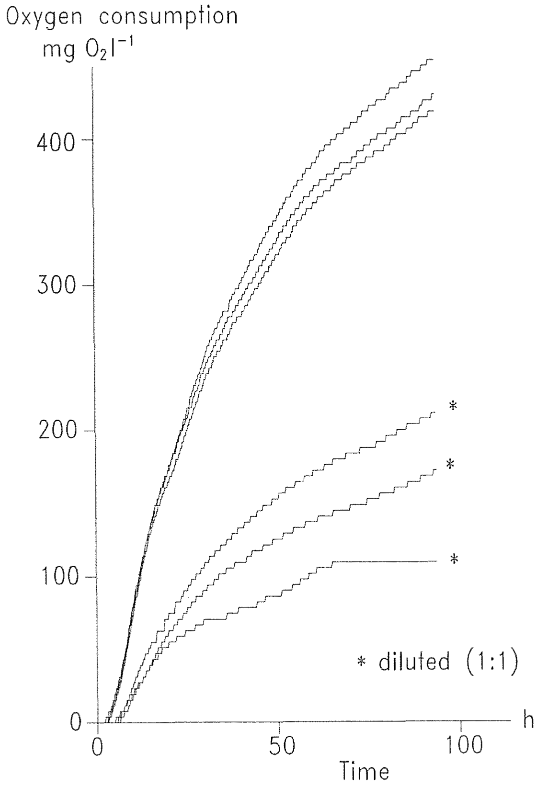

Figure 6.10 Experiment C. Respirometer measurements in sewage with sewer age of 10 minutes.

Table 6.3 Results from experiment A, B and C after respirometer measurements and for the diluted samples also before the measurement.

Experiment	Time d	Alkalinity mg HCO_3^- l^{-1}		COD mg O_2 l^{-1}		TOC mg C l^{-1}
		1:0	1:1	1:0	1:1	1:0
A	6	133	-	78 (22)	-	21 (12)
B	0	175*	88	500*	230	109*
	4	264	132	240 (85)	130	53 (30)
C	0	159*	85	590*	280	134*
	4	220	124	220 (87)	96	47 (29)

* Copy from Table 6.2 ( ) Filtered sample

Determinations in Figure 6.11 were made in two aliquots from experiment B, one fresh and one diluted 1:1 with distilled water.

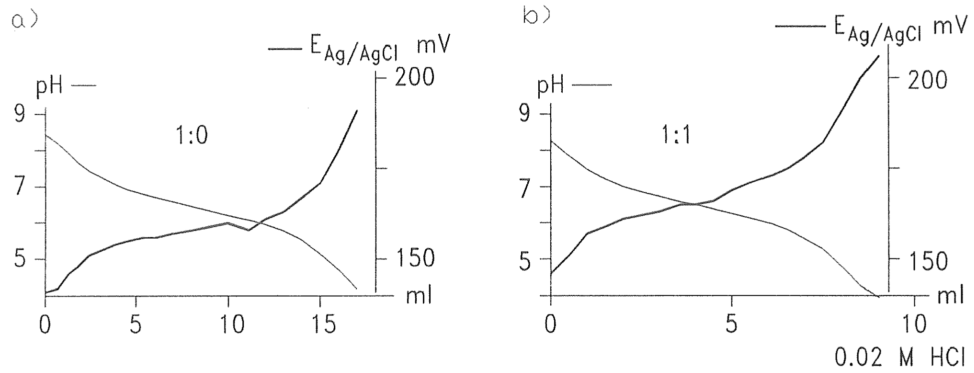

Figure 6.11 Simultaneous pH and potential titration with 0.02 mol l^{-1} HCl in sewage saturated with oxygen.

Registrations in Figure 6.12 were made during two separated titration.

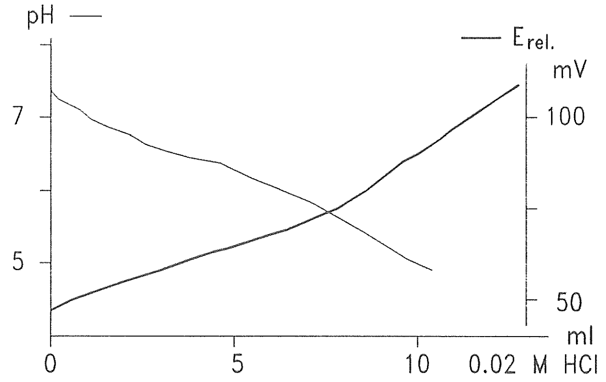

Figure 6.12 Potential and pH titration with 0.02 mol l^{-1} HCl in sewage saturated with oxygen.

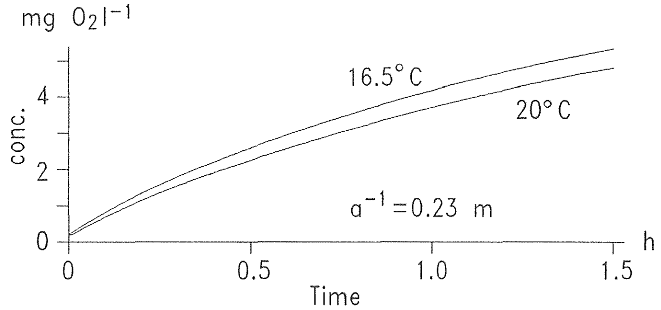

Figure 6.13 Oxygen transfer in the simulated system with distilled water.

6.2.3 Evaluation according to oxygen uptake

The design of the experiment and according to section 3.1 allows three different possibilities to calculate the oxygen uptake (OU) in sewage. In the following section the oxygen uptake in the sewage from the three different experiments will be determined based on oxygen concentration measurement, respirometer measurement and COD analysis. The calculation methods will differ due to oxygen concentration, settling and surface adsorption condition.

1. Oxygen uptake according to the oxygen concentration (section 3.1.1) is calculated by Equation 6.1 modified from Equation 3.1.3 where ΔC is neglected. The results from the other methods were used to calculate the oxygen transfer constant (K_La) beside the K_La calculated for distilled water.

$$OU_x = \sum_{k=0}^{x} \alpha K_L a(\beta C_m - C_k)\Delta t_k \tag{6.1}$$

2. Oxygen uptake according to the respirometer measurement (section 3.1.2) is calculated by Equation 3.1.7 and 3.1.8.

3. Oxygen uptake according to COD analysis (section 3.1.3) is calculated by Equation 3.1.10 in case of excess of oxygen, 3.1.11 in case of oxygen concentration ≈ 0 and finally 3.1.16 in case of oxygen concentration ≈ 0 and with an initially adsorption that not can be excluded.

The K_La values will be given by the slope showing the relation $\ln(C_m - C)$ *vs* time. Thus from data presented in Figure 6.13 the K_La values of distilled water at 16.5°C and 20°C were calculated to be 0.492 h^{-1} and 0.477 h^{-1}, respectively (Figure 6.14).

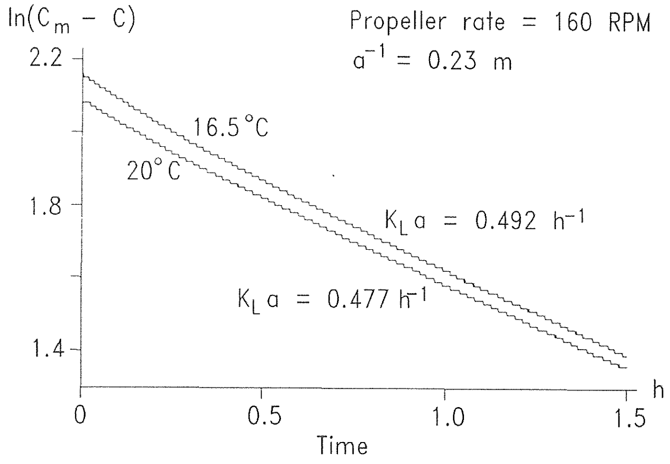

Figure 6.14 ln(C_m - C) *versus* time. Distilled water in the simulated system.

