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MATHEMATICAL MODELLING OF SELF-PURIFICATION OF RIVERS

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Preface

During the last three years a number of studies has been carried out at IIASA which explored the applicability of various methodologies of systems theory and operations research to river quality management. They finally culminated in the book "Modelling and Control of River Quality" by S. Rinaldi, R. Soncini-Sessa, H. Stehfest and H. Tamura. In most cases the applicability of the methods has been demonstrated for the Rhine river. The basis for these examples was a report on identification of a water quality model for the Rhine river, which was published originally in German. In order to provide an easily accessible reference for the above-mentioned studies the English translation of this report is now published together with a sensitivity analysis of the Rhine river quality model.

Abstract

The self-purification process in rivers is described qualitatively. Different ways of representing this process by systems of differential equations are discussed. The parameters of the differential equations cannot be measured directly, but must be estimated from experimental values of the dependent variables. For this problem, called model identification, the quasilinearization technique is recommended and explained. The technique is applied to self-purification models of some simple laboratory studies. A model is given of rivers whose benthos may be neglected. Its dependent variables are: concentration of easily degradable wastes, concentration of slowly degradable wastes, bacterial mass concentration, protozoan mass concentration, and oxygen concentration. Keeping the measurement efforts within reasonable limits, the conditions under which this model can be identified are investigated. Finally, a self-purification model of the Rhine river between Mannheim/Ludwigshafen and the Dutch-German border is proposed. It is shown that the model is consistent with the measured data. The model is used to estimate the consequences of activities such as waste heat disposal or sewage treatment.

Acknowledgements

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This paper is, with the exception of Sect. 4.4, essentially a translation of

H. Stehfest, "Modelltheoretische Untersuchungen zur Selbstreinigung von Fliessgewässern", KFK 1654 UF, Kernforschungszentrum, Karlsruhe, Federal Republic of Germany, 1973.

C O N T E N T S

1. Introduction

In view of the enormous pollution of our rivers it is today imperative that greater efforts toward water pollution control must be made [18]. Uncertainties exist in the selection of measures to be applied to concrete situations. An important factor is the ability of the river to clean itself. This should be used on the one hand, but on the other hand it should not be abused. This optimization problem can only be solved if one can quantitatively describe the self-purification processes; but today one is far away from it. Most of the sanitation programs for rivers are based on the so-called Streeter-Phelps-Equation (e.g., [53]), although one knows today that this equation is only a very crude model of the self-purification process [32] (see also Section 4.2).

The following thoughts are to be a contribution to a more realistic theoretical model of the self-purification process in rivers. The initial question was how waste heat fed into rivers interacts with organic pollution [50]. To start with, the biochemical, physical and mathematical facts were compiled for the laying down of a mathematical model of the self-purification process. Then, several self-purification models, their possibilities and limits, are discussed.

2. Qualitative description of the self-purification processes

2.1 Degradation of the pollutants by bacteria

In the complex process, which is termed self-purification, the first and most important step is the degradation of the pollutants by bacteria (and lower order fungi). Degradation consists of a chemical change, which releases electro-chemical energy. The released energy is used for building up energy rich organic phosphates (especially adenosine triphosphate (ATP)), which in turn deliver energy for the biomass synthesis (reproduction, growth) and for the maintenance of life functions (movement; replenishment of spontaneously degenerated protein molecules etc.). The energy consumption for the maintenance of life functions is described as endogenous respiration. In the creation of new biomass, the pollutants or by-products of their degradation possibly can be used as building materials (assimilation); but normally also other building materials, which can not be derived from the energy donor, must be available in the water (e.g., nitrates, phosphates, and calcium). If an energy donor, or some essential nutrient is not available, the endogenous respiration continues through the degradation of cellular matter (especially that of the reserve substance glycogen [10]). That way the biomass is slowly reduced, because

the degradation products are excreted. The degradation of a pollutant normally consists of a long chain of enzyme catalysed reactions (see for example [10]). The energy producing reactions are exclusively oxydations, and especially oxydations through dehydrogenation. As the last (extracellular) hydrogen acceptor, oxygen is the most important one (aerobic degradation), but under certain circumstances also other substances (e.g., sulphur, CO_2 or fragments of degraded molecules) can be reduced (anaerobic degradation). Organic pollutants are broken up in the course of degradation. Ideally, the end products are purely inorganic (e.g., CO_2, H_2O, NO_3-, SO_4--). The metabolic pathways of the many different degradable pollutants are so arranged that with progressing degradation more and more pathways coincide. Thus, for those metabolic pathways which end up with CO_2 and H_2O, only two possible courses are known: the Krebs cycle and the pentose phosphate cycle [61].

The enzymes, which catalyze the single steps of degradation (and synthesis) are proteins or proteids, which are highly specific to the chemical reaction catalyzed. The ability to synthesize an enzyme is genetically determined, that is why only those compounds which have been present for a long time in nature are biologically degradable. Many compounds which have appeared in the last decades with the development of chemical technology can not be degraded, or only partially degraded; among those are, for example, the chlorinated carbohydrates [28,58]. Only a part of the enzymes, the so-called constituent enzymes, is synthesized by the microorganisms independently of the available nutrients. The other enzymes are inducable, that is, the genetically fixed ability to synthesize them is only realized when the specific substrate (or sometimes others, mostly structurally related compounds) are present.

The transport of the nutrient molecules through the cell walls and the cytoplasmic membranes is also achieved by enzymes; these are called permeases. Ordinary diffusion plays a minor role in nutrient uptake, because the transport has to be accomplished against a concentration gradient.

If the nutrient molecules are very large (e.g., starch, cellulose, protein), a direct transport into the cell is impossible. In this case, the nutrient molecules are degraded outside the cell into fragments which are small enough. These reactions are catalized by exoenzymes, that is enzymes which act outside the cytoplasmic membrance. They can be attached to the cellwalls as well as be released into the surrounding medium. They differ from the endoenzymes by their small molecular weight (10^4 - 10^5 as opposed to 10^5 - 10^6 of the endoenzymes) and by their extremely low cystin and cystein content [76].

There are large differences in the degradation abilities of different species of bacteria. Some bacteria grow in purely inorganic media (autotrophic bacteria), while others are dependent upon organic compounds--sometimes very complicated (heterotrophic organisms). Another classification rests on the differences in energy gains through dehydrogenation: the strictly aerobic bacteria are dependent on oxygen as an hydrogen acceptor, the facultatively aerobic bacteria can do either with or without oxygen, the anaerobic bacteria cannot use oxygen as a hydrogen acceptor, and the strictly anaerobic bacteria will die in the presence of oxygen. Within those opposed groups of aerobic - anaerobic and autotrophic - heterotrophic, there are to be found many other differentiations. For example, the bacteria of the family nitro-bacteriaceae (autotrophic, strictly aerobic) derive their energy solely through nitrification (that is oxidation of ammonia to nitrite, and of nitrite to nitrate), while the also autotrophic and strictly aerobic bacteria of the family beggiatoaceae derive their energy solely through the oxidization of sulphur and hydrogen sulphide [31].

If in a heterogeneous bacterial community all species have the ability to decompose a certain nutrient, in most cases the degradation of that nutrient follows the same metabolic pathway. That is, while the nutrient is decomposed, the heterogeneous population acts like a homogeneous population (see for example [35,93]).

Those bacteria found in rivers show great flexibility in their use of the pollutants [31,43], that is, in the analysis of the self-purification processes one can be quite certain that the bacteria will react like a homogenous population in regard to most pollutants. These assumptions can be realized even when just a few species are able to degrade a substance, because often metabolic intermediates can be used by all bacteria. This is especially possible with the end products of reactions catalyzed by exoenzymes. The bacteria found in rivers are mainly of genus bacillus, aerobacter, pseudomonas, flavobacterium, escherichia, achromobacter, alcaligenes, micrococcus, sphaerotilus, or chromabacterium [31,43,44,65].

The most important exception regarding the collective degradation behaviour are the above-mentioned nitrifying bacteria which oxidize the ammonium or nitrite excreted by other bacteria. Because of their low growth rate, the nitrifying bacteria only play an important part in slowly flowing (e.g. impounded) or overgrown bodies of water [38,65,92,96]. (In overgrown bodies of water the nitrifiers settle on the waterplants). Besides that, their growth is inhibited by numerous pollutants [15], so that their influence on the self-purification process is often negligible.

The kinetics of the degradation process are dependent upon numerous chemical and physical factors. The rate of degradation changes rapidly with temperature, that is, it increases with temperature as long as those enzymes concerned with degradation

are not denatured. Of great importance are the pH values, the O_2 content of the water, the size of the available solid surfaces, and the turbulence. The latter two play an especially great part when exozymes are involved in degradation.

The kinetics of the degradation of a certain nutrient is often specifically influenced by other nutrients or by non-degradable compounds. This influence can consist of the repression of the production of an enzyme. Thus, numerous inducable enzymes, expecially exoenzymes, are only formed when other, more easily degradable nutrients have been used up [76,87]. Also, the activity of enzymes already present can be regulated. This kind of regulation can be achieved through the binding of the regulator molecule to the active site of the enzyme molecule which is then not longer available for the substrate (competitive inhibition [63]); in this case the regulator molecule and the nutrient molecule are normally structually similar. (The special case of the competitive inhibition in which the regulator molecule and the substrate molecule are identical occurs if the metabolic pathways of two substrates merge and the slowest (i.e., rate determining) reaction is in the common part of the pathways [93]). In many cases, the regulator molecules are bound to some other part of the enzyme molecule and activate or inhibit it by changing the form of the molecule (allosteric regulation [63]); in these cases there is, in general, no structural similarity between substrate and regulator molecule. In competitive inhibition, the enzyme activity depends upon the ratio of the concentration of the substrate to the concentration of the regulator; if there is sufficient concentration of the substrate the inhibition can be overcome. On the other hand, in allosteric regulation the enzyme activity depends only on the concentration of the regulator. Allosteric inhibitions and activations also play an important part in the endogenic regulation of the metabolism: the end product of a metabolic pathway acts as an allosteric regulator of the first reaction (feedback) [67]. Many components of sewage influence the metabolism of the bacteria so seriously that they are damaged or die. Such toxic materials are, for example, heavy metals [40,41].

In the realm of bacteria there exist great differences in regard to mobility. There are attached types as well as various types of flagella. The former can also be carried away by flowing water (as can the motile types); be it that they are attached to suspended particles, or be it, that they have been ripped off from the river bed.

2.2 Continuation of the self-purification by higher order links of the food chain, and the influence of the phototrophic organisms

After the total elimination of the pollutants from the river water, the self-purification process cannot be considered finished, because a large amount of energy produced by the degradation has been used to produce new bacterial mass; part of the pollutants even have been directly integrated into the biomass. Should the bacteria die for any

reason, they become new pollutants, which can result in a new growth of bacteria [34]. However, the pollutants, after their conversion into bacterial mass, are no longer in the dissolved state, so that they can be filtered off or sedimented out. The effectiveness of the conversion, measured as the ratio of the chemical oxygen demand of the produced biomass (see Section 4.2) to the chemical oxygen demand of the eliminated material usually lies between 10 and 60% [19,66,81]. The biomass would decrease very slowly in the following due to endogeneous respiration; the death rate would become significant only relatively late [85]. Normally, the self-purification process develops considerably faster, because the bacteria are consumed by protozoa; this already occurs during the bacterial degradation of the pollutants.

The role of the protozoa in the self-purification process was greatly disputed until recent times (see for example [65]), however, recent investigations verified their great importance [12,13,22,51,70,86,95]. Figure 2.1 shows, as an example, the growth over time of the bacterial density and the biological oxygen consumption in a laboratory experiment with river water, in one case with, and the other without, the addition of protozoa [51]. One can see that the oxygen consumption, which can be used as a measure for the physiologically no longer useful freed dissimilation energy, is much larger in the first case. The bacterial density is thereby clearly smaller. (After the first day bacterial and protozoan densities are of the same order of magnitude as that measured in nature. The small amount of bacterial density at the beginning resulted from the fact that in the elimination of the natural protozoa many of the bacteria were eliminated as well). Whether the additional consumption of oxygen is due solely to the digestion of the bacteria by protozoa, has not yet been totally explained. For example in [86], as a result of the measurements, the opinion is stated that the protozoa create a substance which enhances the decomposition activity of the bacteria. However, the importance of the protozoa rests mainly on its 'eating capacity', and only this will be considered in the following. For example, protozoan feeding should be the reason for the reduction of the bacterial concentration in the Rhine River between Mainz and Cologne which is observed during the summer. Figure 2.2a shows the bacterial concentrations along the Rhine River during the summer, calculated as the geometric mean of the measurements taken by the Rhine Water Works during the six summer months of 1967 [3]. Figure 2.2b gives the corresponding figures for the six winter months. The opposite behaviour between Mainz and Cologne in the winter (when the self-purification process is slowed down) shows that the summer-reduction can not solely be caused

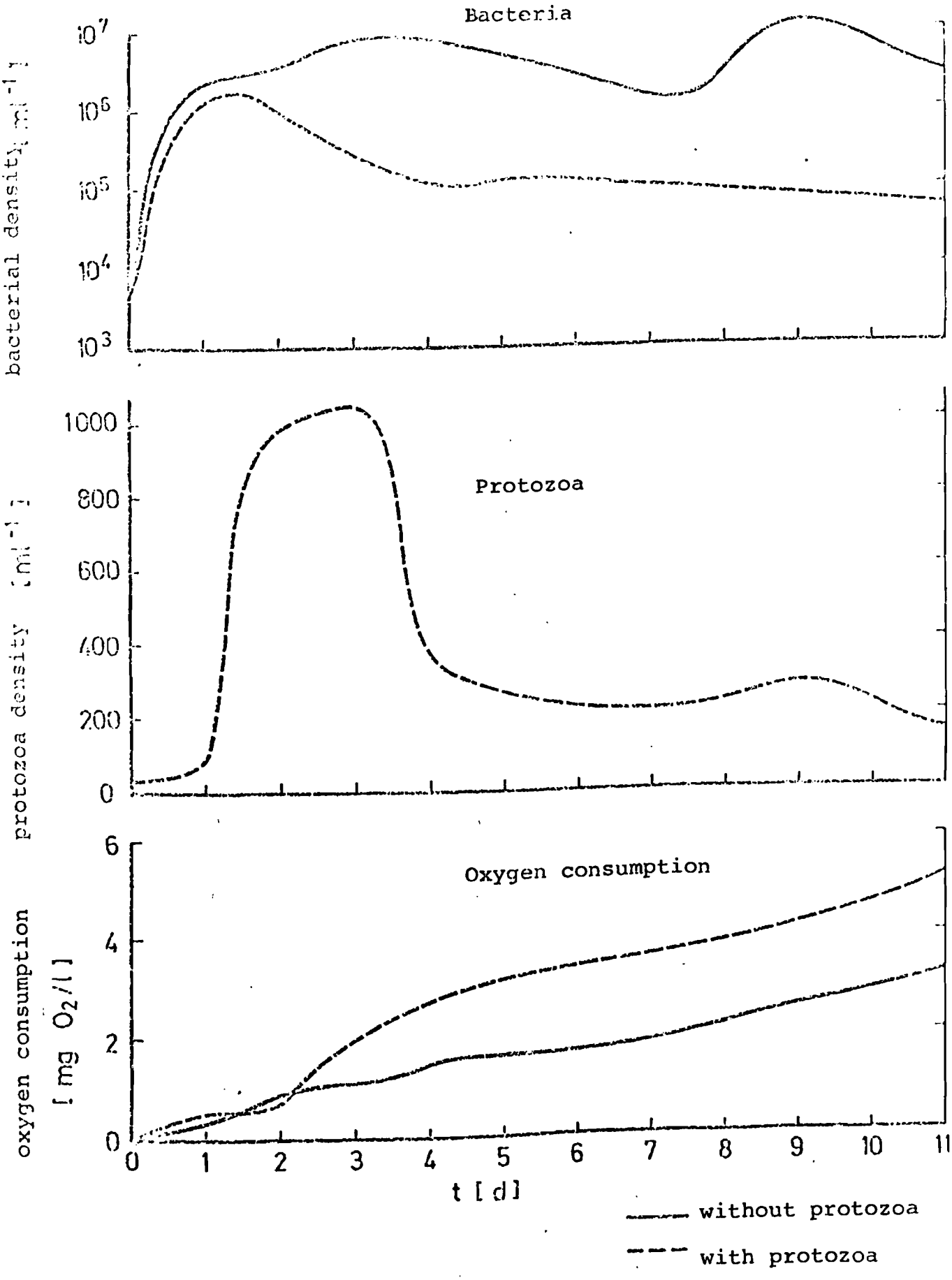


Figure 2.1 Influence of protozoa on bacterial density [51]

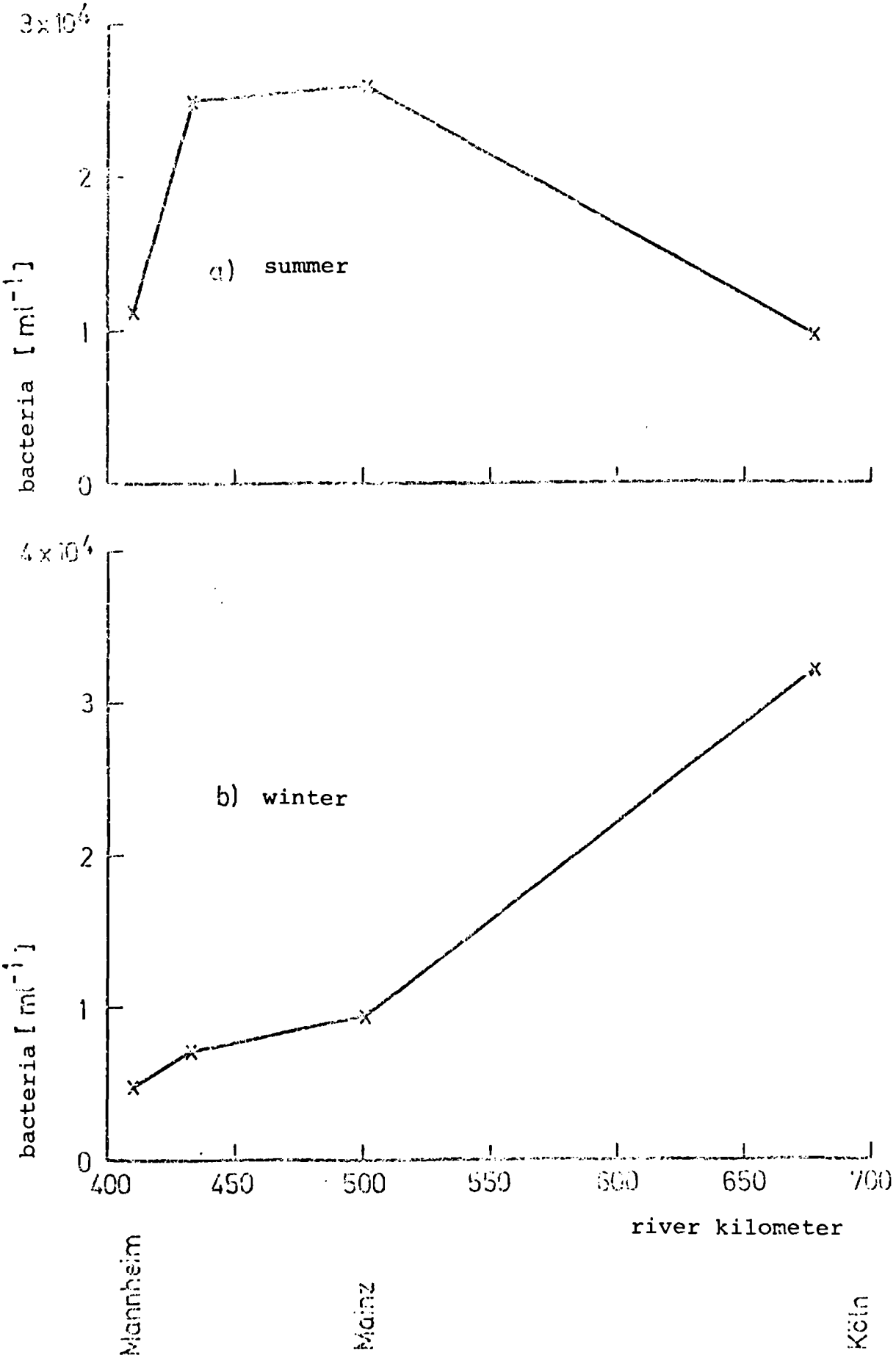


Figure 2.2 Geometric mean values of measured bacterial density in the summer and winter half-year of 1967 for the Rhine River[3]

by differences in the measuring technique (plate count). The curves have very similar shapes for other years, see for example [2].

Among the protozoa feeding on bacteria the ciliates are the most common [13,70]. The flagellates are also frequently found during the self-purification process, but most of them live osmotrophically and use by-products of the bacterial metabolism. Thus, their population dynamics are closely linked to that of the bacteria, and therefore they are not treated separately in the following. While the growth rate of a homogeneous bacteria population can vary greatly according to the differences in degradability of the nutrients, this is not the case with ciliate populations, because their food has in any case approximately the same composition. The differences between the various species of ciliates seem to be greater than among the various species of bacteria which can live on a specific substrate. However, the growth rates of those ciliates which are most important for the self-purification of rivers are close enough to consider all ciliates to act homogeneously [13,70,88] (see Section 4.2). The feeding activity of the ciliates is influenced, just as with the bacteria, by many chemical and physical factors (pH-value, temperature etc.). By and large, the adaptability of ciliates is weaker than that of bacteria; for example, very few ciliates can exist under anaerobic conditions.

The organisms which eat bacteria in turn serve as food for higher organisms, whereby the chemical energy originally brought in by the pollutants is further reduced. These second order consumers are largely raptorial ciliates, rotatoria and phyllopods. Higher order consumers follow, so that one can speak of a food chain (though the structure is not strictly like a chain in the sense that consumers of the n-th order feed only on consumers of the n-1st order).

As with the bacteria, there exist benthic consumers and consumers which are carried downstream by the water; again many of the latter are sessile organisms attached to suspended particles. Among the higher consumers there are motile species which move independently of the water current (e.g. fish).

The higher the order within the food chain, the lower the part of the original chemical energy which the organisms convert. (Assuming the same efficiency for the conversion of consumed biomass to new biomass and a strict chain structure [see above], the chemical energy is reduced from link to link in a geometric progression). Nevertheless, the influence of the higher order consumers upon the dynamics of the self-purification process could be considerable, because they reduce the consumers of the lower order. This, however, is normally

not the case, for two reasons. Firstly, the growth rates decrease toward the upper end of the chain. Therefore those higher consumers which are carried away by the current do not have enough time to reach that high density which could be supported by the nutritional base - the pollutants. Second, with a higher order the consumers become, in general, more and more exacting, so that many of them cannot survive or breed in heavily polluted waters (in single cases the opposite may well occur [16]).

The chemical energy, upon which the food chain is built, stems not solely from the pollutants, but also in part from phototrophic organisms, that is, organisms which are able to use sunlight as an energy source in building new biomass. This organism group contains, beside a few bacteria and many flagellates, algae and higher aquatic plants. Consumers of phototrophs are, among others, herbivorous protozoa, phyllopods, and fish at the upper end of the food chain. In the case of death (often caused by seasonal changes of physical conditions) prototrophs are, of course, decomposed by bacteria.

Although the phototrophs can use sunlight as an energy source, they often use, indispensably or facultatively, organic substances, in some cases even growth is possible in the dark [26,79]. The inorganic or organic substances which the phototrophic organisms take up are, in polluted rivers, to a large extent by-products of bacterial metabolism (CO_2, nitrate [or amonium], phosphates, etc.). Thus, the pollutants act as fertilizers for aquatic flora (eutrophication). In addition to the already mentioned factors which influence the growth rates, light intensity is a most important factor in the growth of phototrophic organisms. Within natural variations of light intensity, the photosynthetic activity is nearly proportional to light intensity. It does not noticeably increase with temperature, as can be expected for a photochemical reaction. On the other hand, endogenous respiration depends on temperature similarly to chemotrophic organisms, so that the ratio between assimilation and respiration increases as temperature decreases [79].

As with chemotrophs, the phototrophs are either benthic or suspended in the body of water. The higher plants are without exception stationary. Since the growth rate of most phototrophs is quite small, the planctonic species are of importance only in very slowly flowing (impounded!) rivers.

Thus the phototrophs counteract the self-purification process in that they produce new organic matter, whose energy comes from sunlight. On the other hand, they also have a beneficial influence on the bacterial degradation: the oxygen formed by photosynthesis can prevent the undesirable anaerobic decomposition (see Section 2.1). Also, the photo-

trophs provide surfaces for bacteria to attach to, so that, as already explained in Section 2.1, in the case of dense water weeds, the bacterial activity can be very intensive directly below a waste water inflow. This effect can be observed especially with slowly growing nitrifiers [38,65]. However, the phototrophs are more exacting about their environment, and if pollution is too great, they can not grow.

2.3 Oxygen balance

All aquatic organisms, with the exception of a few bacteria, fungi, and protozoa, are dependent upon a certain oxygen concentration in the surrounding waters. Thus the oxygen concentration is an important criterion for the quality of river water, and it has to be the aim of all model theory of the self-purification process, to know about the changes of the oxygen concentration over time and space.

Oxygen is consumed, on the one hand, during the aerobic degradation by bacteria and other consumers; on the other hand, oxygen is released by the phototrophic organisms during CO_2 reduction. At the same time, oxygen concentration is influenced by the physical process of diffusion: in abiotic water, diffusive exchange of oxygen between air and water establishes a certain saturation concentration of oxygen in the water. If the activity of organisms cause a deviation from that concentration, diffusion tends to diminish the deviation for rivers. The diffusion stream in the boundery layer between air and water is of greatest interest because it determines the rate at which deviations from the saturation concentration decay. Within the media water and air, the concentration differences are normally quickly equalized by turbulence.

If the decomposition activity of chemotrophic organisms is high, the oxygen consumption, over a longer period of time, can be greater than the biological and physical reaeration through photosynthesis and diffusion. Then anaerobic conditions can result, which are undesirable not only because of the death of many organisms, but also because of the harmful by-product of the anaerobic metabolism (methane, H_2S etc.). (Several organisms suffocate at oxygen concentrations which are considerably greater than zero). During intensive photosynthetic activity, there is a possibility of oversaturation, but this phenomenon relatively seldom occurs in rivers.

The saturation concentration of oxygen increases with the lowering of temperature (see Figure 4.13); apart from that it is little influenced by realistic changes of all other physical or chemical factors. The rate at which deviations from the oxygen saturation level decay is the smaller, the lower the temperature. It also depends upon the substances contained

in the water (see for example [60]) and upon hydrological factors. Also the wind speed and the amount of shipping traffic have an influence, but the importance of this influence is still under discussion.

3. Mathematical basis for model construction

3.1 Description of the self-purification process by means of differential equations

In order to model mathematically the processes described in Section 2, one must first quantify the variables such as bacteria, pollutants etc. It has proved to be useful to characterize them all by mass-concentration; that is by stating the mass of pollutants, bacteria, oxygen etc. which is contained in the unit volume. With the organisms the dry weight will always be given. (The appropriate unit of measurement for all variables will be, as shown in Section 4., [mg/l].)

In order to give an exact description of the influence of the organisms, one should actually state their number and size per unit volume. (The same holds for the insoluble pollutants.) However, it can be seen immediately, that with the product of both, which is proportional to the mass concentration, the eating activity as well as the catchability is essentially characterized. A more detailed description, in view of other unavoidable inaccuracies (see Section 4.), would not be worthwhile. In any case, mass concentration better describes the effects of the organisms than organism concentration (number per unit volume), which is often used [13].

The mass concentrations are in general functions of time t and location (x,y,z). In the following, to indicate location, an orthogonal cartesian coordinate system is used, whose x-axis lies in the direction of the flow, and whose y-axis lies horizontally. The dependence of the concentration upon time and space cannot be given explicitely in an easy manner, one can only determine how the changes in concentration depend upon the concentrations. In other words: one can only formulate differential equations. Normally the concentration changes at a specific time and place depend upon the concentration values at the same place and time. In modelling delays, as they occur for example with degradation by induced enzymes or with the dying of bacteria, differential-difference equations can occur, but each of them can be approximated as precisely as one wants by a differential-equation system. (If one builds a detailed model of all processes, which result in delays, differential equations occur from the beginning.)

In the construction of the differential equations it is useful to differentiate between matter and organisms which are stationary (benthos variables) and those which are flowing in the stream (plancton variables). (This differentiation is an idealization. For example, the heavier suspended particles, which near the bottom of the river are slowly dragged along, are hard to classify.) Benthos variables change solely through degradation or synthesis processes, whereby the transition into plancton (e.g., tearing off) is interpreted as degradation, and sedimentation as synthesis. In opposition, concentration changes of plancton also can be caused by physical transport. Transportation mechanisms which must be considered are the downstream flow of water and the mixing in all three dimensions by turbulence and diffusion. Therefore, the current $\vec{j}_k$, defined as the amount of pollutants, bacteria etc., (k identifies the variable) which per unit time crosses the unit area whose normal lies in the direction of the current, is composed of a flow component $\vec{j}_{kF}$ and a turbulence- and diffusion component $\vec{j}_{kV}$:

$$\vec{j}_k = \vec{j}_{kF} + \vec{j}_{kV}. \tag{3.1}$$

The flow component is

$$\vec{j}_{kF} = c_k \cdot \vec{v}, \tag{3.2}$$

whereby c_k is the concentration and $\vec{v}$ the velocity vector. For the turbulence- and diffusion component one can use the approximation

$$\vec{j}_{kV} = - D\vec{\nabla}c_k, \tag{3.3}$$

which means, that the current is proportional to the concentration gradient. $\vec{\nabla}$ denotes the nabla $(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z})$; D is in the simplest case a constant, but in general a 2nd order tensor. ((3.3) is the classical diffusion ansatz. Diffusion itself does not play a large part in rivers, that is why D does not have the index k. The possibility to use a diffusion ansatz to describe the turbulent mixing is also used to describe the transport of matter in the atmosphere see for example [29,39].)

Based on the law of conservation of mass

$$\frac{\partial c_k}{\partial t} = - \vec{\nabla} \vec{j}_k \tag{3.4}$$

and on the relationship $\vec{\nabla} \vec{v} = 0$, which holds for incompressible fluids, we get for the plancton variables c_k equations of the

form (see also [77])

$$\frac{\partial c_k}{\partial t} + \vec{v}\,\vec{\nabla} c_k = \vec{\nabla}\,(D\vec{\nabla} c_k) + f_k(c_1, c_2, \ldots c_N, x, y, z, t). \qquad (3.5)$$

The functions f_k comprehend degradation and synthesis processes; $c_1, c_2, \ldots c_N$ is the total of the model variables including the benthos variables. Such complicated equations however are virtually impossible to solve with reasonable effort. In most cases those equations which one derives from (3.5) by averaging over the river cross section Q are sufficient. Assuming

$$\overline{\vec{v}\,\vec{\nabla} c_k} = \overline{v_x}\,\frac{\partial}{\partial x}\,\overline{c_k} \qquad (3.6)$$

this averaging, which is indicated by bars, yields

$$\frac{\partial \overline{c_k}}{\partial t} + \overline{v_x}\,\frac{\partial \overline{c_k}}{\partial x} = \overline{\frac{\partial j_{kVx}}{\partial x}} + \overline{f_k}(c_1, c_2, \ldots c_N, x, y, z, t), \qquad (3.7)$$

because of

$$\iint_Q \left(\frac{\partial}{\partial y} j_{kVy} + \frac{\partial}{\partial z} j_{kVz}\right) dy\,dz = \int_{R_Q} j_{kVn}\,ds = 0. \qquad (3.8)$$

The indices x,y,z,n indicate the projections of the vector $\vec{j}_{kV}$ on the coordinate axes and the normal direction of R_Q, respectively. R_Q is the border of Q, of which the line element is called ds. Under the further simplifying assumption $\overline{j_{kVx}} = D_x \frac{\partial}{\partial x}\,\overline{c_k}$ one obtains the equation

$$\frac{\partial \overline{c_k}}{\partial t} + \overline{v_x}\,\frac{\partial \overline{c_k}}{\partial x} = D_x\,\frac{\partial^2 \overline{c_k}}{\partial x^2} + \overline{f_k}(c_1, c_2, \ldots c_N, x, y, z, t), \qquad (3.9)$$

whose transport term can be found for example in [82]. (Similarly, one could simplify equation (3.5) so that the diffusion in x- and z-direction is eliminated. One can find also analogues to this in meteorology [89]. See also [74].)

Equation (3.9) can only be manipulated more easily than (3.5) if one can assume

$$\overline{f_k}(c_1, \ldots c_N, x, y, z, t) = f_k(\overline{c_1}, \overline{c_2}, \ldots \overline{c_N}, x, t) \qquad (3.10)$$

This assumption holds if lateral mixing is much faster than degradation and synthesis. Occasionally the structure of the function f_k is such, that the assumption (3.10) is approximately

fulfilled (see also Section 4.3).

Often one can ignore the longitudinal mixing accounted for by $D_x \frac{\partial^2 \bar{c}_k}{\partial x^2}$, then this equation results:

$$\frac{\partial \bar{c}_k}{\partial t} + \bar{v}_x \frac{\partial \bar{c}_k}{\partial x} = f_k (\bar{c}_1, \bar{c}_2, \ldots \bar{c}_N, x, t) . \qquad (3.11)$$

Solely by simple equations like (3.11) in the following the dynamics of the plancton variables will be described. They are correct if the river is completely homogeneous in y- and z-directions, and no longitudinal mixing occurs.

If one also considers only mean values over river cross sections for benthos variables, one obtains approximately

$$\frac{\partial \bar{c}_i}{\partial t} = f_i (\bar{c}_1, \bar{c}_2, \ldots \bar{c}_N, x, t) . \qquad (3.12)$$

Thus the model equations for the self-purification processes in rivers are coupled partial differential equations of the first order. Their solutions are determined uniquely, if the values of all $\bar{c}_i$ are given at time $t = 0$ for all x and for all t at $x = 0$. In the following, if there is no danger of confusion, c_i will be written instead of $\bar{c}_i$.

If in a river the benthos variables for the self-purification process are unimportant, the model which now consists of equations of forms (3.11) only, is equivalent to the following system of ordinary differential equations [20]:

$$\frac{dc_k}{dt'} = f_k (c_1, c_2, \ldots c_N, t') . \qquad (3.13)$$

This can be easily understood, if t' is interpreted as being the flow time: in a benthosfree river (following simplifying assumptions referred to above), the concentrations at a certain point x_1 are determined uniquely by the concentrations at another point x_0 and the travelling time between both points. Equation (3.13) describes the self-purification dynamics of a benthos free river in the same way as an observer, who is moving along with the current, would see it. (One also arrives at it, if one is looking for the stationary solutions of (3.11), that is $\frac{\partial c_k}{\partial t} = 0$.) In order to simplify the notation, in the following for flow time t' the symbol t will be used as well.

Generally model equations (3.11), (3.12) and (3.13) can only be solved numerically. In the following for systems like (3.13) the Runge-Kutta method [98] is used to solve them; for the models like (3.11), (3.12), which are not dealt with

in this paper, the simple technique of finite differences [1] has proved to be quite useful.

3.2 Model identification by quasilinearization

The functions f_k in equations (3.11), (3.12) and (3.13) contain numerous parameters, whose numerical values have to be determined before one can use the model to solve practical problems. Their number be M. For example, those parameters would be the (nutrient dependent) maximal growth rate of bacteria, the rate at which the bacterial mass reduces as a result of endogenous respiration, or the physical reaeration rate (see Section 4). Their evaluation is called model identification.

Normally one cannot measure these parameters separately without changing the conditions which are relevant for the parameter value. One could, for instance, measure the intensity of endogenous respiration separately, if one removes the bacteria from the nutrient solution and observes them in a non-nourishing medium, it is, however, questionable if the parameter value thus found will hold for the original milieu [37].

Thus it is desirable to determine the parameter values from measurements which have been carried out under natural circumstances and in which therefore the influences of all of the parameters are reflected. This problem represents a general non-linear boundary value problem, which can be solved by quasilinearization [8]. (For further solution techniques see [90] .) In the following, this method as applied to systems of the type (3.13) is described briefly. The application to partial differential equation is not much more difficult, but in the framework of this work not necessary.

In order to arrive at a lucid notation the M parameters which are not shown in (3.13) are included as additional variables by adding to the original differential equations M equations of the form:

$$\frac{dc_k}{dt} = 0 \quad , \quad k = N+1 \, , \; N+2 \, , \; \ldots\ldots \, , \; N+M \, ,$$

If in the functions f_k time t explicitely appears, a further dependent variable $c_{N+M+1} = t$ is introduced, and the system is enlarged by

$$\frac{dc_{N+M+1}}{dt} = 1$$

After all dependent variables have been gathered into the vector $\vec{c}$, the system can be written in the form of

$$\frac{d\vec{c}}{dt} = \vec{f}(\vec{c}), \tag{3.14}$$

whereby $\vec{f}$ is a N+M+1 dimensional vector.
Now the problem of parameter estimation can be formulated as a boundary value problem in the following way: the measured values χ_{kj} of some dependent variables c_k of (3.14) at the instants t_{kj} be given. The number of the measured values of c_k be J_k. The initial values of all dependent variables are to be determined. If more values χ_{kj} are given than are indispensable (that is, in general, more than N+M+1), the initial values shall be determined in such a manner that the sum of the squared deviations is minimal. In this formulation there is no longer any difference between the original variables and the parameters, that is to say, among the given values χ_{kj} could also be the values of certain parameters.