The K_La values in Figure 6.14 were determined in the simulated system at a water depth of 230 mm and a propeller velocity of 160 RPM. The revolution rate was kept constant during the measuring series, whereas due to the repeated sampling of test aliquots the water depth gradually decreased from 250 mm to about 200 mm. This means that the K_La value will vary in a range of 0.44 - 0.55 h^{-1}.

For comparison between different measuring series as well as between different methods to determine the uptake of oxygen a mean K_La value of 0.5 h^{-1} has been chosen.

Experiment A: By regression of OU_t based on COD values only the exponential Equation 3.1.10 was used, as excess of oxygen prevailed during the whole experimental period. The regression gave OU_∞= 194 mg O_2 l^{-1} , τ = 48 h (Figure 6.15) and with a correlation of 0.995 to measured values. Corresponding regression performed according to the method based on the median values from the respirometer study Figure 6.8 gave OU_∞= 117 mg O_2 l^{-1} and τ = 56 h. Considering the low initial COD-content of 244 mg O_2 l^{-1} these results appear to be more probable than those obtained with the COD method.

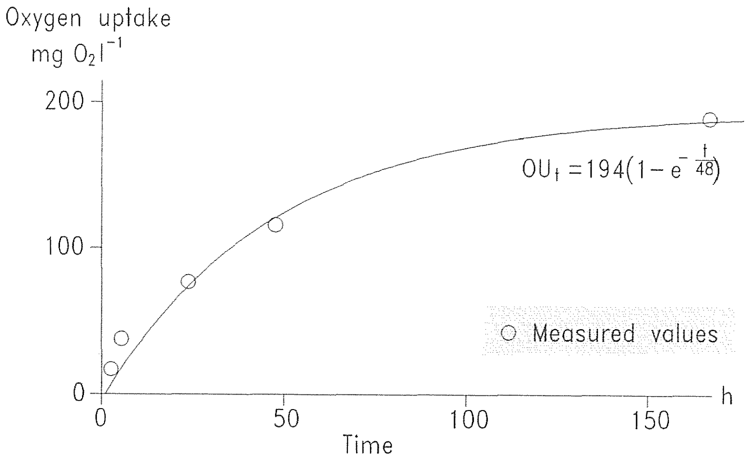

Figure 6.15 Exponential regression of OU_t based on COD, experiment A.

Provided that the results of the COD method are valid, a great part of the suspended material, the biomass included, should be disintegrated. However, with regard taken to the excess of oxygen and the short measuring period a lysis of biomass does not appear more probable in the simulated system than in the respirometer, which is why this cannot be the reason. Here it could be said that the two methods are not comparable, but an analyze of total iron parallel with the COD analysis indicates a sedimentation or an adsorption of material meaning that the aliquot cannot be regarded as representative. The difference is probably related to the rotation rate that allow sedimentation and consequently to a too low rotation rate while sampling. Later on in the experimental series the rotation rate was temporarily increased during the sampling.

Calculations based on the values for oxygen uptake given by the methods based on COD and on respirometer measurement, respectively, gave differing K_La values when using the exponential equations. These values are summarized in Table 6.4 compared with the estimated mean K_La value for distilled water.

Table 6.4 Calculated values of OU, τ , K_La and α based on the result of oxygen concentration, COD analysis, respirometer measurement and the mean K_La value for distilled water for experiment A, the total experimental time is 167.7 h.

Method	OU_∞ mg O_2 l^{-1}	τ h	OU_t mg O_2 l^{-1}	K_La h^{-1}	α m^{-1}
K_La, distilled water	-	-	130	0.5	-
OU_t , COD method	194	48	188	0.72	1.44
OU_t , BOD method	117	56	11	0.43	0.86

In Table 6.4 calculations according the COD method have given an improbable value, i.e. a K_La value of 0.72 h^{-1} which is to be compared with K_La = 0.5 h^{-1} for distilled water. This leads to an α = 1.44 compared to α = 0.86 based on the BOD method which is much more realistic.

In experiment A there was an excess of oxygen during the whole experimental time. This means that graphs on the cumulative oxygen uptake (OU_t) calculated from the three different methods ought to agree, which in fact was not the case. Figure 6.16 summarizes the results obtained with the different methods. The COD method gave considerably higher oxygen consumption than the respirometer method - a result which in itself is not reasonable. However, as discussed above a too low rate of rotations has probably caused unrepresentative sampling.

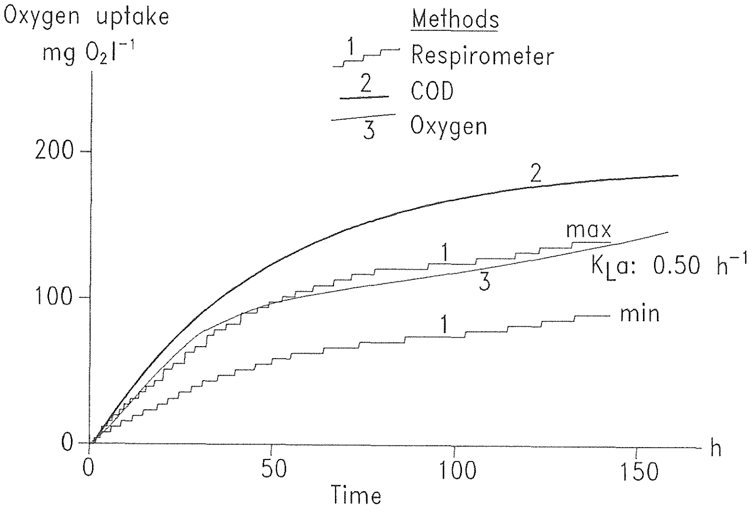

Figure 6.16 Experiment A: comparisions of OU_t from respirometer measurements, COD analysis and registrations of oxygen concentration.

The α value is found to be in the range of 0.86 to 1.0 according to Figure 6.16.

Experiment B. The experimental condition of series B differ from those of series A in so far as oxygen concentration during a longer period was ≈ 0 mg O_2 l^{-1}. This means that the oxygen uptake will follow Equation 3.1.10 at oxygen concentration > 0 mg O_2 l^{-1} and Equation 3.1.11 at concentration ≈ 0 mg O_2 l^{-1}. The exponential regression according to Equation3.1.10 gave $OU_\infty = 257$ mg O_2 l^{-1} and the time constant $\tau = 49$ h. The straight line pertaining to oxygen concentration ≈ 0 mg O_2 l^{-1} will intercept the substrate limiting curve at the times of transition to and from the zero oxygen concentration. The slope of the straight line will give the value for $C_mK_La = 2.86$ mg O_2 l^{-1} h^{-1}. With $C_m = 9.08$ mg O_2 l^{-1} the K_La value will be 0.31 h^{-1}. (Figure 6.17)

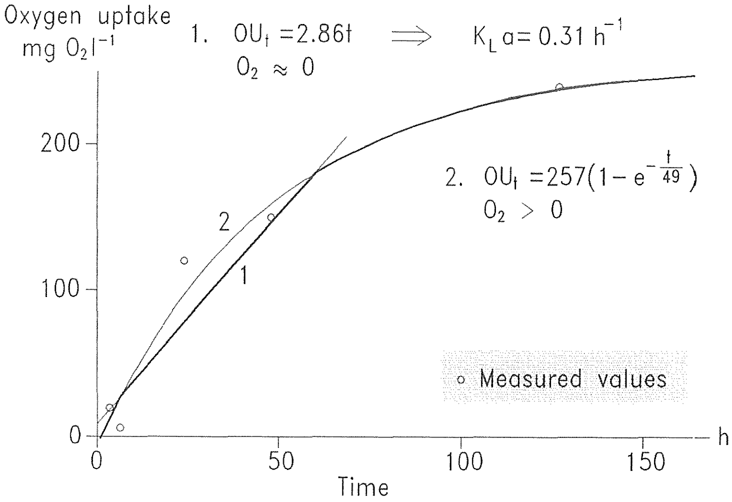

Figure 6.17 Experiment B: regression of data from OU_t based on COD analysis.