The method of quasilinearization consists in calculating iteratively better and better approximations $\vec{c}_n$ to $\vec{c}$ from the differential equations system

$$\frac{d\vec{c}_n}{dt} = \vec{f}(\vec{c}_{n-1}) + J(\vec{c}_{n-1})(\vec{c}_n - \vec{c}_{n-1}), \tag{3.15}$$

starting with an initial approximation $\vec{c}_o$. $J(\vec{c}_i)$ denotes the Jacobi-Matrix of system (3.14):

$$J(\vec{c}_i) = \begin{pmatrix} \frac{\partial f_1(\vec{c}_i)}{\partial c_{i,1}} & \frac{\partial f_1(\vec{c}_i)}{\partial c_{i,2}} & \cdots & \frac{\partial f_1(\vec{c}_i)}{\partial c_{i,N+M+1}} \\ \vdots & & & \vdots \\ \frac{\partial f_{N+M+1}(\vec{c}_i)}{\partial c_{i,1}} & \cdots & & \frac{\partial f_{N+M+1}(\vec{c}_i)}{\partial c_{i,N+M+1}} \end{pmatrix}, \tag{3.16}$$

where the k-th component of $\vec{c}_i$ is called $c_{i,k}$. The least square solution $\vec{c}_n$ of (3.15) can be determined relatively easily, since one is dealing with a linear system: It is

$$\vec{c}_n(t) = X_n(t) \cdot \vec{c}_n(0) + \vec{p}_n(t), \tag{3.17}$$

where X_n is the matrix solution of the system

$$\frac{dX_n}{dt} = J(\vec{c}_{n-1})\, X_n \text{ with } X_n(0) = I. \tag{3.18}$$

(I is the unit matrix) and $\vec{p}_n$ is that solution of the system

(3.15) which satisfies $\vec{p}_n(0) = 0$. (In (3.17) the general solution of (3.15) is represented by the sum of a particular solution, and the general solution of the accompanying homogeneous system (3.18).) If one inserts the expression (3.17) into the necessary conditions for the minimum of the sum of the squared deviations,

$$\frac{\partial}{\partial c_{n,i}(0)}\left(\sum_{k=1}^{N+M+1}\sum_{j=1}^{J_k}\left(c_{n,k}(t_{k,j})-\chi_{k,j}\right)^2\right)=0,\quad i=1,2,\ldots N+M+1, \tag{3.19}$$

one obtains a system of linear equations for the unknowns $c_{n,i}(0)$, which can be solved using a standard method [98] (see Appendix B). (If the boundary value problem is not overdetermined one obtains a linear system with a unique solution by equating expression (3.17) with the boundary values.)

Whether the series of the thus determined $\vec{c}_n(t)$ converges for a boundary value problem at hand, normally cannot be determined from the onset, but has to be decided through numerical trials. The same holds for the question, how sensitive the solution is to changes in the boundary values. Thus the method of quasilinearization becomes an important tool for planning experiments [9]: by simulating several boundary value problems one can find out which variables have to be measured with what accuracy at which places in order to determine the parameters of the model. Besides the convergence of the recursion, the confidence interval for $\vec{c}(0)$ is an important criterion; if one gets very similar sums of squared deviations for rather different $\vec{c}(0)$, one has to impose more restrictive boundary conditions.

The deviations $c_{n,k}(t_{kj})-\chi_{kj}$ can be weighted according to the accuracy of measurement of χ_{kj}, thus the least square condition will be:

$$\frac{\partial}{\partial c_{n,i}(0)}\left(\sum_{k=1}^{N+M+1}\sum_{j=1}^{J_k}\left(g_{kj}\cdot\left(c_{n,k}(t_{kj})-\chi_{kj}\right)\right)^2\right)=0. \tag{3.20}$$

One uses such a weighting, for instance, if the variables, of which measurements were made, have very different values but the maximum relative errors in measurement are about the same for all variables. In this case one could use the weights

$$g_{kj}=\left(\operatorname{Max}\left\{\chi_{kj}\mid j=1,2,\ldots J_k\right\}\right)^{-1}. \tag{3.21}$$

(The weighting of course could also be effected implicitly by a suitable transformation of variables in (3.14). This weighting is applied in the following, unless otherwise noted.)

When determining $\vec{c}_n(t)$ from equation (3.15), the preceding approximation $\vec{c}_{n-1}(t)$ has to be known for the entire range of t. This can be achieved by storing $\vec{c}_{n-1}(t)$ as a sufficiently dense table function, however with large systems the computational effort becomes prohibitive. One can also newly evaluate at each iteration step the $\vec{c}_i$, i=0,1,...n-1, simultaneously with $\vec{c}_n$. This technique is used in solving the boundary value problems of the following sections.

If the solution of the system (3.18) has components of very different orders of magnitude one can get into numerical difficulties in determining $\vec{c}_n(o)$ from (3.19). This can be avoided by using other initial values for X_n (see [8]). In the cases which are dealt with in the following, this did not occur.

It should also be mentioned, that instead of $\vec{c}_{n-1}(t)$ in equation (3.15) one can also use solution of equation (3.14) with the initial vector $\vec{c}_{n-1}(0)$. This showed similar convergence characteristics but was not explored further.

4. Mathematical Models of the Self-purification Process

4.1 Models of a few simple laboratory experiments

For setting up a mathematical model of the self-purification process on the basis of measured values, the functions $f_i(c_1,...c_n,t)$ in (3.11), (3.12), and (3.13) still have to be specified. These functions have to reflect the processes which are described qualitatively in Section 2. Whether one has used adequate functions, can best be tested with simple laboratory experiments, in which the discussed mechanisms are isolated. Therefore a few of them are discussed in the following. Based on these experiments, the quasilinearization technique could be tested, too.

The simplest self-purification system consists of a homogeneous bacterial population in a completely mixed solution which contains a single energy supplying substrate, as well as those inorganic substances necessary for bacterial growth. The corresponding model is a differential equation system of the type (3.13) for the three variables: substrate concentration S, bacterial concentration B, and oxygen concentration O:

$$\frac{dS}{dt} = - \frac{a_{11}\, S}{a_{12} + S}\, B \tag{4.1}$$

$$\frac{dB}{dt} = a_{21}\, \frac{a_{11}\, S}{a_{12} + S}\, B - a_{22} B \tag{4.2}$$

$$\frac{dO}{dt} = a_{31} (O_s - O) - a_{32} \frac{a_{11}\, S}{a_{12} + S}\, B - a_{33} a_{22} B\,. \tag{4.3}$$

Here a_{ik} are the parameters, and O_s is the oxygen saturation concentration. The right side of equation (4.1) is the well-known Michaelis-Menten-expression [63,93] : for a single enzyme catalyzed reaction it can be derived from the law of mass action, provided that the enzyme-substrate complex disintegrates slowly into the reaction products and the enzyme. Thus there first appears, instead of bacterial mass density, the concentration of the enzyme. For a sequence of enzyme catalyzed reactions, under certain assumptions there appears the same expression for the rate with which the original substrate is degraded; the reaction parameter and the enzyme concentration in it are those of the slowest reaction of the sequence [14,93] . Thus equation (4.1) results, assuming that the substrate is degraded along a single metabolic pathway, and that the bacterial concentration is proportional to the enzyme concentration.

The Michaelis-Menten-expression is used in the following also for cases in which the suppositions which led to it are not fulfilled with certainty. Then it represents a two parameter approximation to an expression, about which one knows only that it will behave like $S \cdot B$ for low substrate concentrations (probability of enzyme-substrate molecular collision), and in the case of greater substrate concentration it is proportional to B and independent of S (maximum rate for metabolic reactions).

The first term on the right hand side of equation (4.2) is the same as $a_{21} \cdot \frac{dS}{dt}$, that is, it is assumed that the ratio between the amount of substrate degraded and the amount of newly formed biomass is constant [39,66]. The second term on the right hand side of equation (4.2) takes into account the decrease of the bacterial mass through endogenous respiration (see Section 2.1) [24].

On the right hand side of equation (4.3) are listed all processes which affect oxygen balance: first the physical reaeration, which is proportional to the oxygen deficit [94]; the oxygen consumption in nutrient degradation, which is supposed to be proportional to $\frac{dS}{dt}$; and finally the oxygen consumption in endogenous respiration, which is assumed to be constant per bacterial mass unit [11].

Equations (4.1) - (4.3) are based on the assumption that the changes in oxygen concentration are not so great that they would influence the degradation kinetics. This especially excludes the occurence of anaerobic conditions.

The next more complex self-purification system results, if instead of homogeneous bacterial population a heterogeneous one is used. In many cases no complications arise because the nutrient is degraded in the same manner (see Section 2). One can use the same model equations (4.1)-(4.3).

Such a system was investigated experimentally in [34], where glucose was used as the nutrient. Figure 4.1 gives the measured values of one of the experiments. (In fact, oxygen concentration was measured continuously, but the chosen points of Figure 4.1 represent the curve sufficiently.) The dashed line gives the function S(t) calculated by Gates et al. [33] from equations (4.1) and (4.2), whereby $a_{22} = 0$ and the other parameters were fitted by a graphical method [33]. The following parameter values were given in [34]:

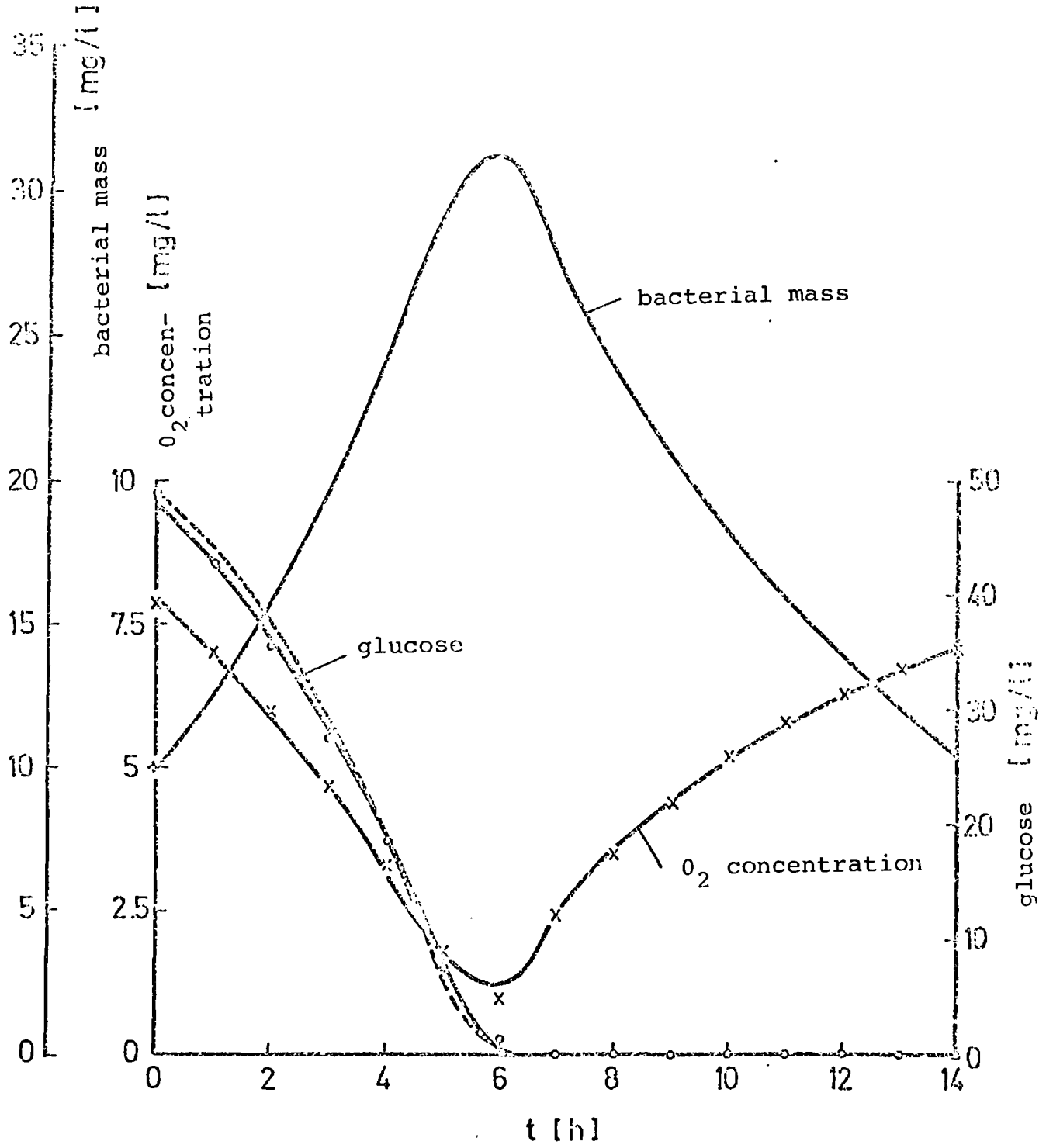
$a_{11} = 0.680$ [mg Substr./mg Bact./h] $a_{12} = 7.80$ [mg Substr./ml]

$a_{21} = 0.5$ [mg Bact./mg Substr.]

Also, the values for a_{31} and a_{32} were given, the former resulted from a control run in distilled water:

$a_{31} = 0.23$ [h^{-1}] $a_{32} = 0.273$ [mg O_2/mg Substr.].

If one tries to evaluate all the parameters of the model (4.1) - (4.3) through the quasilinearization technique (see Section 3.2) from the given measurements, it may happen that unreasonable parameter values result (e.g. negative values for a_{12}, a_{22}, or a_{31}), unless the initial approximation is very good. That is to say, if all parameters are completely free for optimization, the given measurements are not sufficient for a unique solution of the boundary value problem.



o + x measured values from Gates et al.[34]

nutrient curve calculated by Gates et al.[34]

solution of the model equations using optimal parameter values

Figure 4.1 Model identification for the degradation of glucose by a heterogeneous population in a laboratory experiment.

The difficulty cannot be overcome by increasing the number of measurements of S and O. If, however, the parameter a_{31} is fixed at the value 0.23 given in [34], the quasilinearization method yields, for a large range of initial approximations, the following parameter values a_{ik}:

i \ k	1	2	3
1	0.48	2.3	
2	0.79	0.14	
3	0.23	0.25	0.10

The units used are as above, mg/l and h. The initial values of the parameters may differ by more than a factor of 2 from the optimal values, without the $\vec{c}_i$'s (see 3.15) converging into other values. In Figure 4.1 the solutions of equations (4.1) - (4.3), which resulted from model identification, are given as solid curves. One can see that they fit the measured data very well.

Most remarkable is the sharp decline of the bacterial mass density after glucose depletion; this hardly could be attributed to endogenous respiration, especially since oxygen consumption is low at the same time. This fast decline is also reported in [34], even though values for the bacterial mass were given as functions of time for one run only. It is ascribed to bacterial death, although the chosen method of biomass determination allows for other interpretations as well.

If one, in addition to a_{31}, also fixes the value for a_{33}, then for $a_{33} = 0.67$ the model identification yields the following parameter values a_{ik}

i \ k	1	2	3
1	0.474	2.3	
2	0.51	0.013	
3	0.23	0.26	0.67

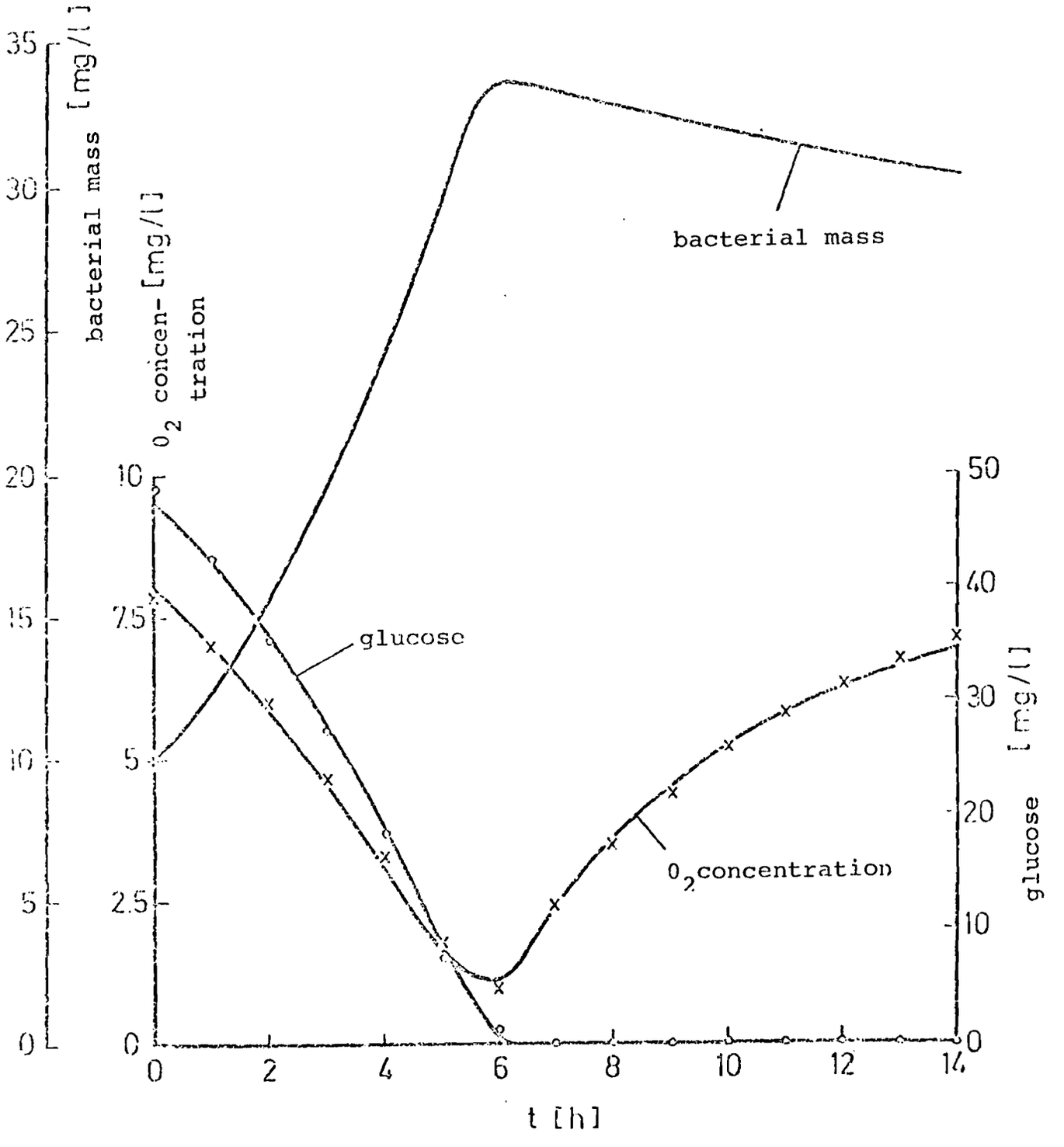
and the curves in Figure 4.2. The curves fit the measured values practically as well as the curves of Figure 4.1, although some of the parameter values differ considerably. That is, the parameter estimation based on measurements of S, O, and the initial value of B is quite uncertain, even if a_{31} is fixed. The parameter values given in [34] must thus be similarly inaccurate, because with the last discussed model ($a_{33} = 0.67$) approximatly the same parameter values as in [34] should result, since a_{22} is so low ($a_{22} = 0$ in [34]!). The uncertainties of the parameters given in [34] (especially $k^m = a_{11} \cdot a_{21}$ and $K = a_{12}$) are therefore considerably larger than expected from the variations of the given values. (However, for another experimental run given in [34] the parameter values were not as different.)