Corresponding exponential regression using the results from the respirometer measurement gave $OU_\infty = 286$ mg O_2 l^{-1} and the time constant $\tau = 72$ h. These values are higher than those achieved with COD method due to the fact that the time employed in the simulated sewer was 30 h longer than in the respirometer. In general, series of shorter duration seem to give values for OU_∞ and τ at exponential of results from respirometer measurements. However, the differences are of no great significance when OU_∞ and τ are calculated according to the oxygen method (Table 6.5).

Table 6.5 Calculated values of OU, τ , K_La and α based on the result of oxygen concentration, COD analysis, respirometer measurement and the mean K_La value for distilled water Experiment B, the total experimental time is 127 h.

Method	OU_∞ mg O_2 l^{-1}	τ h	OU_t mg O_2 l^{-1}	K_La h^{-1}	α m^{-1}
K_La, distilled water	-	-	402	0.5	-
K_La, COD method	-	.	249	0.31	0.6
OU_t , COD method	257	49	232	0.30	0.6
OU_t , BOD method	286	72	237	0.29	0.6

The different K_La value agrees notably well whether COD method or respirometer method has been used. The α value were found to be 0.6.

The oxygen uptake noted with the different methods are summarized in Figure 6.18.

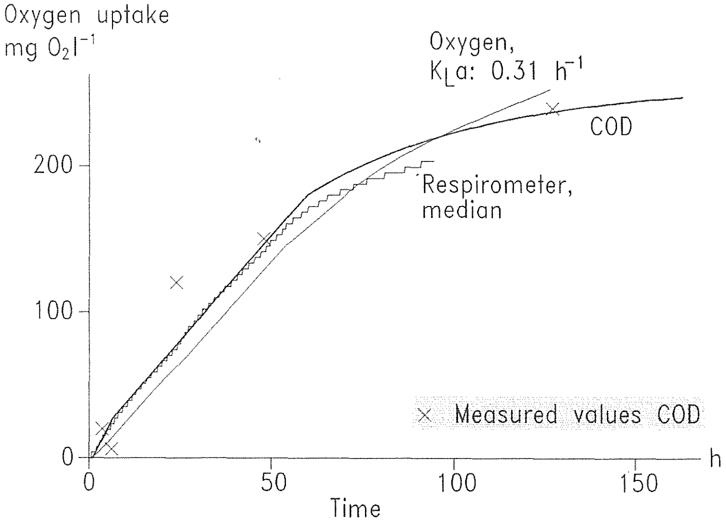

Figure 6.18 Experiment B: comparisons of OU_t from respirometer measurements, COD analysis and registration of oxygen concentration.

Experiment B shows that the difference in COD measured in sewage at two different points of time is comparable to the biochemical oxygen consumption of the mean time, provided that at least the beginning and final conditions are aerobic. The result in the simulated system indicates a somewhat lower oxygen uptake during the period of zero oxygen concentration. However, this is compensated by the fact that the decrease of the oxygen uptake rate shows up later in relation to the decrease of the oxygen consumption in the respirometer.

The determination of consumption of oxygen in the respirometer is principally the same as determinations based on measurements of the oxygen content - the principle is the transferred amount of oxygen equals the consumed amount. The oxygen concentration method is thus a method comparable with the two other methods. Consequently, knowing the K_La value the rate of oxygen consumption in the sewer net can be continuously determined.

Experiment C. In contrast to previous experimental series, in series C the oxygen concentration has been ≈ 0 during the major part of the experimental period, which means a linear regression of oxygen uptake.The exponential oxygen uptake is during a period of about 7 h and with 3 measured values of COD. The number of values will be too few for an useable regression. Considering the conclusion made from experiment B that the COD method and the respirometer method are comparable during periods of oxygen excess it is possible to use the results from the respirometer measurement. Exponential regression of the median BOD graph gives $OU_\infty = 527$ mg O_2 l^{-1} and $\tau =$ 41 h.

The transition between exponential and linear oxygen uptake takes place at $t = 6.7$ h giving $OU_{6.7} = 50$ mg O_2 l^{-1} this corresponds to a K_La value in the size of 0.7 h^{-1} which must be unreasonable due to the value in distilled water. However, by direct reading of respirometer values a more reasonable value of $OU_{6.7} =$ 30 mg O_2 l^{-1} is obtained. A linear oxygen uptake starting at 6.7 h and a $OU_{6.7} = 30$ mg O_2 l^{-1} will give differences of up to 80 mg O_2 l^{-1} between measured and calculated values. Such differences are too great to only depend on analysis errors. (See Figure 6.19). In this case the initially adsorption is not negligible which is why Equation 3.1.16 is used. To solve the equation the five first values of the apparent oxygen uptake have been used.

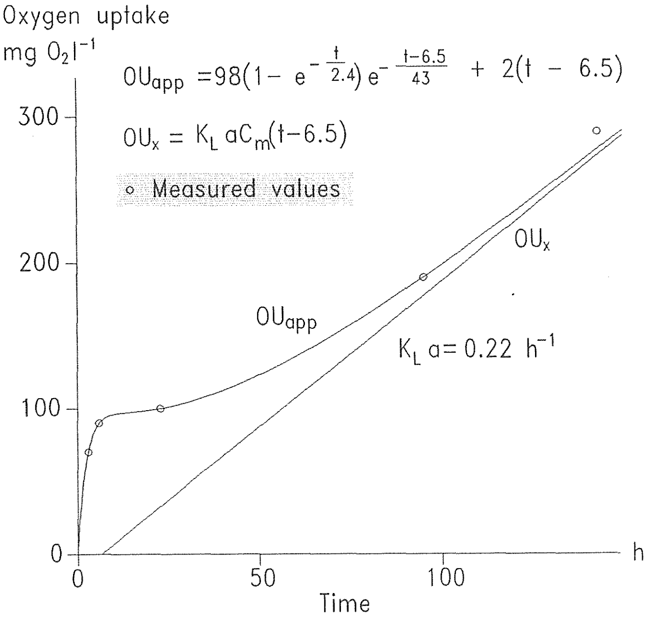

Figure 6.19 The apparent oxygen uptake OU_{app} and the estimated oxygen uptake OU_t according to Equation 3.1.16

Equation 3.1.16 gave $COD_{max}^{ads} = 98$ mg O_2 l^{-1} , the time constant for the adsorption of COD $\tau = 2.4$ h, lag time for the oxygen uptake $T_2 = 6.5$ h, the time constant for the oxygen uptake in the biofilm $\tau_2 = 43$ h and finally the oxygen transfer value $K_L a C_m = 2.0$ h^{-1} mg O_2 l^{-1} (Figure 6.19). According to the respirometer measurement the lag time for oxygen uptake should be about 2 h and according to the oxygen concentration measurement the oxygen uptake should be exponential for the first seven and a half hour. A correction of the constants would give slightly different values but this is not considered here.

About the respirometer method, it must be said that exponential regression gives a poor correlation at low values of t ($t < 10$ h) owing to the lag time (Figure 6.10)

Calculation of $K_L a$ using the result from COD method gave with the oxygen method the following results (Table 6.6).

Table 6.6 Calculated values of OU, τ, K_La and α based on the result of oxygen concentration, COD analysis, respirometer measurement and the mean K_La value for distilled water. Experiment C: the total experimental time is 148 h.

Method	OU_{ads} mg O_2 l^{-1}	τ h	OU_t mg O_2 l^{-1}	K_La h^{-1}	α m^{-1}
K_La, distilled water	-	-	642	0.5	-
K_La, COD method	-	.	290	0.23	0.45
OU_t , COD method	98	43	232	0.22	0.45

The α value was found to be 0.45 according to Table 6.6

The oxygen uptake noted with the different methods are summerized in Figure 6.20

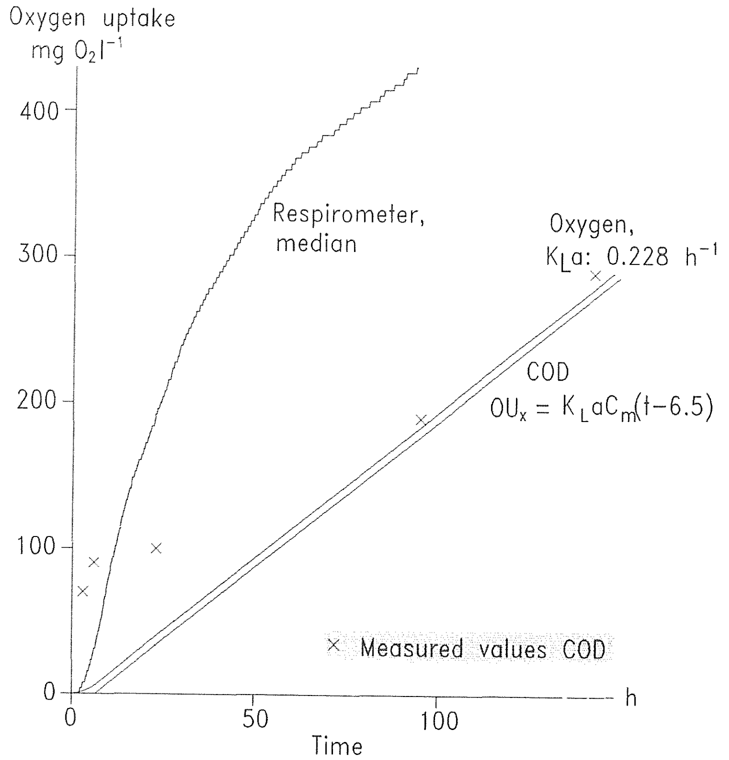

Figure 6.20 Experiment C: comparisons of OU_t from respirometer measurements, COD analysis and registration of oxygen concentration.

One of the most serious weakness in determing the oxygen uptake using this method is the risk for systematic errors due to the standard deviation of the COD value. (For COD value at 500 mg l^{-1} the standard deviation is 16 mg l^{-1}, for COD value at 50 mg l^{-1} the standard deviation is 12 mg l^{-1}). The potential discrepancy between the measured and real value of COD_0 will not be possible to eliminate in the continued calculation but will remain as a systematic error.

The excess of oxygen in-sewers will depend on the consumption rate and the oxygen transfer rate. The consumption rate for the sewage in experiment A, B and C is shown in Figure 6.21.

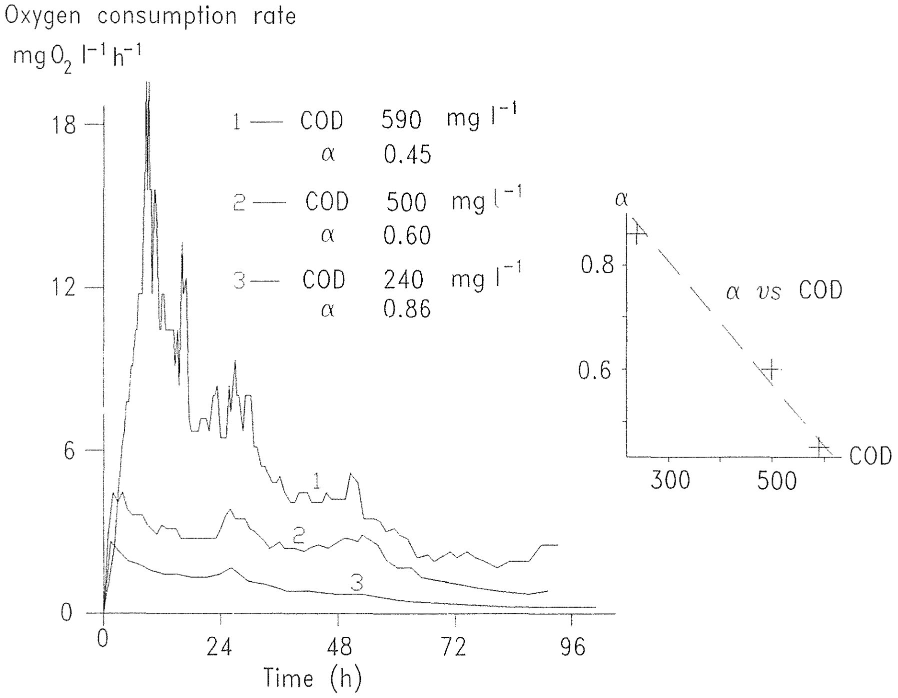

Figure 6.21 Biological consumption of oxygen in wastewater measured in a respirometer. From experiment 1) C, 2) B and 3) A.

The results shown in Figure 6.21 express a low oxygen consumption rate. Even with a COD-content of 590 m O_2 l^{-1}, the consumption is in the range of 6-12 m O_2 l^{-1} h^{-1} during the first 48 hours, except for the initial phase. To understand the diagram given in Figure 6.21 it is necessary to consider that a biofilm is always present on the walls of the sewer. This was initially not the case in the respirometer, a condition which is displayed by the great increase in the rate of oxygen consumption during the first day. The adsorption of organic material and microorganisms to the respirometer walls starts immediately, and as many aerobic heterotrophs have generation times of about one hour, the consumption of oxygen will increase until available nutrients are limited.

To balance the oxygen consumption of this primary wastewater relatively low K_La-values are required. Typical in laboratory experiments is the range of 0.2 - 1.2 h^{-1}. However, Taghizadeh-Nasser[45] determined K_La-values experimentally for sewers, in the range of 4-8 h^{-1} depending on the water depth, with lower values for high depths. Clean water was used in these experiments. Even if correction for the α-value is done the oxygen transfer rate is greater than the consumption rate.

The conclusion is that, at least at the start of the transport in the sewer net, oxygen transfer will not be the limiting factor for the biological processes.

Something that can be noted in this context, figure 6.21, is that the α-value seemed to be linear dependent of COD in the range of these experiments.

6.2.4 Evaluation according to pH and alkalinity

The alkalinity in experiment B and C (Table 6.2) increased slightly during the experimental time in spite of the fact that the pH-value varied in both increasing and decreasing directions. From a theoretical point of view it seems more likely in-sewer that an aerobic degradation should be accompanied by an increase or maintenance of alkalinity than a decrease (section 3.2.2). However, it might also be possible that consumption of fatty acids would cause an increased alkalinity, though this can hardly explain a temporary decrease of the pH value. A comparison of the alkalinity values in experiment A after 167 h shows that the alkalinity value in the simulated sewer was 60 mg HCO_3^- l^{-1}, and the alkalinity value in the respirometer was 130 mg HCO_3^- l^{-1}. This difference seems to due to that the buffering capacity is partly derived from the suspended matter. This would probably also permit a decrease of pH in the water phase in spite of an increase of the total buffering capacity.

6.2.5 Evaluation according to potential measurement

The conductivity was found to increase during the measuring periods probably due to mineralisation appearing as a consequence of the degradation. However, considering the long measuring times and the comparatively small measuring volumes it seems possible that part of the increase has been caused by leakage from the electrodes.

Figure 6.22 shows the pH-dependence of the redox potential as determined under oxygen saturation in three different sewage waters. From Nernst's equation for the reaction $O_2 + 4\ H^+ + 4\ e^- = 2\ H_2O$ ($E_h = 1230 - 59pH + 15\log[O_2$ at 25°C)] a slope of 59 mV/pH unit was to be expected. However, as can be seen in Figure 6.22, this is obviously not the case. The explanation can be that the potential is not determined by a chemical equilibrium but by the kinetics between anode and cathode reactions occurring at the surface of the electrode.

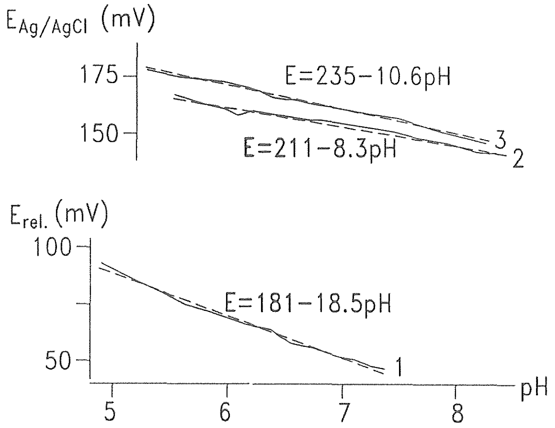

Figure 6.22 Open circuit potential *vs* pH (1). Sewage 10 min in-sewer age (2) Sewage, the same as in experiment B (3) Sewage as in B but diluted with distilled water 1:1. The samples were saturated with oxygen at 20°C.