In order to obtain more accurate estimates of the model parameters measured values of bacterial mass density as a function of time have to be used, too. If these values really drop as quickly after glucose depletion as reported in [34], the model (4.1 - 4.3) is inadequate, because it seems unlikely that at the outset of the experiment the proportion of the bacteria dying per time unit is the same as after glucose depletion. One should examine the causes of the dying, and put them into the model. Lack of food cannot be considered as the cause for such rapid decline of the bacterial mass [84], even though a model, into which this process was included tentatively, simulated the laboratory system very well, and showed the reincrease of the bacterial mass density, which is mentioned in [34].

The next higher order of complexity in the self-cleaning system is achieved by adding another nutrient, or by adding bacteria consumers.

If a further nutrient is added, which also is degraded in the same way by all species of the heterogeneous bacterial population, several possibilities exist for degradation kinetics, depending upon the nutrient combinations. It is possible that both nutrients are independently degraded according to the Michaelis-Menten kinetics. This has frequently been observed [93], especially if the degradation processes are quite dissimilar, as for instance in a nutrient combination of carbohydrate and protein. The equivalent model can be derived from equations (4.1) - (4.3), if one adds an equation like (4.1) for the second nutrient and the appropriate terms to equations (4.2) and (4.3).

In other cases the nutrients inhibit each other, whereby, as described in Section 2.1, there exist two possibilities: the competitive and the allosteric inhibition. Analogous to the Michaelis-Menten-expression used for the simple enzyme



o + x measured values from Gates et al.[34]

——— solution of the model equations using optimal parameter values

Figure 4.2 Model identification for the degradation of glucose by a heterogeneous population in a laboratory experiment with fixed parameter $a_{33} = 0.67$

catalyzed reaction, one also can derive easily expressions which describe the reaction kinetics of these inhibited reactions [63]. For the competitive inhibition the espression reads:

$$\frac{dS}{dt} = - \frac{a_1 S}{a_2 + S + a_3 I} E , \qquad (4.4)$$

while the allosteric inhibition has the expression

$$\frac{dS}{dt} = - \frac{a_1 S}{(a_2 + S)(1 + a_3 I)} E \quad . \qquad (4.5)$$

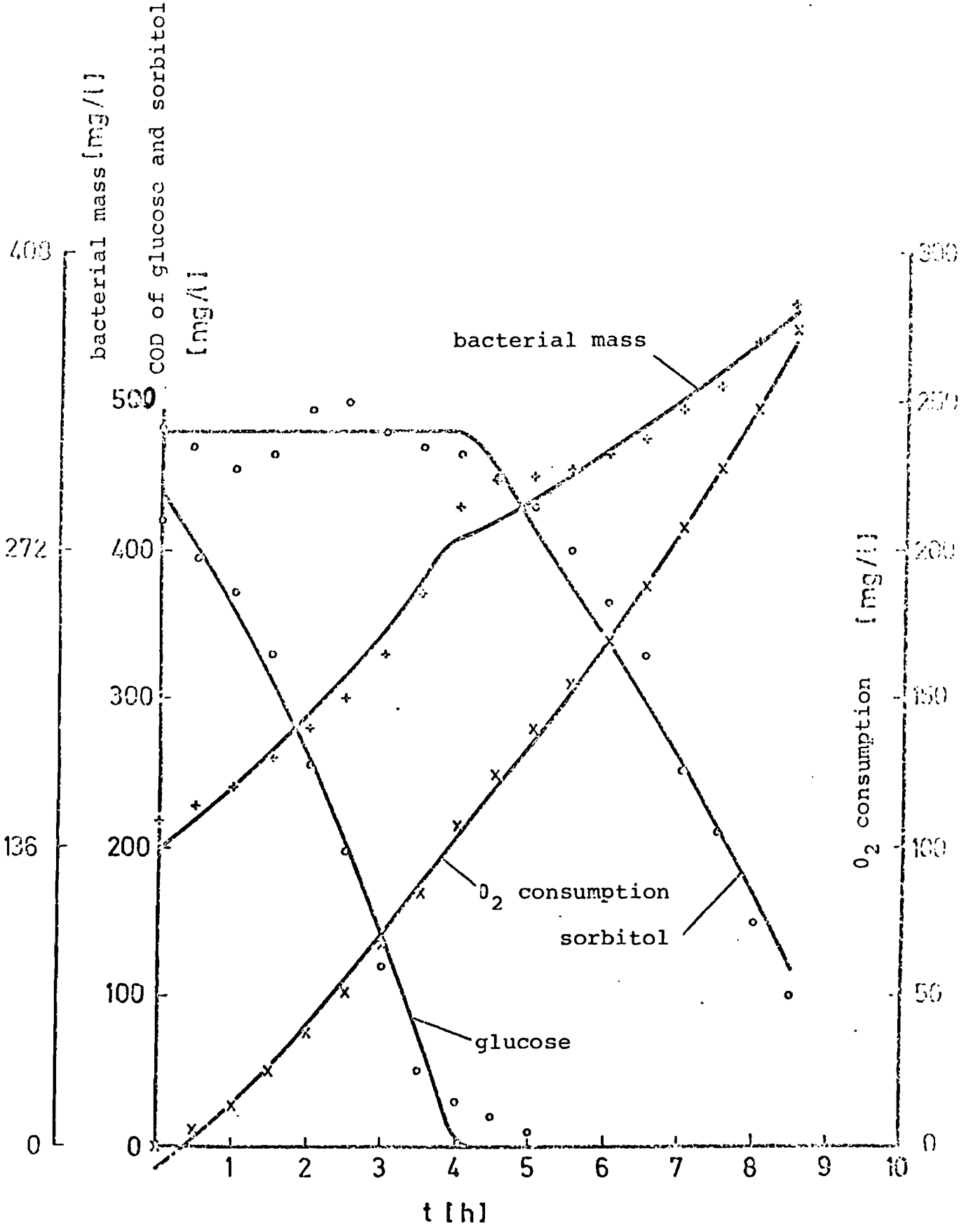
In both cases E is the enzyme concentration and I the concentration of the inhibitor, which in this case is another nutrient or one of its degradation products. Expression (4.5) is only valid if the affinity of the enzyme to the inhibitor is exactly as strong as to the nutrient. (For a more general expression see [63].) Formulae (4.4) and (4.5) can be used, like the Michaelis-Menten-expression, for enzyme catalyzed reaction chains and thus for the bacterial degradation of a nutrient [14,40,41,93].

A laboratory experiment, in which the degradation of one nutrient is inhibited by another, was examined in [36]. The nutrients were sorbitol and glucose. With bacteria acclimatized to glucose, the sorbitol was only degradated when the glucose had completely disappeared. Figure 4.3 shows the results of this experiment. Glucose values are given also for t > 5 h in [36] - they are about 10 mg/l. It is, however, most likely that these appear not as a result of the glucose, but come from a metabolic by-product, because in a control run, using a sorbitol-free medium, the 'glucose values' at large t-values stayed also well over 30 mg/l. (The glucose concentration was measured using the anthrone test [68].)

To model mathematically the laboratory experiment, an allosteric inhibition was assumed. The model thus has the following form:

$$\frac{dS_1}{dt} = - \frac{a_{11} S_1}{a_{12} + S_1} B \qquad (4.6)$$

$$\frac{dS_2}{dt} = - \frac{a_{21} S_2}{(a_{22} + S_2)(1 + a_{23} S_1)} B \qquad (4.7)$$



o + x measured values from Gaudy et al.[36]

——— solution of the model equation using optimal parameter values

Figure 4.3 Model identification for the degradation of a glucose-sorbitol mixture by a heterogeneous population in a laboratory experiment [36]

$$\frac{dB}{dt} = - a_{31} \frac{dS_1}{dt} - a_{32} \frac{dS_2}{dt} - a_{33} B \qquad (4.8)$$

$$\frac{dV}{dt} = - a_{41} \frac{dS_1}{dt} - a_{42} \frac{dS_2}{dt} + a_{43} a_{33} B . \qquad (4.9)$$

S_1 is the glucose and S_2 the sorbitol concentration; V is the accumulated oxygen consumption. S_1 and S_2 are (as in the experiments of [36]) measured by the chemical oxygen demand (COD). The biochemical reactions underlying the process cannot be considered completely known, thus the use of the kinetic expression for the allosteric inhibition in Model (4.6) - (4.9) is not imperative. It is certain, however, that the degradation process of sorbitol leads at first through dehydrogenation and phosphorylation to fructose-6-phosphate [52,72]. (The order of the two reactions depends upon the bacterial species. Both possibilities should be realized in the heterogeneous population used in [35] and [36].) Fructose-6-phosphate is in a "fast" equilibrium with glucose-6-phosphate, the first intermediate product of glucose degradation [10]. Because of this early amalgamation of the metabolic pathways of glucose and sorbitol, the number of the possible inhibition mechanisms is relatively small. (That one is dealing with an inhibition rather than a repression (see Section 2.1), can be recognized by the fact that the population adapted to glucose can utilize sorbitol at a high rate immediately after the glucose has been used up, whereas in a pure sorbitol medium the degradation only begins very slowly, because the corresponding enzymes have to be formed first.) The simplest explanation of the kind of inhibition included in model (4.6) - (4.9) is that besides glucose-6-phosphate also free glucose enters the cells and there allosterically inhibits the sorbitol degrading enzymes. The non-occurance of the inhibition in 'old' sorbitol adapted populations [36] can be the result of the changed permeability of the cellwalls for free glucose. However, the inhibition of the sorbitol degradation could also be the result of an excess glucose- and fructose-6-phosphate-level. Then in the degradation of sorbitol one of the first two reactions would determine the rate so that the glucose- and fructose-6-phosphate-level would be quite low [72].

As in the previous example, it is here not possible to determine all the parameters of the model (4.6) - (4.9) uniquely on the basis of measurements of the dependent variables alone. However, the parameter determination is possible if one assigns estimates to parameters a_{12}, a_{22}, a_{23}, a_{33}, and

a_{43}, which in the process of model-identification are treated in the same manner as the measured values of the dependent variables (see Section 3.2) If the following estimates are used

$$a_{12} = 5.0$$

$$a_{22} = 10.0$$

$$a_{23} = 1.0$$

$$a_{33} = 0.1$$

$$a_{43} = 0.35$$

and their weight (3.21) is multiplied by 0.02 then, using the quasilinearization technique, the curves of Figure 4.3 result, and the parameter values a_{ik} are:

i \ k	1	2	3
1	0.557	5.47	
2	0.260	9.40	1.04
3	0.515	0.631	0.0968
4	0.194	0.290	0.367

The given estimates were taken, as far as they are related to endogenous respiration, from the control runs with sorbitol-free medium as described in [36]. (In these control runs the degradation of the biomass after the glucose depletion has been observed.) The remaining estimates are based on many different experimental results, which all lie in the order of mg/l (see for example [10]). The factor of 0.02 mentioned above was entered because of the relatively high uncertainty of the estimates. It is apparent that model (4.6) - (4.9) reproduces the measured values quite well. However, also here the sensitivity of the sum of squared deviations to changes of some parameters is quite small, this holds especially for a_{23}. (This low sensitivity is already indicated by the fact that the initial parameter estimates are only slightly changed in the model identification despite the very small weights.)

In determining the parameters based upon the values given in [36], it was assumed that the concentration of the suspended solids is equal to the concentration of the viable bio-mass, i.e., that the proportion of dead bacteria in the suspension is negligible. Little is known about the extent, causes, and kinetics of the dying of bacteria. In the literature one can find, depending upon the experimental conditions, values for the ratio of suspended solids to viable biomass, which are close to 1, as well as much greater values [11,25,37,85]. Because of the low value of a_{43} one

can suspect that the term $a_{33}B$ in equation (4.8) comprises not only endogenous respiration, but also cell lysis; thus a remarkable proportion of the suspended solids could be dead biomass.

If one does not enlarge the system given by equations (4.1) - (4.3) by a further nutrient, but by protozoa feeding on bacteria, one gets the model equations

$$\frac{dS}{dt} = - \frac{a_{11} S}{a_{12} + S} B \qquad (4.10)$$

$$\frac{dB}{dt} = - a_{21} \frac{dS}{dt} - \frac{a_{22} B}{a_{23} + B} P - a_{24} B \qquad (4.11)$$

$$\frac{dP}{dt} = a_{31} \frac{a_{22} B}{a_{23} + B} P - a_{32} P \qquad (4.12)$$

$$\frac{dO}{dt} = a_{41}(O_S - O) - a_{42} \frac{dS}{dt} - a_{43} \frac{a_{22} B}{a_{23} + B} P - a_{44} a_{24} B - a_{45} a_{32} P, \qquad (4.13)$$

where P is the concentration of the protozoa mass, because the population dynamics of the protozoa can be described in a similar way as those of the bacteria [21,22,23]. However, this model was not tested with measured values. In that (as well as for more complex models) the results given in [12,13,51,70,86] could be used. It would also be desirable to validate self-purification models for the case where toxicants are present. The essential kinetic expressions for these models should be equations (4.4) and (4.5), depending upon the inhibition mechanisms [40,41].

4.2 Model for benthos-free rivers

Models for rivers are especially simple if one can ignore the benthos variables, because then the equations are ordinary differential equations (see equation (3.13)). According to Section 3.1 benthos denotes the total of the river organisms and materials which are stationary. In this sense, those rivers can be considered benthos-free, which flow fast and which are deep; also the quality of the river-bed plays a major role. To ignore benthos variable c_k, c_k need not be very small compared with the corresponding plancton variable. If, for example, the bacterial density on the river bottom is so high that the c_k values (c_k is the mean value over the river cross-section (see Section 3.1!)) is of the same order of magnitude as the concentration of the plancton bacterial mass, c_k can, under certain circum-

stances, be ignored, because the water layer immediately next to the river bottom--compared to the major portion of water--moves only slowly, so that material exchange between the benthos bacteria and the free-flowing water is relatively small. Furthermore, in thick bacterial colonies the lower parts are poorly supplied with nutrients [97].

Up to now the self-purification of benthos-free rivers has been usually described using the Streeter-Phelps model (see Section 1), in which it is simply assumed that the oxygen demand for biological oxydation (BOD) of the organic waste decreases according to a first order reaction (see also equation (4.3)).

$$\frac{dBSB}{dt} = -k_1 \, BSB \tag{4.14}$$

$$\frac{dO}{dt} = k_2 \, (O_s - O) - k_1 \, BSB \tag{4.15}$$

It is obvious, however, that this simple model, in which, for example, bacteria concentration is not present, describes the self-purification only incompletely. Figure 4.4 illustrates this [32]: even though k_2 was measured separately, and k_1 was determined for each of the three purification stages such that the sum of the squared deviations is minimal, the solution of (4.14) and (4.15) does not fit the experiment results. If the measurements used for the parameter estimation are so poorly reproduced, it is only natural that an extrapolation to different experimental conditions (e.g., different temperature) becomes doubly problematic. There have been some attempts to improve upon the Streeter-Phelps model by adding empirical corrections (which in some cases are intended to account for benthic variables) to the analytical solutions of (4.14) and (4.15) [73,96]. Since, however, the dynamic character of the self-purification process was not taken into account, it is doubtful if more than data reproducing models have resulted.

While on one hand the Streeter-Phelps model is too crude, it is, on the other hand, in general impossible to take into account every pollutant in detail (as in model (4.6) - (4.9)), because of the large number of pollutants. The aggregation level of the model has to be such that the data basis for the model identification can be supplied with a reasonable measurement effort.

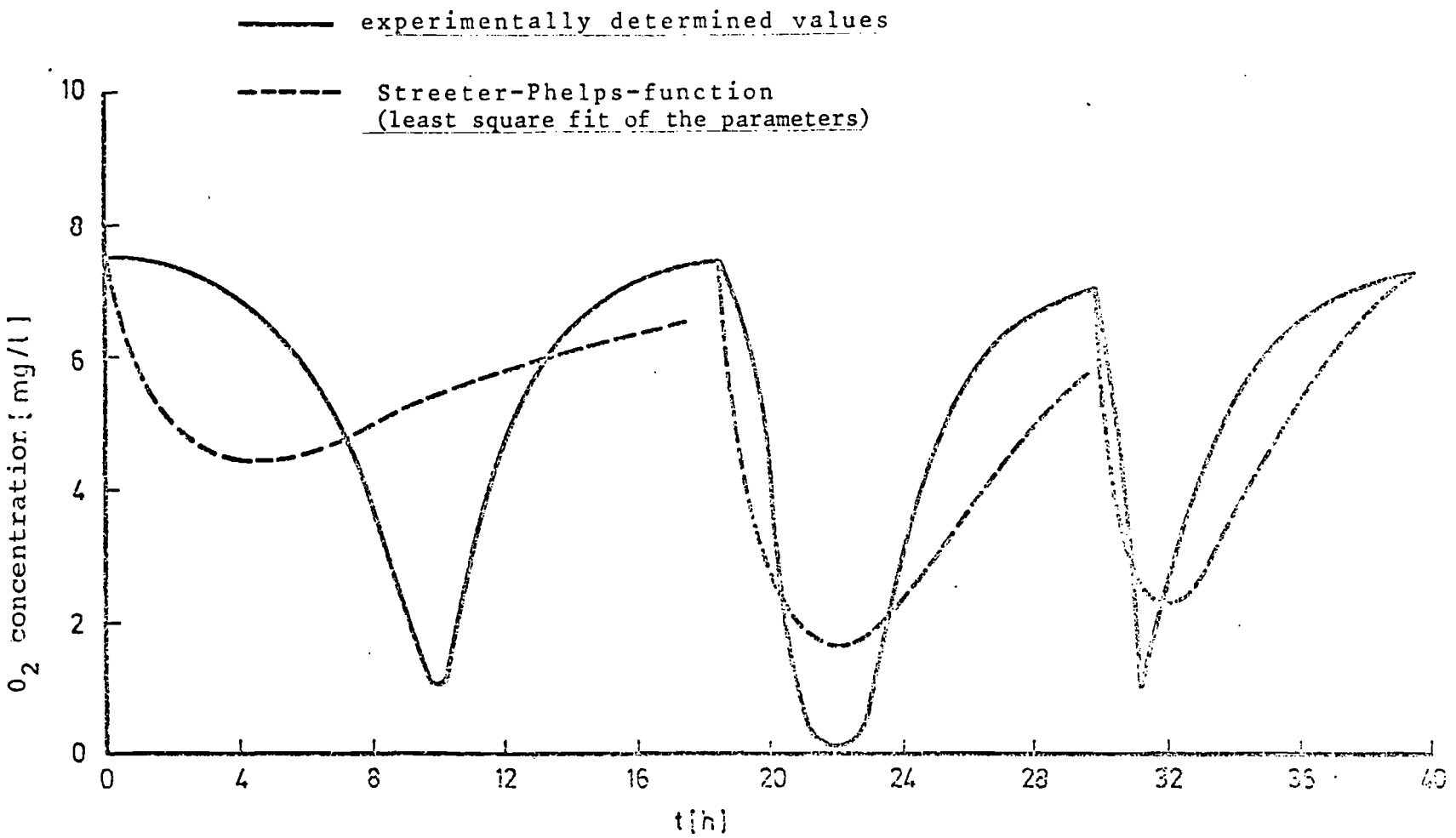


Figure 4.4 Description of measured oxygen sag curves by means of the Streeter-Phelps-equation [32]

The organic pollution, as the basis for the growth of heterotrophic bacteria, practically can only be measured in total. One measure could be the oxygen demand for the complete chemical oxidation of organic materials (COD), another one is the amount of organically bound carbon (TOC). (For techniques of measurement see [27,64]. Measuring of COD with potassium permanganate should, however, not be used because only a small part of the organic substance is oxidized [7].) COD is more useful as a measure of organic pollution for modelling self-purification processes than is TOC, because COD reflects the stepwise degradation of the substance, while TOC could, for instance, only change in the last step of oxidation. Thus in the following the term "organic pollution" means COD. (However, by and large the ratio of COD to TOC remains nearly constant in the course of the self-purification process [58].)