Recalling the equation in section 3.3 concerning ΔE/ΔpH this will be $-(b_cB_a / (b_a + b_c)$ in the case of activated controlled electrode reactions or $-b_c$ in the case of an anodic mass transport controlled reaction and consequently $-b_a$ in the case of a cathodic mass transport controlled reaction. According to the slopes in Figure 6.22 it is found that ΔE/ΔpH in the three measurements (1, 2 and 3) are -18.5, -8.3 and -10.6, respectively, thus indicating varying courses of the velocity determining electrode reactions. It seems reasonable that the pH dependence found in the first sewage sample (1) should differ from the other as this sample was taken at a different time and therefore probably would have had a different composition. In the last two measurements (2 and 3) agreeing values of ΔE/ΔpH were to be expected as the measurements were made in an ordinary sewage sample and in a dilution 1:1 of the same sample. This points to a simultaneous appearance of more than one not negligible anode reaction, the Tafel slopes which had shifted differently due to the dilution. In addition, there is also the risk that dilution will bring suspended substances into the solution. Finally, for correct comparisons the measurements should have been performed in solutions with the same ionic strength, which however, was not the case.

The cathodic reaction is assumed to be constituted by the oxygen reduction and the anodic reaction mass transport controlled. The expected potential shift is ~60 mV per pH unit or pH independent. In this case an Au electrode was used which means that the pH independent step is expected to be the rate determining step. This will lead us to an anodic reaction with pH depended compounds.

For sample A in Figure 6.5 the pH is relatively constant about 80 mV vs Ag/AgCl or 0.3 V vs the hydrogen electrode. If this would be a potential of equilibrium the expected value would be ~0.5 according to the following calculation:

$$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O \qquad E^0 = 1.23\ V$$

$$E_{eq} = E^0 + RT/4F\ \ln[O_{2(aq)}][H^+]^4 \qquad (6.2)$$

where $O_{2(aq)} = 8$ mg l^{-1} with MV. = 32 g mol^{-1} $\Rightarrow [O_{2(aq)}] = 2.5 \cdot 10^{-4}$ mol l^{-1}
and $pH \approx 8$

Consequently it is a mixed potential where the oxygen reduction is kinetically controlled. Because of the variation or lack of variation in potential with variating oxygen concentration it can be suspected that in this case oxygen reduction is negligable as cathodic reaction. The dominant cathodic reaction may, for example, consist of a reduction of Fe^{3+}.

In Figure 6.23 a relation between the relative potential and oxygen concentration is obvious. Regression of the potential according to log $[O_2]$, pH and log(time) for oxygen concentration > 0 mg O_2 l^{-1} gave the following result:

$$E_{Ag/AgCl} = -600 + 55 \log[O_2] + 88\ pH + 42 \log[time] \qquad (6.3)$$

The result of observed vs predicted is presented in Figure 6.23

The time dependent term in Equation 6.3 will correspond to COD' dependent term and HCO_3^- dependent term in the equation based on equilibrium controlled conditions (Equation 3.2.23). Under kinetically controlled conditions the time dependent term will correspond only to the COD' term (Equation 3.3.17) representing the anodic reaction which presumed to consist of degradable compounds. The substitution of COD' with time is motivated by the results in section 6.2.3 that shows a time dependent reduction of COD.

Supposing that oxygen is the cathodic reaction and controlled by electron transfer and the anodic reaction is mass transport controlled. In this case the Tafel slope would be ~60 mV which means that the cathodic reaction would be pH dependent. Consequently i_{lim} for the anodic reaction will pH depend in an order of 2.5.

The other case is that the cathodic reaction is mass transport controlled. In this case the cathodic reaction can be pH dependent or not but the oxygen concentration will follow the Tafel slope of the anodic reaction.

In Figure 6.7 the potential measurement was carried out with two different electrodes, one platinum and one gold. The results from the two electrodes follow each other but with a certain discrepancy. Even here the oxygen reduction seems to be a dominant reaction. At a low oxygen concentration it is reasonable that the cathodic reaction will shift to some other reaction. Which reaction will not be evident from these experiments.

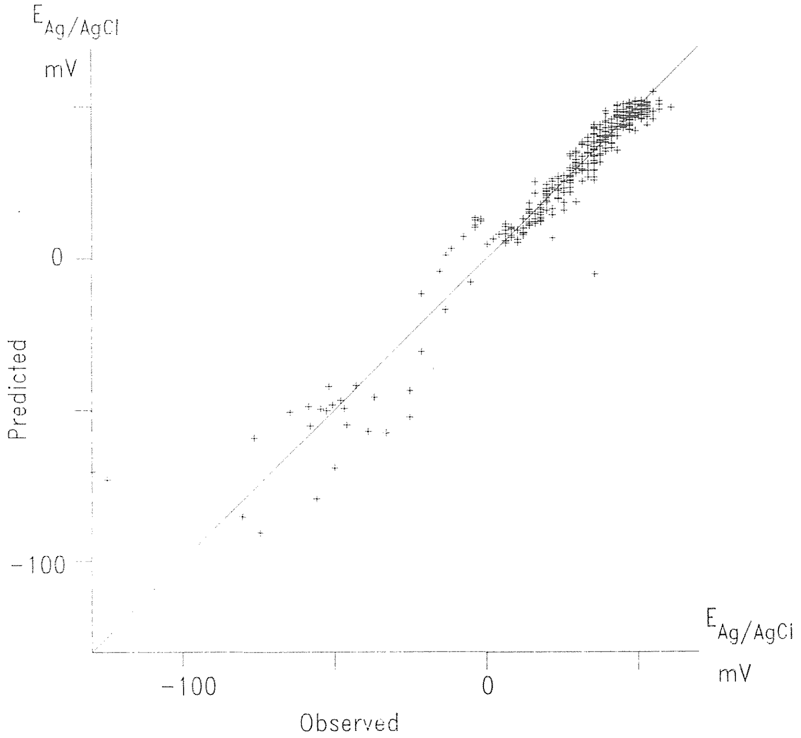

Figure 6.23 Observed vs predicted from regression in experiment B of potential according to pH, oxygen concentration and time.

6.3 *In situ* measurements at two consecutive points in a sewage tunnel

6.3.1 Experimental design

For the purpose of these experiments three requirements seemed necessary (1) practically no fresh sewage is to be delivered into the net between the two test points, (2) electrical power is to be made available at the test points with reasonable expenses and efforts, and (3) the distance between the test points is to be long enough, i.e. giving rise to a transportation time long enough, to facilitate the processes involved in degradation. With regard taken to these requirements Partille and Slamby were chosen as test points. These two places are connected with a sewage tunnel of 7455 m corresponding to a transportation time of 4 h (Figure 5.4). In this tunnel the sewage is only mixed with a small delivery from Björndammen ca 2500 m downstream from Partille and naturally also inleaking ground water. In this study the delivery from Björndammen has been regarded as negligible as well as the dilution with inleaking water.

Automatic measurements of temperature, conductivity, pH, oxygen concentration and redox potential were made in the channels of the equipment specially built for this experiment and placed at the two test points (see section 4.1.3). After passing the channel, sewage was sampled for manual determination of alkalinity and determination of COD in the laboratory. In the latter case the samples were preserved for shorter storage by addition of 2 m 4 M H_{S4} to 200 m sewage sample. It was decided that test samples for manual analyses should be taken during the period when the load on the sewer was changing from low to high, starting with a series of 6 samples with intervals of ca 10 minutes, then after 1 h an additional series of 6 samples with the same intervals of ca 10 minutes. pH and conductivity was registered on printers parallel with the automatic registration.

The time needed for transportation of sewage between the test points was determined with the aid of package chips. At a fixed time they were dropped into the sewer at point Partille. Notations were then made of the time they arrived at point Slamby. It was found that the transportation times of the different chips varied considerably, more than 2 h between the arrival of the first and the last chip. However, the main part of the chips arrived within half an hour. The great spread of the chips is probably caused by electrostatical adhesion to the tunnel walls. Regarding these observations the average transportation time was settled to be the same as noted for the front of the main group of chips.

Different problems had to be considered at point Partille and point Slamby, respectively. The test point Partille presented a certain disadvantage as all sewage passing the point comes from a number of pressure pipes independent from each other, which means an intermittent sewage delivery during periods of low sewage production. At these times air will be pumped into the sewage sampling equipment and thus causes oxygenation of the water. During the remaining time the sewage flow varied but this caused no problem. At point Slamby the problem was a tendency towards reduced water flow caused by obstruction of the strainer in front of the sampling pump. This is not the case at point Partille, probably because, here, the velocity of the water is higher, leading to self-cleaning of the strainer.

The results of this study have been completed with data from the automatic registrations of influent sewage to the Rya wastewater treatment plant and at Slamby where a specially constructed vessel was used.

Further, in a later experiment performed at point Slamby use was made of the instrument carrying vessel described in section 4.1.3. The open circuit potentials measured here were compared with those registered in corresponding influent routinely measured at the Rya wastewater treatment plant. The expression "corresponding influent" means that the actual time at Slamby corresponds to an actual time at the plant of x - the transport time from Slamby to the plant. In this case the only results that will be presented here are the potential measurement and the oxygen concentration.

6.3.2 Experimental results

Figure 6.24 and Figure 6.25 present the automatic registration of temperature, pH, conductivity, oxygen concentration and redox potential performed at point Partille and point Slamby, respectively. The times when the test samples were taken have also been marked on the figures. Owing to problems in connection with the registration the processing of the data presented in the figures has been slightly different. Strongly fluctuating signals from the electrode to the logger at point Partille caused disturbances in data storage and consequently several values fell outside the measuring area. These disturbances were dealt with and the result controlled against the values obtained on the printer (Figure 6.26). In addition, values have been deleted which were suspected to have fallen outside the measuring area. However, even in Slamby the measuring values fluctuated, though to a considerably lesser degree. The changeover time could be illustrated by smoothing the Slamby curve on 5 values.

Table 6.6 shows the results of the determinations of alkalinity and COD in the test samples. The time of both test points are related to each other as the Slamby time was adjusted with regard to the calculated transportation time of 4 h between Partille and Slamby, which means that the test samples taken at the two test points were assumed to have emanated from the same sewage package.

Figure 6.27 presents the automatic registration of oxygen concentration and potential measurement at Slamby correlated to the potential measurement at Rya wastewater treatment plant.

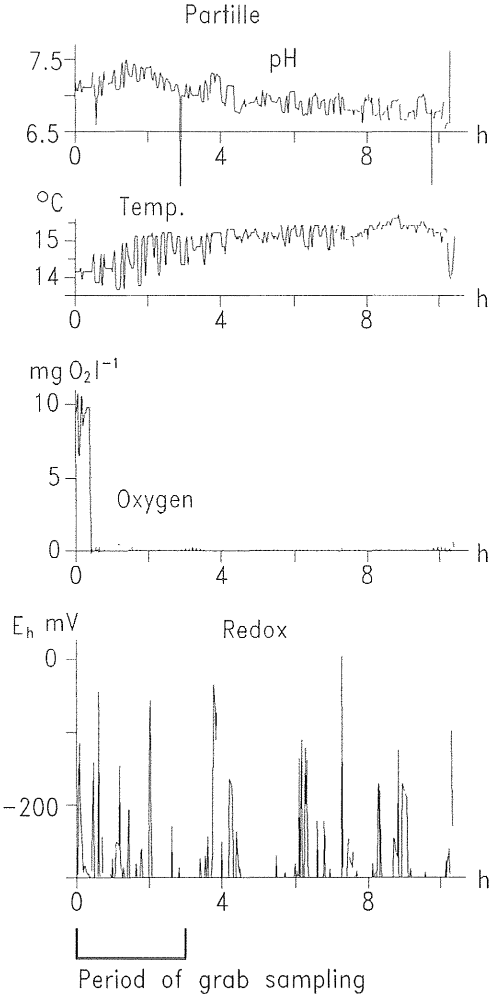

Figure 6.24 Sample point Partille. pH, temperature, oxygen concentration, redox potential and conductivity.

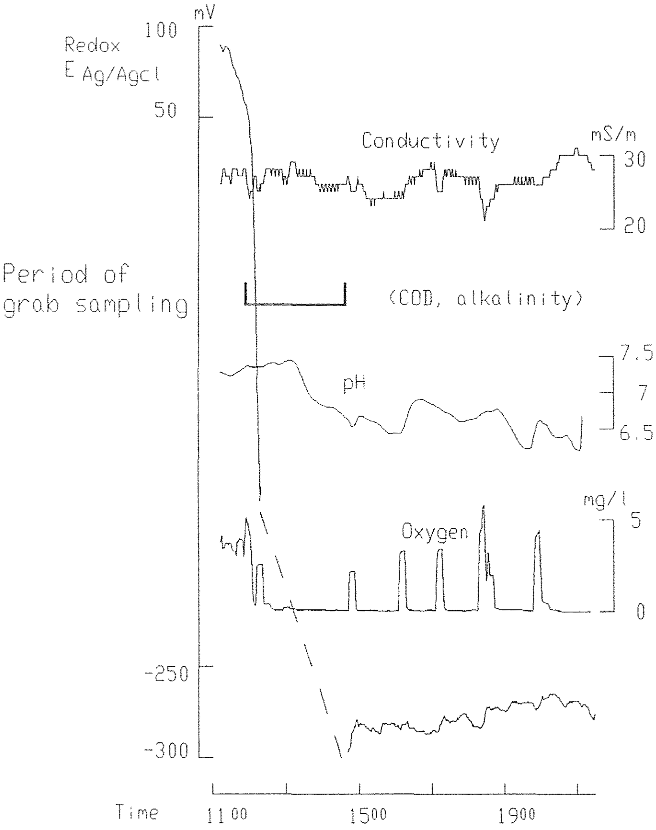

Figure 6.25 Sample point Slamby. pH, temperature, oxygen concentration, redox potential and conductivity.