Possibly, apart from the total COD, one also could determine with reasonable effort the amount of biologically non-degradable substances. One would have to have water samples undergo intensive bacterial degradation for a time which is considerably longer than the flow time of the river, and after that again determine the COD. (The COD of the non-degradable pollutants could also be determined approximately as the difference between the total COD and the long-term BOD, but one has to consider that those pollutants which are at first integrated into the bacterial biomass are oxidized very slowly [95].) However, the model identification described in the following is also possible if one or only inaccurate values of the COD of the non-degradable substances are available.

In the determination of the bacterial mass density a taxonomic differentiation is not tolerable as well, so that for model identification only values for the total bacterial mass are available. As pointed out in Section 2.1, it is not a bad approximation if one considers all bacteria to be acting collectively. As a measuring method neither the direct counting (because of the high expenditure), nor the plate count [15] (because of the large errors) can be used. The measurement through the ATP content, using luciferin and luciferase, or similar methods, seem to be appropriate[49]. (It appeared, however, that ATP measurement can be disrupted by the presence of certain compounds contained in industrial waste water [59].) Perhaps the bacterial mass could also be determined by measuring the oxygen consumption after the addition of a relatively large amount of bacteria consumers.

If part of the pollutants are present in an undissolved, suspended form, then in determining the COD the living biomass is inevitably encompassed. Thus the COD values have to be corrected for the results of the biomass determinations.

Also higher organisms, if they have to be considered at all, have to be amalgamated into larger groups. Counting seems to be the only practical way to measure them. In the following, only the protozoa are incorporated in addition into the model, because, as explained in Section 2.2, the higher order links of the food chain are not of great importance. The phototrophics are also left out, because their planctonic forms do not play a large role in rivers (see Sections 2.2 and 4.3).

Finally, for model identification, the values of oxygen concentration are usually available, they can be obtained easily in various ways [15,17].

A model, which is to be identified on the basis of measurements of COD, bacterial mass density, protozoan mass density, and oxygen concentration may well contain more than these variables. Likewise no measured bacteria curve was used in the identification of model (4.1) - (4.3) which contains the bacterial mass. (Only the initial value of B was used. This would not have been necessary if one had accepted an unknown, constant factor in the function B (t).) Because of the various degradation kinetics of the numerous pollutants it would be desirable to differentiate between easily and slowly degradable materials in the river model. In the following they are denoted by $N_1(t)$ and $N_2(t)$, respectively. Thus COD values are values of N_1+N_2. The Michaelis-Menten-expression should describe the degradation kinetic of N_1 well (see Section 4.1). One of the expressions (4.4), (4.5) should be more realistic for the degradation kinetic of N_2, where N_1 acts as inhibitor; it is well known that those enzymes which catalyze the degradation of slowly degradable pollutants are only formed after the more easily degradable materials have been used up [76]. (For a large part those materials which are difficult to degrade (e.g., humic acids [42]) only come into existence during the degradation process of easily degradable materials.) To describe the degradation process of N_2 expression (4.4) is used, because it gives a better fit. In other cases expression (4.5) may be more appropriate; the comments made in the following about the model are also then valid. In any case, the kinetic expressions for inhibition should be considered only as approximations with three parameters, which reproduce the essential characteristics of the inhibition: for small N_1 the result for N_2 is the Michaelis-Menten-Kinetic; for high N_1 the degradation of N_2 is blocked. The difference between (4.4) and (4.5) consists in the following: in the first instance

the maximum degradation rate of N_2 is independent of N_1; in the second instance this is not the case.

All the assumptions discussed above lead to a model of the benthos-free river which is shown in Figure 4.5, and which is to be identified on the basis of measured values of N_1+N_2,B,P, and O.

It is assumed thus far that water inflows into the river during the time of interest do not change the concentrations considerably. Otherwise one has to add the corresponding source terms on the right hand sides of the model equations. For instance, in case of an increase of COD through a single sewage effluent at flow time t_o the following terms have to be added to the first two equations, respectively:

$$\alpha \cdot z \cdot \delta (t - t_o) \tag{4.21}$$

$$(1 - \alpha) \cdot z \cdot \delta (t - t_o), \tag{4.22}$$

where z is the given COD concentration increase and $\delta(t-t_o)$ is the impulse function. Parameter α denotes the ratio under which the discharged pollutants are apportioned to N_1 and N_2. If we can look upon many effluents on a river reach as a single distributed source with constant density one can use these terms also but with rectangular shaped functions instead of $\delta(t-t_o)$.

A complete set of measured values for the aforementioned variables seems not to exist thus far for larger river reaches. Thus in order to test the usefulness of model (4.16) - (4.20), and in order to clarify the questions of planning measurements raised in Section 3.2, a river was simulated on a computer which delivered the necessary measured values. This simulated river is discussed in more detail in Appendix A. It contains 30 different pollutants, all of them having different degradation kinetics (mutual inhibitions according to expressions (4.4) and (4.5), purely additive degradation, formation of exoenzymes), as well as two protozoa types with different metabolic dynamics. The kinetic parameters were generated within realistic ranges by a random number generator. In Figure 4.6a the values obtained from this "river" are reproduced. The values of the total organic pollution were corrected for the non-degradable pollutants by subtracting the pollution values at t = 145 h (see above).

$$\frac{dN_1}{dt} = -a_{11}\frac{a'_{31}\,N_1}{a_{32}+N_1}\,B \qquad (4.16)$$

$$\frac{dN_2}{dt} = -a_{21}\frac{a_{33}\,N_2}{a'_{34}+N_2+a'_{35}N_1}\,B \qquad (4.17)$$

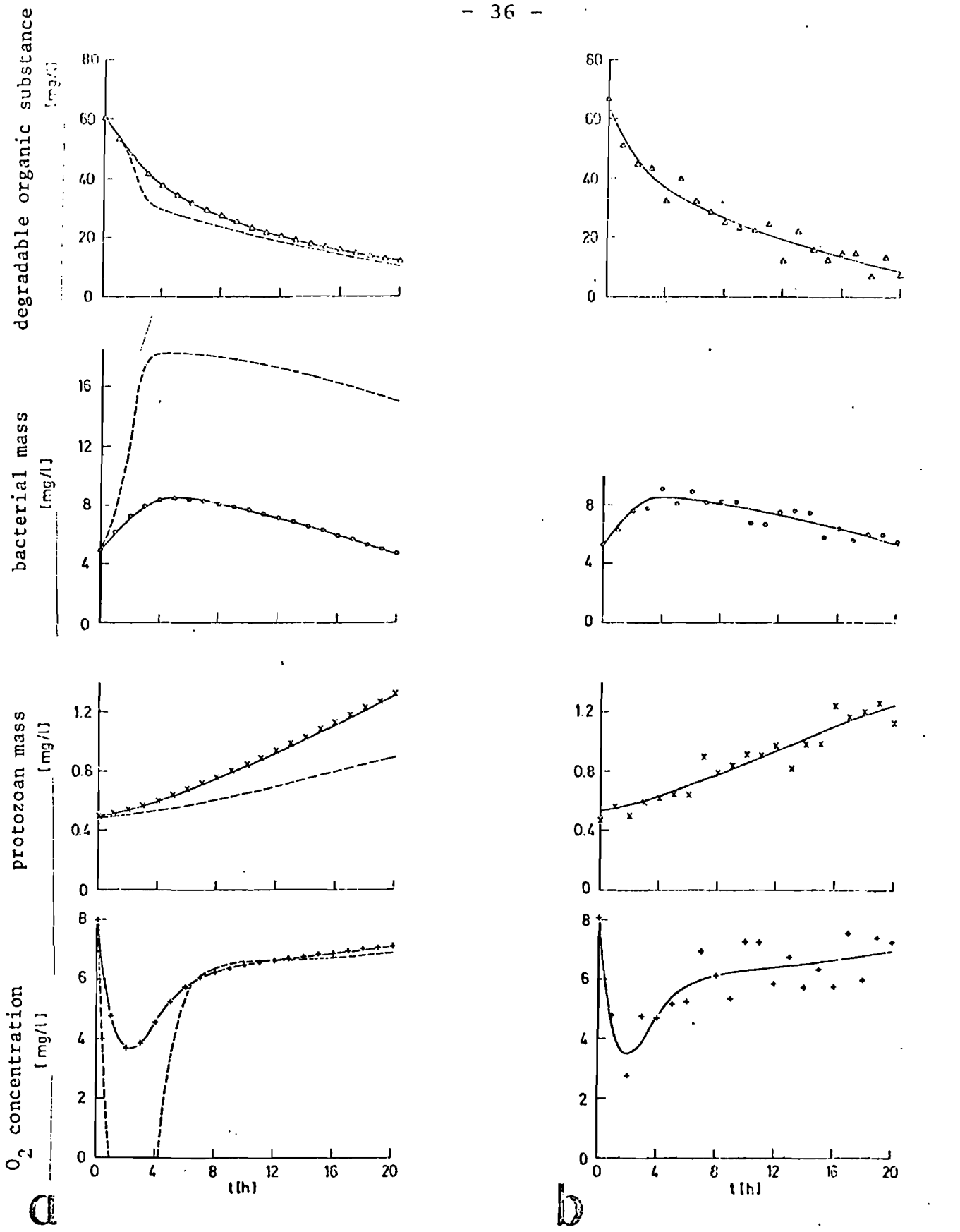
$$\frac{dB}{dt} = \frac{a'_{31}\,N_1}{a_{32}+N_1}\,B + \frac{a_{33}\,N_2}{a'_{34}+N_2+a'_{35}N_1}B - a'_{36}\,\frac{a'_{41}\,B}{a'_{42}+B}\,P - a'_{37}\,B \qquad (4.18)$$

$$\frac{dP}{dt} = \frac{a'_{41}\,B}{a'_{42}+B}\,P - a_{43}\,P \qquad (4.19)$$

$$\frac{dO}{dt} = +a'_{51}\,(O_S - O) - a_{52}\,\frac{a'_{31}\,N_1}{a_{32}+N_1}\,B - a_{53}\,\frac{a_{33}\,N_2}{a'_{34}+N_2+a'_{35}N_1}\,B \qquad (4.20)$$

$$- a'_{54}\;a'_{37}\;B - a'_{55}\;\frac{a'_{41}\,B}{a'_{42}+B}\,P - a'_{56}\,a_{43}\,P$$

Figure 4.5 Model equations for the benthos-free river



▵ • x + measured values from the simulated river

——— solution of the simple model using optimal parameter values

- - - - - initial approximation

Figure 4.6 Model identification for a benthos-free river

a "measured values" without errors
b "measured values" with errors

As could be expected from Section 4.1, the parameters of models (4.16) - (4.20) can only be uniquely determined if estimates for some parameters are given. Model identification, for example, is possible, if the primed parameters in equations (4.16) - (4.20) are given the values from the second following table, and if these values are weighted by $0.003 \cdot g_o$, where g_o is again the weight according to (3.21). The solid curves in Figure 4.6a show the solution of Model (4.16) - (4.20) using the optimal parameter estimates. The parameter values a_{ik} are:

i \ k	1	2	3	4	5	6	7
1	4.12						
2	5.41						
3	0.543	19.5	0.0769	21.0	0.996	2.52	0.0479
4	0.179	8.21	0.0331				
5	1.05	3.08	3.27	1.04	1.03	1.01	

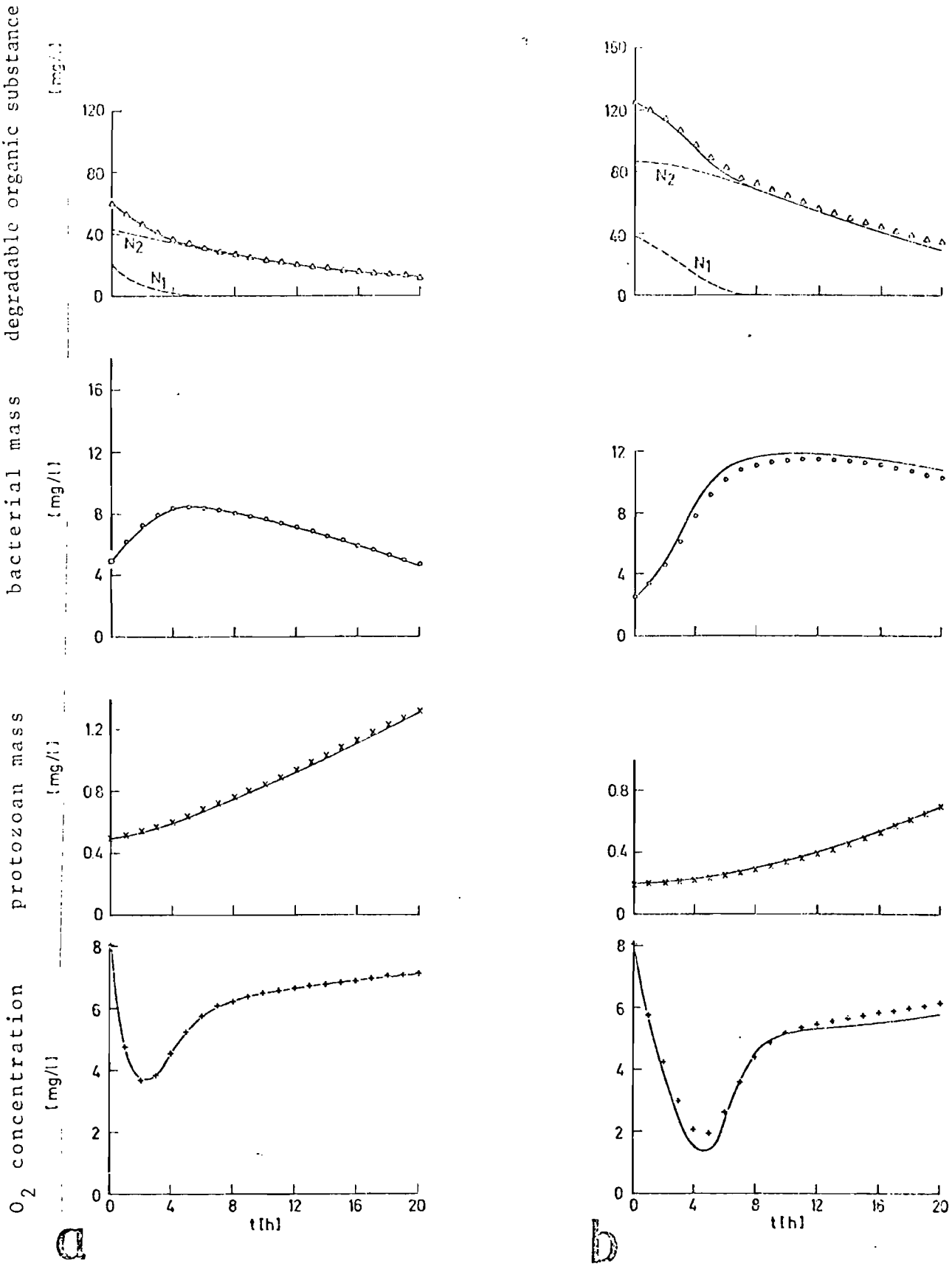
while the initial guesses were

i \ k	1	2	3	4	5	6	7
1	2.0						
2	2.0						
3	0.5	2.0	0.07	20.0	1.0	2.0	0.04
4	0.135	15.0	0.04				
5	1.0	4.0	1.0	1.0	1.0	1.0	

(the dashed curves show the initial approximations $\vec{c}_o(t)$ (see Section 3.2).) It is apparent that the simple model reproduces the "measured values" well. Model identification is possible in the same manner if the "measured values" have considerable errors; Figure 4.6b gives an example. The solution functions have not been changed too much from Figure 4.6a, the same holds true for the parameter values. The PL/I computer program, which in the case of Figure 4.6b solved the model identification problem, can be found in Appendix B along with a program description.

In selecting the parameters, for which approximate values are to be prescribed, one has to ask whether reasonable guesses for the parameters in question are available. For instance, it is better to use an approximate value for a_{31} than for a_{32}, because one knows that a_{31} is of the same order of magnitude, but below the largest known growth rate of bacteria at the given temperature, while for a complex nutrient mix very little can be predicted about a_{32}. (If one gives an approximate value for a_{32} rather than for a_{31} a model identification would also be possible if all other circumstances remain unchanged.) Also one can use the kinetic parameters for the interaction between bacteria and protozoa, which have been found in laboratory experiments, as measured values for the model identification; but it is desirable to leave parameter a_{43} totally free, because the term $a_{43}.P$ is to account approximately for the influence of higher order links of the food chain. Parameters a_{51} and a_{37} cannot be left completely free, although it would be desirable (see below and Section 4.3, respectively), because unreasonable parameter values can result if the measured values are subject to errors as in Figure 4.6b. However, since the weight of the guesses is very small (see above), the coupling of the parameter values to the measured values is not very restricting. Summing up, it can be stated that on the basis of measurements of total COD, bacteria, protozoa, and oxygen, model (4.16) - (4.20) can be identified, although this model distinguishes between easily and slowly degradable COD. (This also holds in the case where the non-degradable substances were not eliminated. However, the fit of the measured values is not as good.)