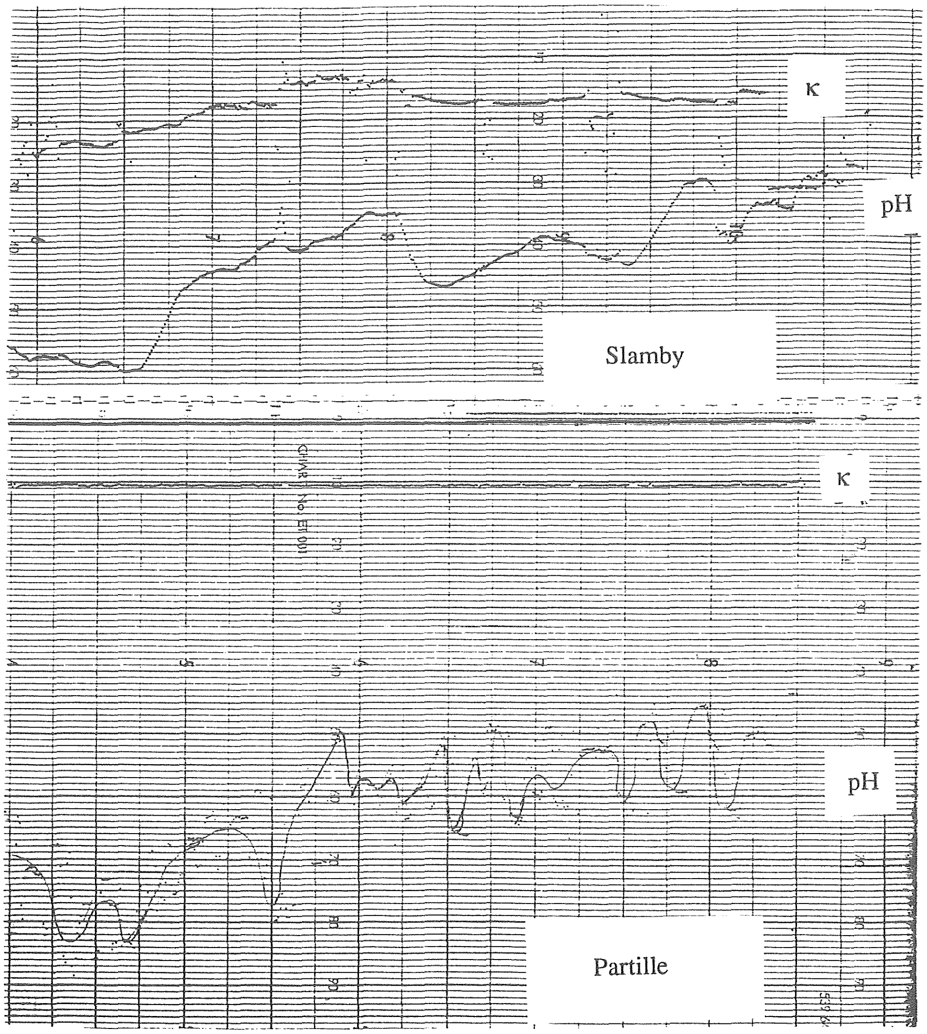

Figure 6.26 Printer data obtained at Partille and Slamby.

Table 6.7 Results from period of grab sampling in Partille and Slamby

Partille				Slamby			
Time min	Local time	Alkalinity mg $HCO_3^- l^{-1}$	COD mg O_2 l^{-1}	Time min	Local time	Alkalinity mg $HCO_3^- l^{-1}$	COD mg O_2 l^{-1}
0	07:41	264	182 (190)	0	11:55	255	204 (203)
13		209	280	14		275	254
27		242	492	25		289	294
39		314	420	33		302	359
51		355	269	43		306	362
61		276	395	54		330	345
125		352	868	112		283	1200
135		236	404 (490)	123		264	1170
145		224	487	134		250	879
154		317	1480	143		248	856
169		382	2630	151		249	1086
180		287	1641	160		241	1402

( ) Determination of COD by the method of Dr Lange

The chips were released into the sewage at point Partille at 07:30. A few of the chips arrived to point Slamby between 11:15 and 11:30. Thereafter they came in clusters. Based on the observations the mean time needed for the transportation of sewage from Partille to Slamby was estimated to be 3 h 45 min. The sewage at time 0 in Slamby in Table 6.7 will correspond to the sewage at time 30 minutes in Partille. Manual measurements of the temperature gave 15.1°C in Partille and 13.4°C in Slamby.

Figure 6.27 shows the determination of redox potential and oxygen in sewage at Slamby compared with the influent at Rya wastewater treatment plant. The measurement at Slamby was between 10:28 and 09:47. The measurement at Rya started 10 hours later. The break in the Rya potential graph is due to electrode cleaning.

Remarks to the results: the time coordination of the grab sampling between the sampling points (Partille and Slamby) was not good enough to make it possible to determine the degradation extent during the transport.

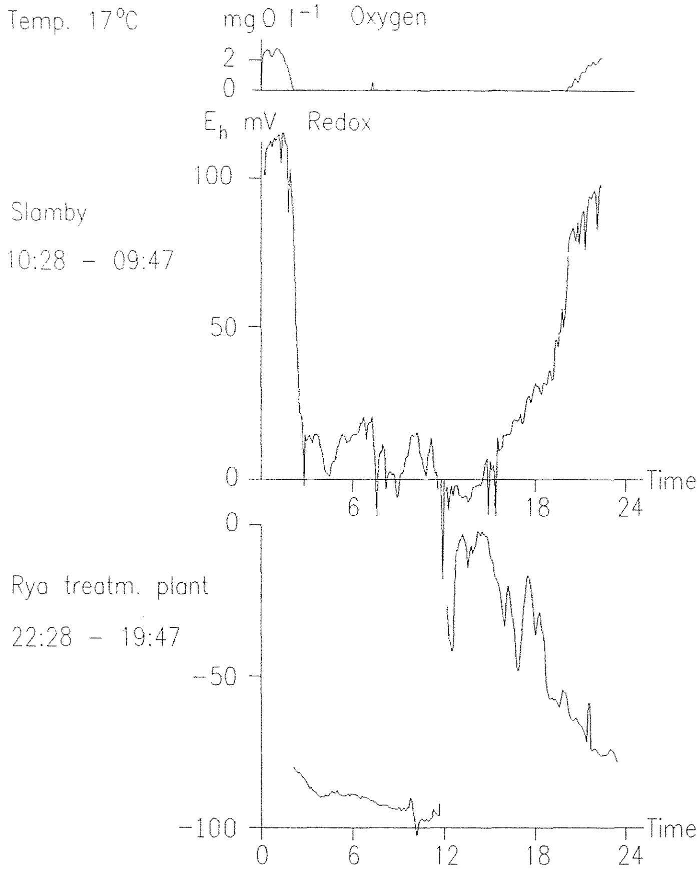

Figure 6.27 Determinations of redox potential and oxygen in wastewater at Slamby and Rya wastewater treatment plant.

6.3.3 Evaluation of field measurements

Lack of oxygen was found during 3/4 of the day. In spite of this, as nitrate/nitrite are not available, the degradation in sewers is dependent mostly on aerobic respiration, Table 3.1. Thus the content of oxygen being the limiting factor. This might possibly lead to incomplete oxidation of organic material, i.e. causing a decrease in the energy supply by exchanging one pollutant for another.

Measurements in the sewer very close to a primary wastewater pipe usually showed an excess of oxygen. This is quite natural because of the high oxygen content (9 mg O_2 l^{-1} is not unusual) in unpolluted water. This means there is an oxygen reserve that will take about 30 minutes to consume for the microorganisms in a wastewater with an oxygen consumption rate of 18 mg O_2 l^{-1}. Furthermore, the homogenisation of the water is not sufficient to make suitable material available to the microorganisms. A somewhat contrasting condition was found by measurements in sewers at points 6 h downstream from the primary pipes. The lack of oxygen for several hours, displays the potential of oxygen demand in wastewater. The organic material is at this location readily available for microorganisms thus creating an oxygen demand larger than the oxygen transfer. Compared with the result in 6.2.3, that the α - value seems to be linear dependent of the COD value, it can be said that the oxygen transfer rate decreases when the oxygen demand increases.

At point Slamby the break point between aerobic and anaerobic conditions seems to be around a COD concentration of 350 m O_2 l^{-1}. The COD mean value in the influent at Rya wastewater treatment plant is 435 m O_2 l^{-1} according to section 2.2 this is surprisingly high enough to give an anaerobic condition during the whole day (Figure 6.27) Dirasian[62] has shown a general decrease in redox potential along the sewer which also indicates a more anaerobic condition.

The results described in Figure 6.27 were obtained at a temperature of 17°C. The influence of the temperature on the potential value is shown in Figure 6.28. Figure 6.28 shows the daily variation of the potential, measured in the influent sewage at Rya wastewater treatment plant. The mean value of three days in winter and summer, respectively, is presented.

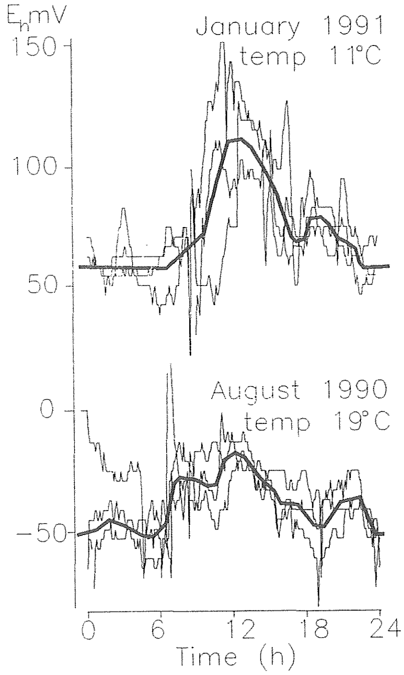

Figure 6.28 The daily variation of redox potential in sewage arriving at the treatment plant.

It can be concluded the that oxygen content in sewage decreases with increasing distance from the user[8]. Figure 6.27 shows the oxygen content and redox potential in the sewer at a point 6 hours downstream from the user. Here, lack of oxygen was found during 75% of the day. The redox potential varied irregularly during these periods. According to table 3.1 it seems reasonable to suppose, if at all, that only sparse fermentation will take place and then only in the biofilm and sediments. The degradation in the sewage is thus a result of aerobic and anaerobic respiration. Considering that the concentrations of nitrite and nitrate are too low to be of practical significance, and the redox potential too high to signify a notable reduction of sulphate, it can be concluded that degradation in sewers is almost entirely the result of aerobic respiration, the content of oxygen being the limiting factor.

A comparison of the measurements discussed above with values obtained in wastewater entering the sewage plant gives a more complete picture. Normally this primary effluent has a redox potential in the range of -300 to +100 mV[62] and -200 to +200 mV (operational data from the sewage treatment plant, 1990). This indicates a water, lacking oxygen as well as nitrite and nitrate, in which both the reduction of sulphate and fermentation can take place. General daily variations (mean value of three days) of the redox potential and temperature are: in winter, 5 to 150 mV and; in summer -75 to ±0 mV (Figure 6.28). Therefore during the warmer part of the year, the section of the sewer net closest to the sewage plant will continuously be lacking oxygen, a condition which will favour reduction of sulphate and fermentation.

The long transport of wastewater from densely populated suburbs to a large sewage plant will decisively influence the quality of the water coming into the plant. Figure 6.29 illustrates the development of microbiological activity through the sewer net.

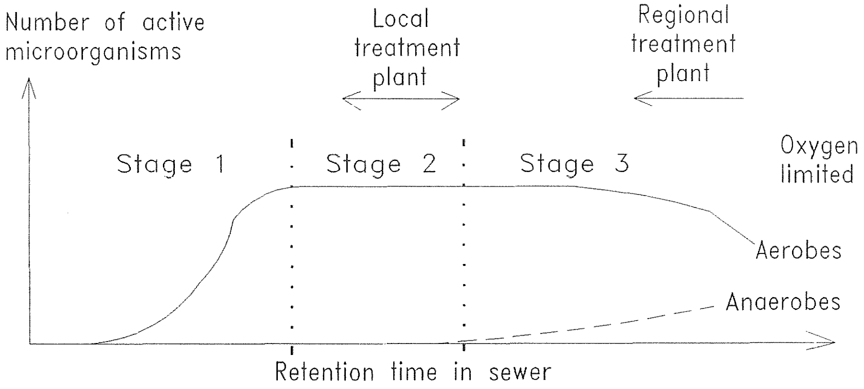

Figure 6.29 The probably development of active microorganisms in a sewer.

The processes in the sewage during the transport in the sewer net can be described in three stages:

Stage 1. The aerobic microorganisms reproduce and the activity is limited by the number of microorganisms.

Stage 2. The oxygen transfer rate is insufficient compared to the microbiological oxygen consumption rate. The activity is limited here by oxygen transfer.

Stage 3. The anaerobic microorganisms reproduce, while the aerobic decrease. Some of the aerobic activity will be substituted by chemical oxidation.

These three stages are only valid if the concentration of readily biodegradable substance is high enough. Otherwise the activity in stage 2 will be substrate limited and stage 3 will never happen. Because of the daily variation of the substrate content, stage 3 will not have any decisive importance. Unless the sewer net is of a size so that the daily variation is equalized in parts of the sewer net, then the oxygen limiting condition will last for several days to one month and stage 3 will be of importance. This is illustrated in Figure 6.30. This shows the difference between the effluent to a local treatment plant and a regional treatment plant.

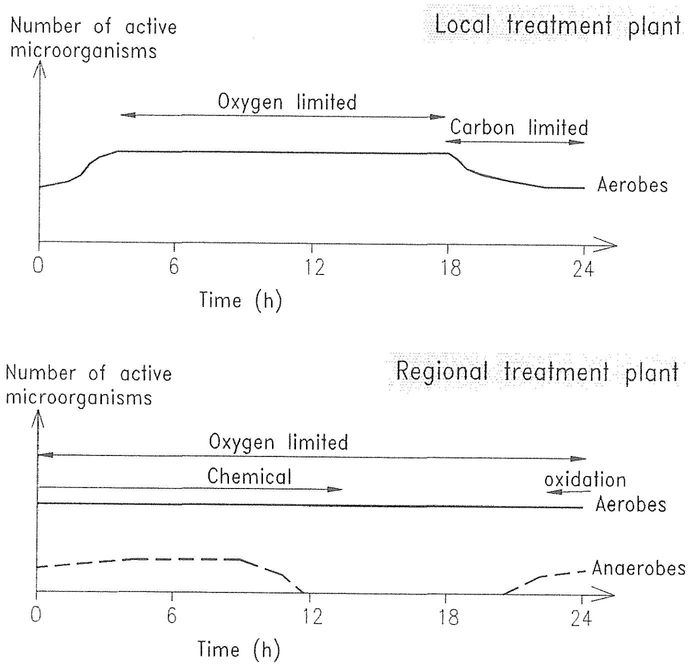

Figure 6.30 The daily variation of the active microorganisms in primary effluent at a regional wastewater treatment plant.

7 CONCLUSION

From this study it is evident that it is difficult to determine the quality of sewage. If the sewage is classified according to Henze's presentation (Table 2.1) then, for instance, the sewage in experiment C is classified as normal according to COD determination and as concentrated according to the respirometer measurement. For the characterization of sewage, the quality concept needs to be defined in two parts: one that defines the present concentration of pollutants and one that defines the capacity for change.The capacity for change of the sewage will be of greatest importance not only during transport in sewers, but also during the collection and preservation of sewage samples. In this study it can be concluded that:

* Freezing as a method of preserving sewage samples for later analysis of BOD is not a reliable method. The BOD results will be affected by the time between sampling and analysis and the BOD concentration of the fresh sewage will not be measured accurately.

* The sampling procedure affects the measured COD value since adsorption to the walls of the sampling device occurs. The collected sample will be affected by adsorbtion thus yielding low COD values for the bulk sample.

With the models in this thesis and the laboratory set up, it is possible to simulate isolated in-sewer processes such as decomposition rate and adsorption rate of organic material both an excess of oxygen and at a shortage of oxygen. In addition to this, it is possible to determine the α value of the oxygen transfer and how to use in-sewer redox potential measurement. With this laboratory set up it can be concluded that:

* The oxygen transfer α value is strongly correlated with the COD concentration.

* The degradation rate in sewage seems to be correlated to the rate of the organic material in the sewage to adsorb on surfaces. This is logical as the time factor for the degradation of adsorbed organic material is one tenth of the rate for the total degradation in sewage (Figure 6.19).

Consequently, the degradation of sewage during transport in the sewer net work will be mainly dependent on a combination of the adsorbability of organic material and the oxygen transfer rate.

Further studies might consider the relationship between sewage adsorbability and the concentration of easy degradable material. Such studies may lead to an instantaneous method to determine kinetic characteristics of sewage.

Evaluation of the redox potential measurement (e.g., open circuit potential or mixed potential) in this study is only in the development stage. In spite of this it is stated in this study that:

* Oxygen concentration is strongly correlated to the open circuit potential.

- The open circuit potential is correlated to a time factor which here is explained as the change in soluble degradable material according to the results from the COD method.

Another explanation for the time dependence could be an altering of the electrode surface. However, this area needs more research. After further studies it may be possible to use the open circuit potential for a continuous determination of the quality of the sewage related to the dominant oxidation and reduction reactions in the sewer. An interesting thought might be to try to imitate different microorganisms by combining electrodes made of different materials. I am convinced that with further research and with the present knowledge from electrochemistry, it is possible to solve many of the problems in characterization of sewage.

Furthermore, from the *in situ* measurement it can be concluded that aerobic degradation in sewers is oxygen limited because of a low α - value rather than a high oxygen consumption rate.

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