The purpose of a model is not only to reproduce measured values, but also to predict the system behaviour under circumstances for which no measurements have been made. Figures 4.7 and 4.8 give two examples for the application of the identified model to changed conditions. In one case the initial values were changed, in the other case the solution is extrapolated beyond the time up to which values were used for model identification. (Of course, the second case can be looked upon as one with changed initial conditions.) In both cases (which have quite different kinetics) the simple model (4.16) - (4.20) fits the simulated river quite well even under changed conditions. Several further numerical experiments of this kind have given similar results. However, the quality of the fit certainly depends upon the structure of the complex river model used (see Appendix A). Opposed to that, the



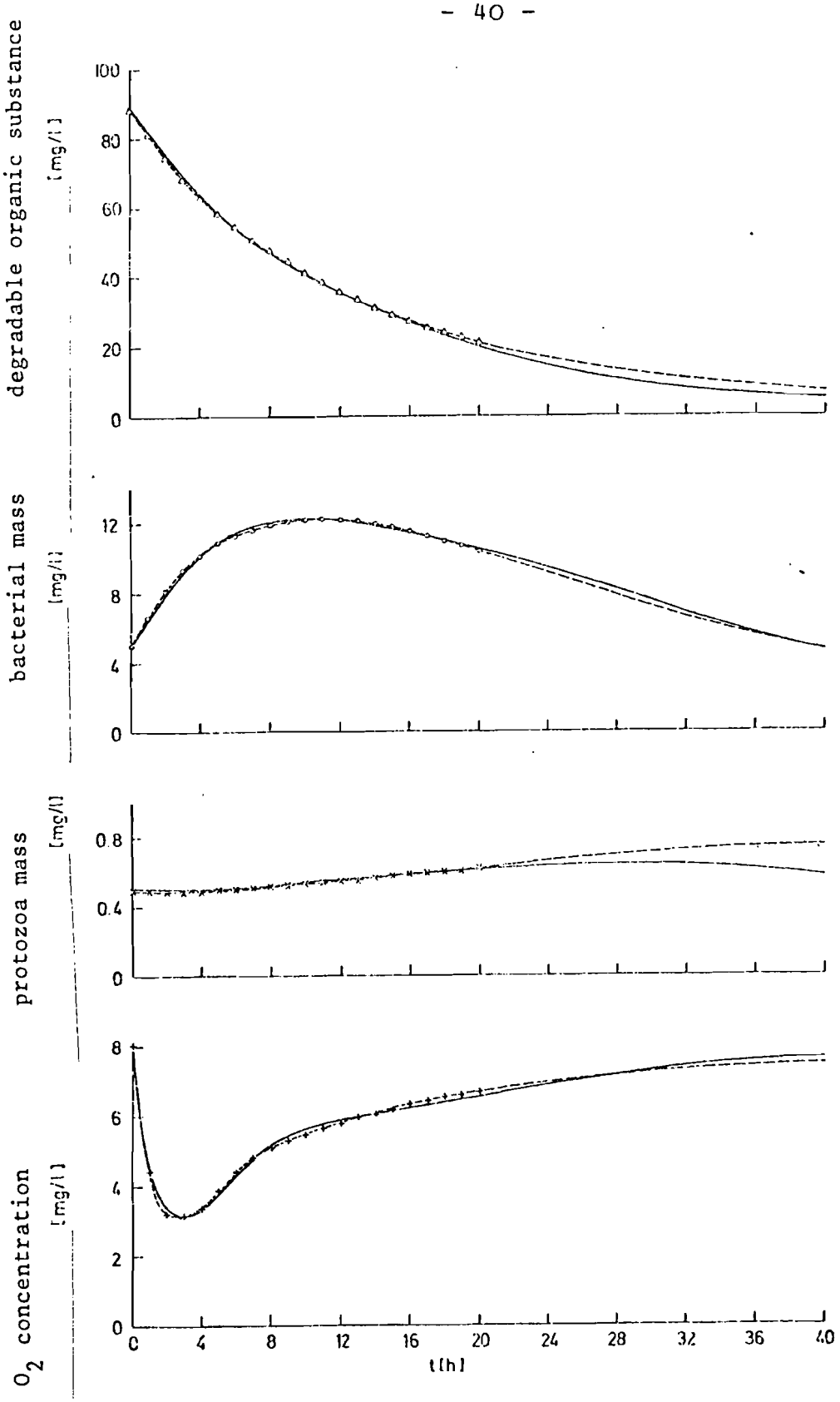
• • × • self purification in the simulated river

——— solution of the simple model using optimal parameter values

• • × • self purification in the simulated river with changed initial values

——— solution of the simple model using changed initial values but old parameters

Figure 4.7 Model identification for a benthos-free river: validity of the optimized model for changed initial values



∆ ∘ × + "measured values" used for optimization
solution of the complex river model
solution of optimized simple river model

Figure 4.3 Model identification of a benthos-free river: Comparison between the complex and the optimized simple model extrapolated beyond the range of the optimization

conditions formulated above for the model identification should not be affected by any realistic change of the complex river model.

One can also use several sets of measured values which have been obtained from the same system under different circumstances for model identification (for instance the "measured values" of Figure 4.7a and b). Then one has to state the equations for the variables which have changed as many times in system (3.14). The uncertainty of the parameter estimation is thus smaller, it may be even possible to dispense with prescribing approximate parameter values. Such cases have, however, not been worked out. The model identification procedure also has not yet been applied to situations with several waste water affluents on the river reach under investigation. (The reach must not be too short, because otherwise the dividing of the pollutants into N_1 and N_2 is too uncertain.) If one wants to consider many affluents with various values of α (see (4.21) and (4.22)) a unique model identification based on measured values from the river will probably be impossible. One then has to observe the self-purification in river samples, and based on the values thus gained one can determine the parameters. These in turn can be entered as estimates (perhaps with a higher weight) into the model identification process which uses the "in-situ" values.

One can use the same proceeding if one wants to determine the physical reaeration rate a_{51} without prescribing an approximate value for it. (This corresponds to the method usually applied in the determination of k_2 in equation (4.15) [32].) Great uncertainty about the size of this parameter exists, especially for large rivers, which cannot be simulated in laboratories [71].

Another open problem is the inclusion of nitrification into the model and the determination of the conditions under which the identification of such a model is possible. Especially interesting is the question if one can dispense with measured values of nitrifying bacteria mass density, if values for NH_4^+, NO_2^-, NO_3^-, and organic nitrogen are given.

Also the question how a degradation inhibition by toxicants can be recognized and taken into consideration has to be cleared up (see Section 4.1). In these cases several sets of measurements for different dilution ratios (i.e., different river discharges) will have to be used (see [55]).

In closing, it is worth mentioning that the separation of the total pollution into easily and slowly degradable materials also can be used to characterize the degradation characteristics of a specific waste water.

4.3 Model for the self-purification process of the Rhine River between Mannheim-Ludwigshafen and the Dutch-German border

The Rhine River with its large discharge and its great flow velocity can be looked upon as a benthos-free river. The statement made in Section 4.2 can be applied to it, that self-purification data measured so far are not sufficient for model identification. There are many measured values available, but most of them give only very indirect information about the self-purification process. For example, measurements for additional consumption [56] are hard to interpret, because of the unknown preference of the bacteria to the nutrients added as compared to the nutrients already present. The same applies to the measurements of the biological oxygen demand, even solely because of the difference in temperature between the river and the sample. The many values of $KMnO_4$ - and $K_2Cr_2O_7$- demand, which have been measured so far, encompass usually only the COD of the dissolved substances, in addition, with the $KMnO_4$ test only a small part of the organic substances is oxidized. Similarly the plate count results are hardly suitable as a measure of bacterial mass in the river, as a comparison of the plate counts with various nutrient media shows [91]. At most, some conclusions can be drawn by comparing values which were obtained under the same stipulations.

In order to identify a model corresponding to equations (4.16) - (4.20) one must have, as explained in Section 4.2, measured values for N_1+N_2, B, P and O, which were taken from the very same water body as it flows downstream, and which allow for a fairly accurate averaging over the river cross-section. Furthermore, if there are sewage effluents or other inflows, measured values of those variables for the inflows must be given. If necessary, parameter estimates have to be determined in the laboratory (see Section 4.2).

Before collecting these data some exploratory examinations concerning the applicability of model (4.16) - (4.20) would be useful. It must be examined whether those organisms higher than the bacteria consumers play an important part; this could be observed best on the Lower Rhine. Even the role of the bacteria consumers themselves needs to be verified. It would be worthwhile to examine nitrification more carefully, although it is most likely that it can be neglected

in the Rhine River. The NH_4^+ - concentration reaches such values that a complete oxidation would greatly influence the O_2 content [5,57]; but because the nitrifiers are inhibited by some pollutants [15] and also grow fairly slowly [38] nitrification will not become very intensive. In working out a model one has to face also the possibility that the toxic influence of some sewage effluents has to be considered separately (see Section 4.1), or that dealing with mean values across the river section (see Section 3.1) turns out to be too inaccurate. The conditions for dealing with mean values across the river section, however, are fulfilled better than it may seem in view of kilometerlong waste water plumes; the terms for bacterial growth in the model equations are constant for large concentrations of pollutants; that is, within the sewage plume they may be barely larger than outside it. (Degradation inhibition by toxitants, which is reduced by increasing dilution, acts similarly.)

Despite the many missing measurements and the partly unverified suppositions, it was tried to formulate a model of the self-purification process of the Rhine River between Mannheim and the Dutch-German border, based on equations (4.16) - (4.20) and on the available data. Such a model, of course, cannot deliver quantitative results, and an optimization of waste water inflows based on it would hardly make sense. But it can facilitate discussions of the problems of water pollution control in the Rhine River Basin, because it will reproduce the essential characteristics of the self-purification process in that river. The model points out especially which possibilities a better validated model offers, and which points should be examined more detailed.

The model equations, which correspond very closely to equations (4.16) - (4.20) (Figure 4.5), are reproduced in Figure 4.9. Equation (4.25) for the nondegradable pollutants, the terms for the inflows (sewage or tributaries) in the first three equations, and the term a_{67} in equation (4.28), which approximately accounts for the biogenic aeration, are all new compared to Model (4.16) - (4.20). Thus it is assumed that the inflows only change the pollution concentrations, and that the biogenic aeration along the river remains constant. The first assumption certainly must be corrected for a quantitative model, at least as far as the Neckar and Main tributaries are concerned, because, apart from pollution, they also bring in a large bacterial mass; the second assumption is of less importance because biogenic aeration is relatively small (see below.) The parameter values were chosen such that the few values which were measured or which could be derived from measured values are best reproduced. Con-

$$\dot{N}_1 = -a_{11}\frac{a_{41}\,N_1}{a_{42}+N_1}\,B + a_{12}\,a_{13} \qquad (4.23)$$

$$\dot{N}_2 = -a_{21}\frac{a_{43}\,N_2}{a_{44}+N_2+a_{45}N_1}\,B + (1-a_{12})\,a_{13} \qquad (4.24)$$

$$\dot{N}_3 = a_{31}\,a_{13} \qquad (4.25)$$

$$\dot{B} = \frac{a_{41}\,N_1}{a_{42}+N_1}\,B + \frac{a_{43}\,N_2}{a_{44}+N_2+a_{45}N_1}\,B - a_{46}\frac{a_{51}\,B}{a_{52}+B}\,P - a_{47}\,B \qquad (4.26)$$

$$\dot{P} = \frac{a_{51}\,B}{a_{52}+B}\,P - a_{53}\,P \qquad (4.27)$$

$$\dot{O} = a_{61}\,(O_S - O) - a_{62}\frac{a_{41}\,N_1}{a_{42}+N_1}\,B - a_{63}\frac{a_{43}\,N_2}{a_{44}+N_2+a_{45}N_1}\,B \qquad (4.28)$$

$$- a_{64}\,a_{47}\,B - a_{65}\frac{a_{51}\,B}{a_{52}+B}\,P - a_{66}\,a_{53}\,P + a_{67}$$

Figure 4.9 Model equations of the self-purification processes of the Rhine River

sidering the incomplete data basis, which promised equally good fit of the measured values for a great variety of sets of parameter values, the parameter values were determined by trial and error within realistic variations, not by the formal method of model identification. In looking back, however, it must be stated that it would have been probably more efficient to have used a model identification program with sufficiently many prescribed parameter estimates. Figure 4.10 shows the solution of the model. The corresponding, very simple computer program is given in Appendix C. The model is supposed to describe the self-purification dynamics in the Rhine River at a temperature of 20°C and a discharge of about 1.25 times the mean discharge (about 2500 m^3/sec in Cologne [17]). The pollution corresponds to the situation in 1969. Those parameters which are assumed to be constant along the entire river section were given the following values a_{ik}:

i \ k	1	2	3	4	5	6	7
1	2.6	a_{12}	a_{13}				
2	3.4						
3	0.05						
4	0.48	20.0	0.1	20.0	3.0	3.0	0.06
5	0.36	12.0	0.07				
6	a_{61}	1.6	2.4	1.0	2.0	1.0	0.07

Thus the maximum growth rate of the bacteria, $a_{41} + a_{43}$, is 0.58 h^{-1}, which gives a generation time of a little more than one hour; this is a realistic value at T = 20° [10]. Endogenous respiration given by a_{47} is probably a bit high with 0.06; but the values given in the literature vary greatly [11,14,37,66,75]; moreover, possible dying of bacteria because of toxicants can be taken into account by a higher value of a_{47}. The ratio between degraded organic pollutants (measured as COD) and newly created biomass, which is 2.6 and 3.4 respectively, lies also within the range marked out by many experimental results [66]. The saturation constants a_{42} and a_{44} amount up to several mg/l for single substrates [10,34,87], yet since N_1 and N_2 encompass many nutrients, the parameter values chosen had to be somewhat larger. (For example, should N_1 encompass n nutrients which have the same concentration

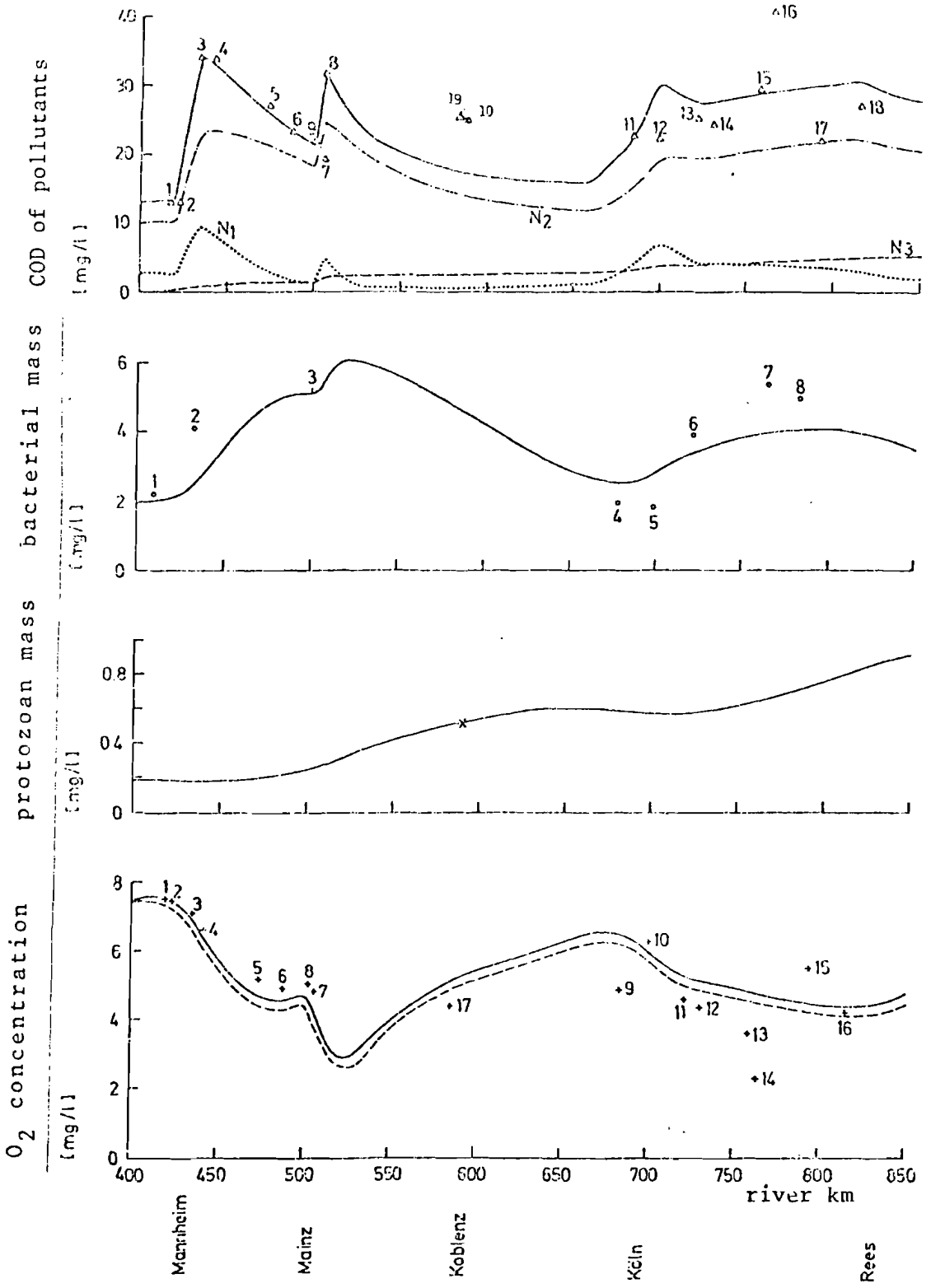


Figure 4.10 Solution of the self-purification model of the Rhine River for standard conditions ($T=20^{o}C$, $Q=1.25MQ$)

as well as the same kinetic behaviour, and which are purely additively degraded, then the saturation constant for N_1 would be exactly n times as large as that for the single nutrient). The inhibition constant a_{45} was finally chosen such that at values N_1, for which $a_{41}\ N_1/(a_{42}+N_1)$ was smaller than a_{43}, no substantial inhibition can any longer occur. The values for a_{51} and a_{52} were chosen in accordance with [22]; those values given in [88] for the maximum growth rates of various ciliates are, however, without exception smaller. The value of a_{67} is based on the value of 1.6 $mgO_2/(l \cdot d)$ given in [54] for the biogenic aeration near Koblenz, which was measured using the light and dark bottle technique. The dotted line in Figure 5.10 shows the oxygen concentration without regard for biogenic aeration. It is apparent that the biogenic aeration in relation to physical aeration is not very important (the above-mentioned value was even measured at the hight of summer), so that no large error occurs if the changes of biogenic aeration along the river and the diurnal variations of photosynthetic activity are ignored.

For parameters a_{12}, a_{13}, and a_{61}, the river section was divided into 12 reaches, in which these parameters were considered constant. Parameter a_{13}, which depicts the hourly concentration increase of the degradable substances by waste water discharges, is calculated from the amount A of organic waste which occurs per hour and river kilometer, from the river discharge Q, and from the flow velocity v (see Appendix C):

$$a_{13} = \frac{A \cdot v(Q)}{Q}$$

A is given in Figure 4.11. One can clearly recognize four major pollution sources: Mannheim-Ludwigshafen (at the mouth of the Neckar); Mainz-Wiesbaden (at the mouth of the Main); Bonn-Cologne-Leverkusen; and the Ruhr district. The values are just estimates which are based on measurements of COD in the river (see below) and the changes along the river of the number of inhabitants living in the river catchment area. The Emscher River, which at this time still represents an important point source of pollution at river kilometer 800, was not taken into account because of the huge treatment plant currently under construction. It is assumed that the Mosel River at the confluence with the Rhine exhibits the same qualities as the Rhine River at this point, as far as self-purification variables are concerned. A comparison of the values for Braubach (Rhine R.)

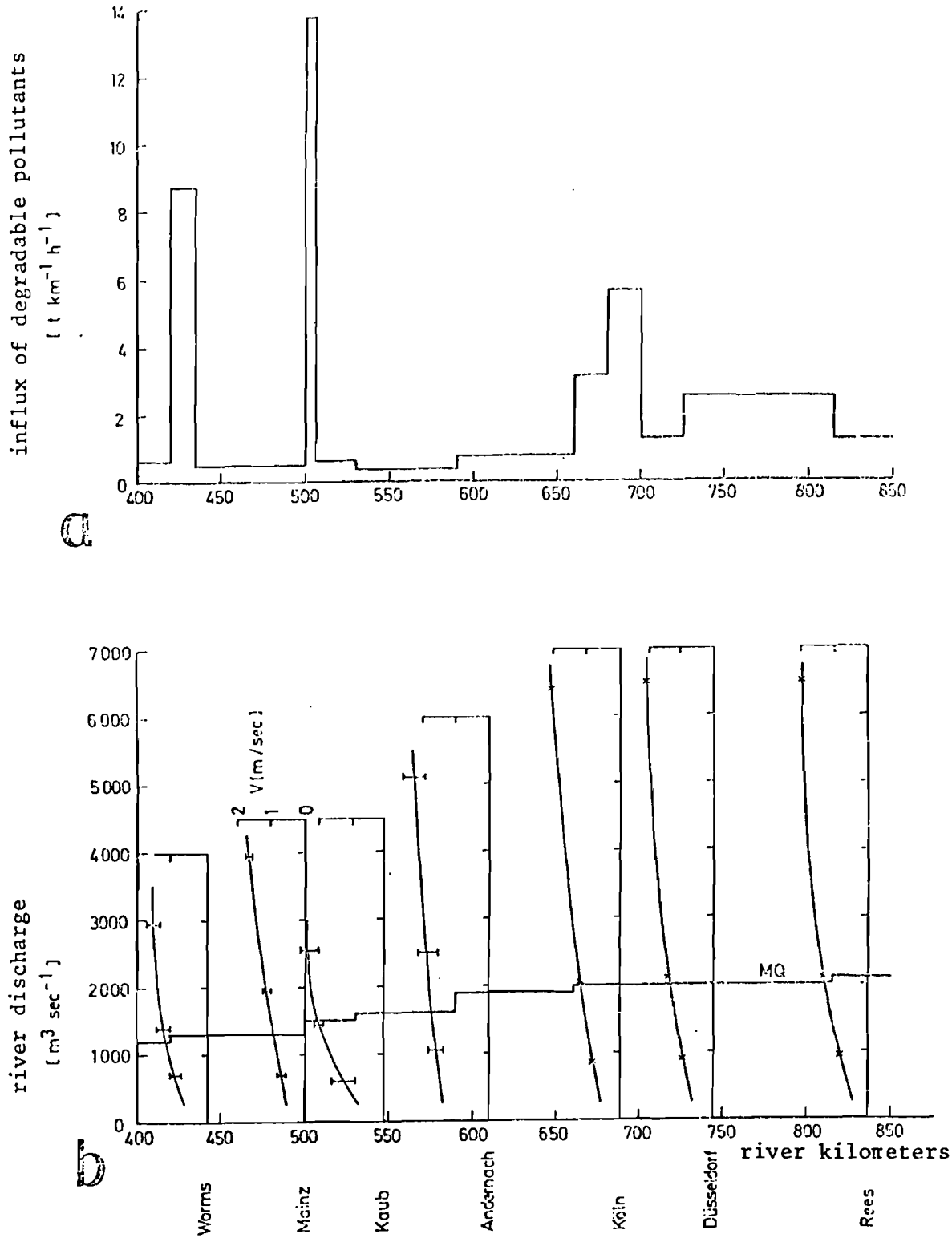


Figure 4.11 Assumptions used in the self-purification model of the Rhine River

a Assumptions on the amount of waste (in tons COD) which flows in per river km and hour

b Dependence of the flow velocity upon the river discharge at various gauging stations as well as approximation for mean discharge MQ

and Koblenz (Mosel R.) in [78] shows that this assumption is reasonable. The somewhat smaller pollution of the Mosel River is certainly compensated by the pollution of the city of Koblenz. Figure 4.11 gives the flow velocities v as a function of the river discharge for various water level gauges. They were communicated over the phone by the concerned Water- and River Traffic Offices, and give essentially the ratio of river discharge to cross-sectional area. Based on these functions, the flow velocity was estimated for the 12 reaches, they are given in Appendix C for the case which is shown in Figure 4.10 ($Q=1.25 \cdot MQ$). The mean discharge MQ was approximated by the solid line step function in Figure 4.11 [17]; changes of the river discharge in relation to the MQ were in the model always made such that the ratio Q/MQ was independent of the location.

Parameter a_{12}, which determines the ratio of easily to slowly degradable pollutants, was set at 0.5 (that is 1:1), with the exception of the reaches between km 420 and 435, and km 500 and 506. For the latter reaches $a_{12} = 0.4$ was assumed, which takes into account that in the Neckar River and Main River, which confluence in these reaches, the ratio of N_1 to N_2 has decreased as a result of self-purification.

The values of parameter a_{61} can also be found in Appendix C; they are all near 0.25, with downward deviations in the Mainz-Bingen area and upwards deviations in the Bingen-Koblenz area. The values seem to be slightly high, but they lie within the range marked by values given in numerous publications [71]. It is assumed that parameter a_{61} is independent of the river discharge, because when that is changed two effects occur which compensate each other approximately: an increase of Q results in a greater water depth, which results in a smaller a_{61}; on the other hand, as turbulence increases, a_{61} increases. (The empirical formula for a_{61} given in [48]

$$a_{61} = c \cdot \frac{v}{h^{3/2}} (1.0241)^{T-20}, \qquad (4.29)$$

whereby h is water depth, T is temperature (in ^{o}C), and c is constant, gives, for example, a result independent from Q, if one assumes a symmetric right triangle as the river profile, and the relationship $v(Q) = Q^{3/7}$ (see Figure 4.11b).)

The numbered points given in Figure 4.10, which come from different sources, are now to be explained in more detail.

COD values:

COD values were available -- with one exception -- for the dissolved substances. All these were multiplied with factor 2, in order to get an estimate for the total COD. Indications of the amount of suspended organic pollutants are given by the measurements taken by the Union of Rhine Water Works (ARW) of the volatile suspended solids [4,5,6,7]. These measurements lump together the active biomass and the suspended organic pollutants, the latter resulted, by the way, partly from dissolved pollutants through adsorption, coagulation, and precipitation processes. If one assumes 1.5 to 2 times their weight for the COD of the suspended substances (in 1969 the ratio COD/TOC for the dissolved substances amounted to 2.5 [5]), then the COD of the calcination losses of suspended solids is about the same as the COD of the dissolved substances [5]. A similar relationship results if one compares the ARW-measurements of the COD near Koblenz [6] with the COD measurements for Braubach in [78], which were gained from an unfiltered sample. (For this one has to chose consistent temperatures and river discharges.) In all cases, except for the samples taken at Wiesbaden, the samples were taken near the water surface. Since the suspended material, despite the relatively strong turbulence, seem to settle to a certain degree, the mean values of the suspended organic substance concentration over the river cross-sections are in reality considerably larger than the measured values. A comparison of the measurements at Mainz and Wiesbaden confirms this. At Wiesbaden, where the measurements were taken near the river bottom, the concentration of suspended organic substance is approximately 2-3 times as large as at Mainz [5]. (The ratio between both values depends upon the river discharge: it increases with decreasing discharge, that is, with decreasing turbulence. That is the reason why the annual mean of the volatile suspended solids at Mainz for 1971 is lower than the value for 1970 (when the discharge was substantially larger), while the opposite occured at Wiesbaden [7].) This means, that the COD of the suspended substances is considerably larger than that of the dissolved substances [5]. It seems therefore reasonable to assume that the total COD is twice as high as the COD of the dissolved substances, and that the thus not considered part of the suspended organic matter is active biomass. The values 1 to 7 are based upon measurements taken during two Rhine trips on 69-08-26 and 69-09-09 [57]. River discharge and temperature were nearly the same as those assumed in the model (see above). The samples were taken at times which correspond approximately to the flow time. Value 8 is based on measurements in the Main River,

which were taken on the same trip, and on the mixing ratio on both these days. Points 9 - 18 are based on the ARW measurements of the COD of the dissolved substances in August 1970 [6]. Discharge and temperature at this time are approximately the same as during the Rhine trips described above. (For 1969 COD measurements of the ARW are available for only a few points [5]. For August they are similar to points 9 - 18.) Point 19 was measured from an unfiltered sample by the International Commission for the Protection of the Rhine River against Pollution on 69-07-10 (discharge and temperature are comparable!) Even though this sample was taken from near the surface, the value was not raised (see above), because the differences in concentration of suspended solids are certainly not as great as for example near Mainz and because this value should not encompass the active biomass, which would require a downward correction of the measured value.

Bacteria Measurements:

The points give apart from a common factor the geometric mean values of the plate counts taken in the summer half of 1967 by the ARW [3]. (Such measurements were not completely available for the following years.) Part of them are shown in Figure 2.2. Because of the inaccuracy of the technique one cannot draw conclusions about the absolute size of the biomass from the plate count results, thus the common factor was chosen arbitrarily, so that the values best fit the model curve. If one takes as the mean bacteria size the volume of a cylinder of radius 0.5μ and of the height 4μ, and the dry weight in g to be a fifth of the volume in ml [10], the plate count figures from [3] make up only about 1/150 of the total bacterial mass. This low percentage results partly from the deficiences of the plate count technique: only a part of the bacteria can grow on the nutrient medium; and the lumps of bacteria which often occur in rivers are usually not resolved during the measurement, so that many colonies come from more than one cell. One also has to consider that the samples were taken from near the surface; the differences between the plate count results at Mainz and Wiesbaden (see above) are substantial [5].

Protozoa Measurements:

The only indication of the actual protozoa density in the Rhine River are a few measurements of the number of ciliates among the suspended solids near Koblenz from the year 1968 [42]. The results in the summer were 10^5 - 10^6 organisms /ml of settled solids. According to the ARW reports [6], the dry weight of suspended solids near Cologne is about 30 mg/l. Assuming that this corresponds to 0.30 ml/l undried settled solids (which is fairly realistic [45]) one gets a

ciliata density of $3 \cdot 10^4$ - $3 \cdot 10^5$/l for the Rhine water near Koblenz. If one assumes a ratio of 1:5 between dry and wet weight of ciliata (as for the bacteria) then one gets the value of 0.5 mg/l in Figure 4.10, if, for instance, the ciliates are spheres with a radius between 0.013 and 0.027 mm. The size corresponds to many observations [65], so that one can say that the curve of Figure 4.10 is certainly not wrong by orders of magnitude.

Oxygen measurements:

The oxygen concentrations 1 - 7 were measured on the Rhine trips on 69-08-26 and 69-09-09 [69]. Values 8 - 16 are mean values of the ARW measurements taken during August and September 1970 [6]. (Only 2 measurements were taken each month, that is why the values of September have also been used, even though the discharge and the temperature did not fit the assumptions of the model as well.) Value 17 was taken under the same conditions as the COD value 19 (see above.)

On the whole the fit between the values and the curves is satisfactory. This holds especially for those values which were taken during the Rhine trips at times corresponding to the flow time. The great variations in the lower Rhine are probably due to single sewage effluents; actual averaging over the river cross-section should make them dissapear. Even though there is such a good fit, it should be once again emphasized that the model described is too uncertain to draw quantitative conclusions from it.

In order to test if the model reacts correctly to changes in the underlying conditions, the two essential parameters which are subject to natural fluctuations - temperature and discharge - were changed.

In changing the temperature the biochemical reaction rates change according to the Arrhenius-law

$$v(T) = c_1 \cdot e^{-c_2/T}$$

as long as the temperature is not so high, that the proteins become denatured [47]. Figure 4.12 shows how well the bacteria follow this law [46]. (See also [47].) (In [46] the measured values were plotted using a wrong abscissa unit, therefore the curve for the activated sludge showed a sharp bend.) Similar T-dependencies were measured for endogenous respiration [11] and for the growth rates of protozoa [88]. According to these measurements, when $T = 20^oC$ was changed to $T = 10^oC$ the maximum growth rate and the parameters a_{47} and a_{53} were halved, when changed to $T = 25^oC$ they were multiplied by the factor 1.6. The changes of a_{61} for a

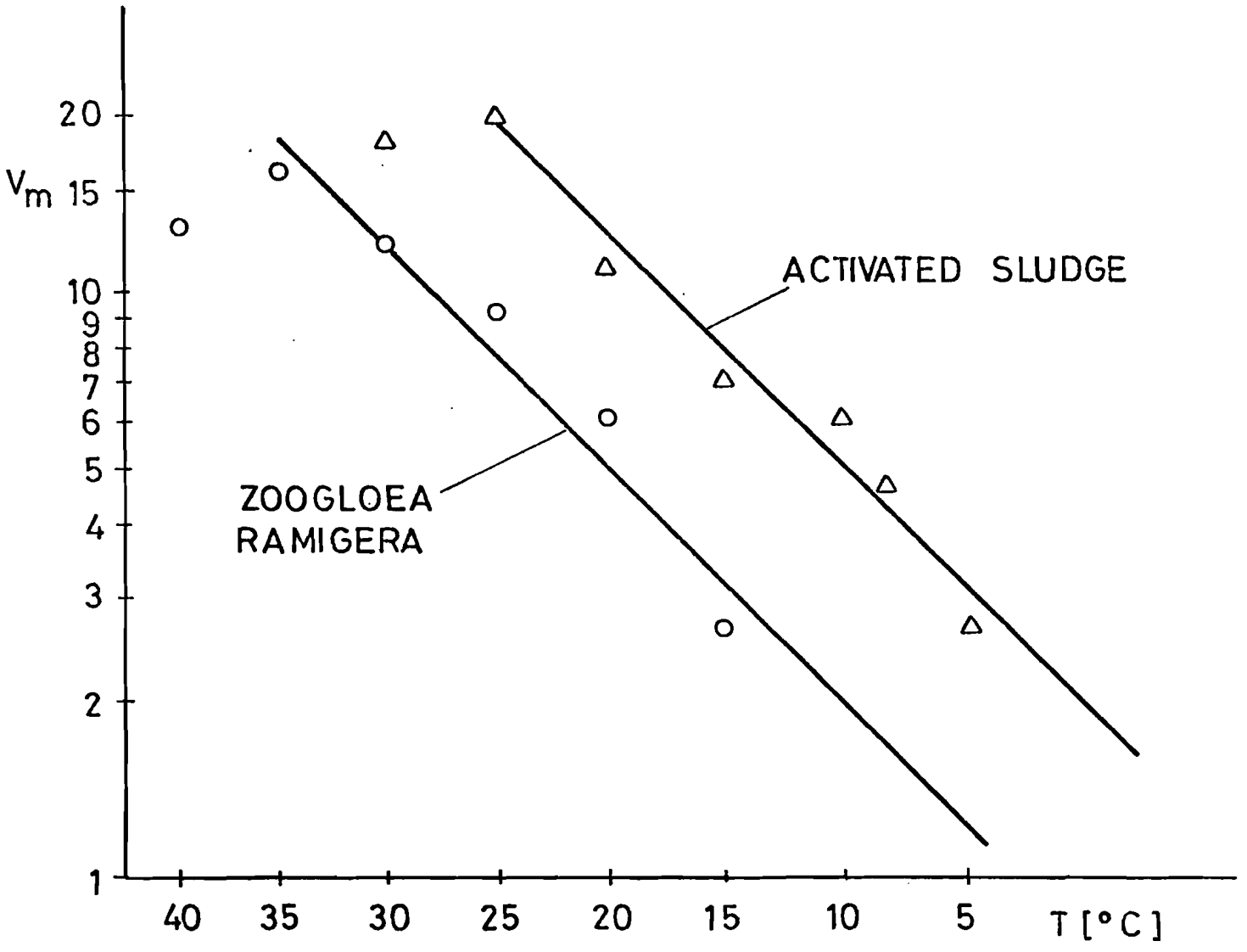


Figure 4.12 Temperature dependence of the maximum bacterial growth rate for homogenous and heterogenous populations

specific river [62] as well as the changes of 0 with temperature are shown in Figure 4.13. However, for the T-dependency of a_{61} in model (4.23) - (4.28) the relationship (4.29) was used. The remainder of the parameters were regarded as being independent from temperature. With that the solid curves of Figure 4.14 resulted for T = 10°C and unchanged discharge. The COD concentration at Cologne now is considerably smaller than at Mainz; whereas at T = 20°C the values were practically the same. A similar relationship is shown by the COD measurements which were taken on the one hand in January and December and on the other in September 1970 [6]. The density of the bacterial mass at the lower temperature is considerably larger at Cologne than at Mainz, whereas at T = 20°C the opposite occured. This behaviour is confirmed also by the measurements (see Figure 2.2 and [2]). The oxygen values at Cologne are now slightly lower than at Mainz, whereas earlier the opposite occured. This tendency cannot be observed at the values in [6], probably because of the small number of measurements taken.

Figure 4.15 shows the model solutions for temperature T = 25°C. The self-purification performance has risen considerably, especially near the Dutch border, whereas the oxygen concentration near Mainz and at the lower Rhine has considerably worsened. The O_2 minima have moved upstream. An increase of the water temperature of the Rhine River by 5°C is under discussion in connection with fresh water cooling of power plants [50]; Figure 4.15 shows, even though there are uncertainties in the model, that the influence of such a small artificial heating has a serious influence upon the oxygen concentration. With a smaller discharge anaerobic conditions could result at Mainz (see below).

The changes in the self-purification process caused by a decrease of the discharge to 0.77 MQ are shown in Figure 4.16. The consequences of this decrease are governed by two effects: the dilution ratio for the discharged pollutants is changed, and the flow times between the pollution sources are changed. Both effects result for a decrease in discharge in an increase of the relative degradation performance over a certain river section. In Figure 4.16 this is clearly shown by the curves between Mannheim and Mainz. In the lower Rhine this is less pronounced because of the feeding activity of the protozoa, thus the COD concentration increase in the lower Rhine is slightly larger than at Mainz. This tendency can also be detected, for example, by a comparison of the ARW values for September 1970 and 1971 [6,7], although this is not as strongly apparent. This is perhaps an indication that one must consider higher order links of the food chain.

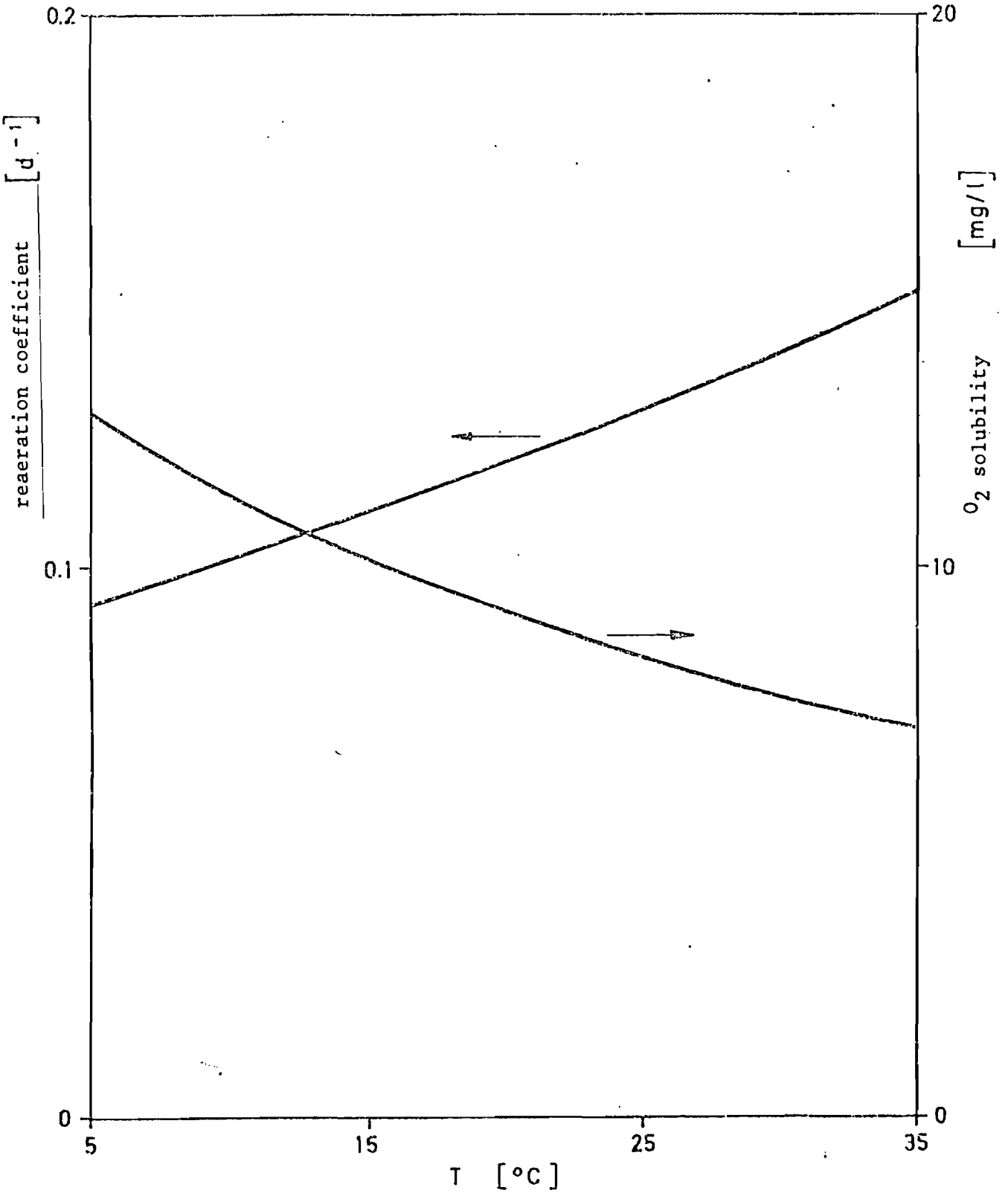
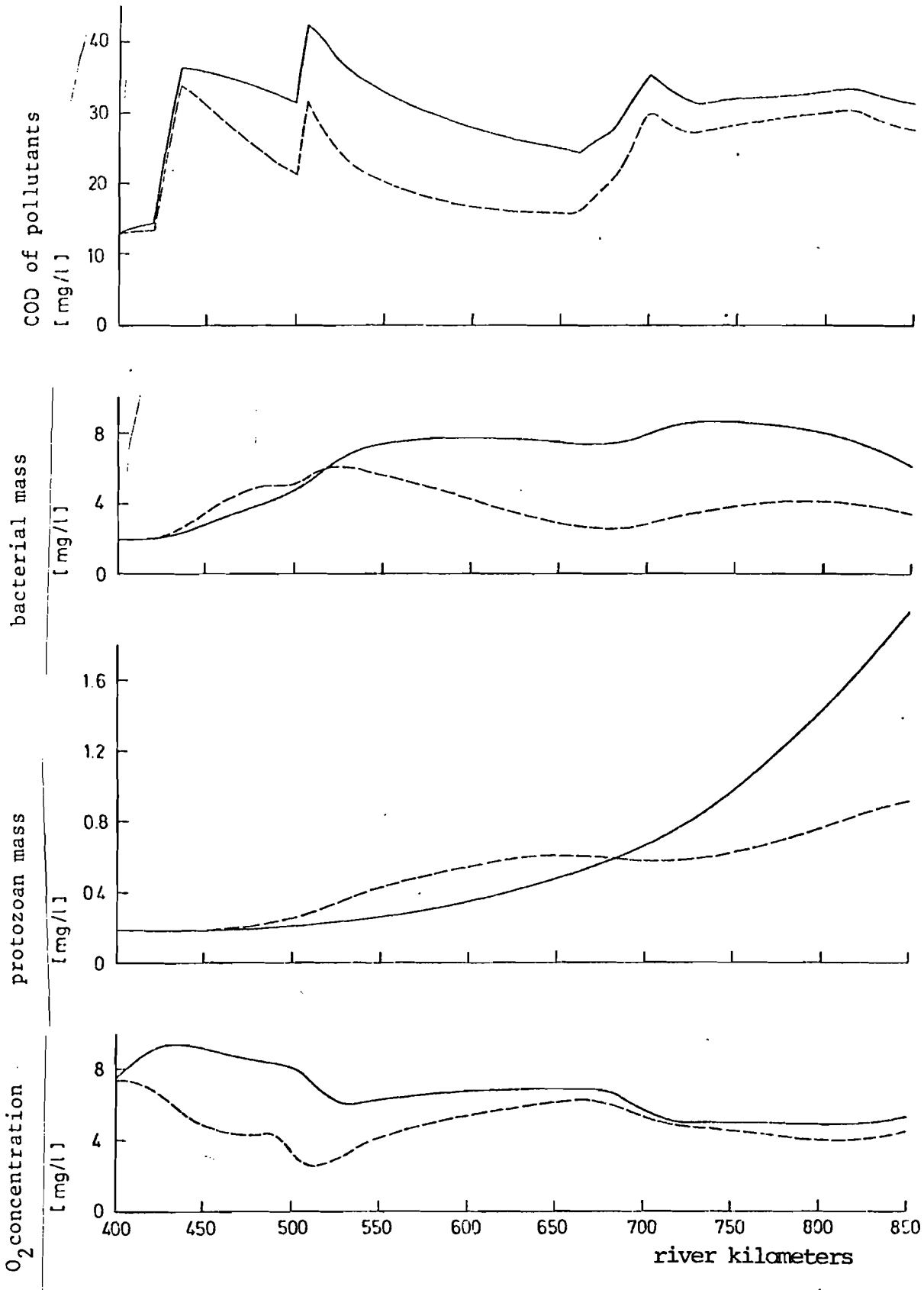


Figure 4.13 Temperature dependence of oxygen saturation concentration and of the reaeration coefficient in a special case 62



----- T = 20°C

——— T = 10°C Q = 1.25 MQ

Figure 4.14 Changes in the self-purification behaviour of the Rhine River when temperature is lowered

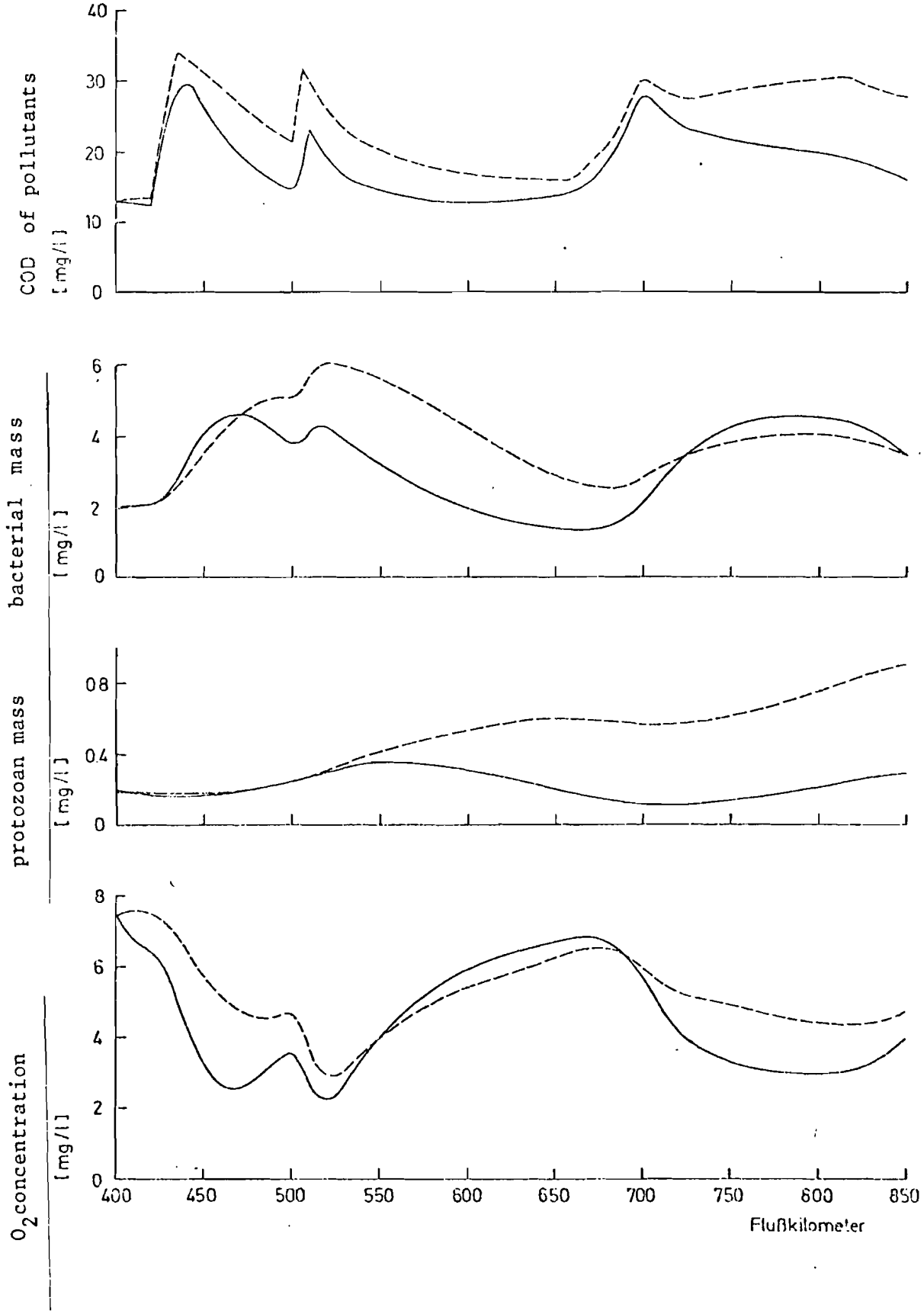


Figure 4.15 Changes in the self-purification behaviour of the Rhine River when temperature is raised

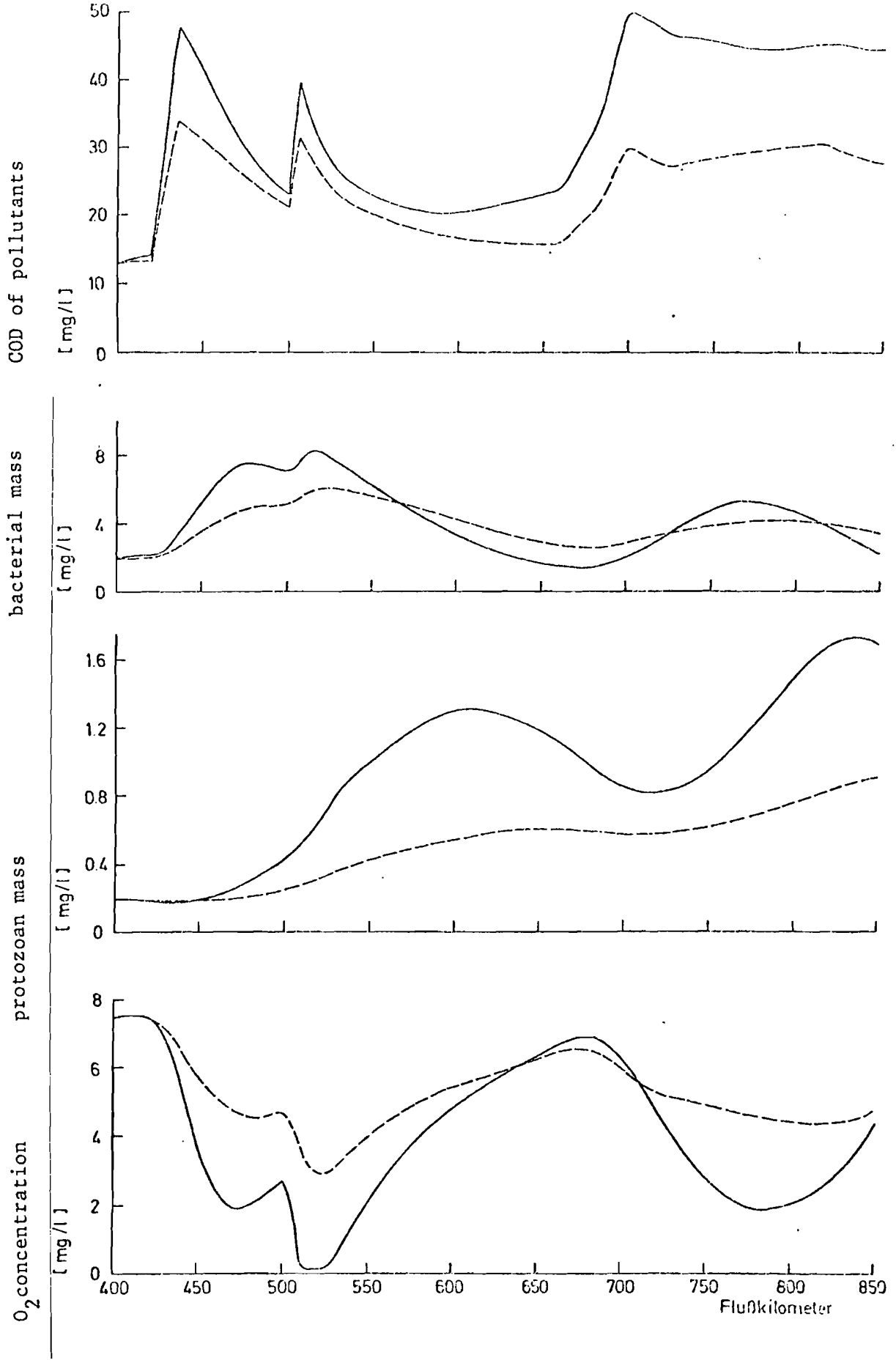


Figure 4.16 Changes in the self-purification behaviour of the Rhine River if discharge is lowered

One other reason could be the slightly higher temperature in September 1971. The oxygen concentration for Q = 0.77 MQ at Mainz reaches 0 (which causes the organisms in the model to cease all metabolic activities except endogenous respiration.) Altogether, the O_2 values of the lower Rhine are now higher than the ones at Mainz, whereas at Q = 1.25 MQ they were about the same. This is also verified by the ARW measurements taken in September 1970 and 1971 (See [7], p.30.)

In closing, two examples are to be discussed, which show the facilities offered by a model like the one discussed for water quality management. Figure 4.17 shows the changes in the self-purification process of the Rhine River, if the easily degradable component of the waste water discharges is reduced by 50%. A similar case could become reality, if in the future solely biological sewage treatment plants are established, because the remainder from the sewage treatment plants consists of slowly degradable materials, moreover, biological treatment plants will be built preferably where a large fraction of easily degradable material in the sewage promises a high degree of purification. Figure 4.17 shows that even though the total COD inflow has been reduced by nearly 25% the COD concentration in the river nowhere decreases remarkably, and that in some sections it even increases considerably. Figure 4.17 shows this effect comparatively mildly. With somewhat different, but still realistic parameter values in (4.23) - (4.28) substantially higher increases of the COD concentration can occur [83]. The cause of the rise is the decrease of the growth rate of the bacteria relative to the protozoa consumption rate and to the endogenous respiration. The practical consequence of this behaviour of the model (which is certainly independent from the uncertainties of the model) must be to eliminate also the slowly degradable compounds from the waste water. Otherwise the difficulties, for instance, for drinking water production in the Lower Rhine Region could increase even though there would be a reduction of sewage influx.

Figure 4.18 shows the self-purification processes in the case where the COD load from the Main River is reduced by 50%. According to the discussion of Figure 4.17 and the opinion presented occasionally in literature, that moderate pollution increases the self-purification ability [56], one could be afraid that in the lower Rhine this could lead to an increase in pollution. Figure 4.18 shows that this does not have to happen. Because of the lower bacterial density downstream Mainz, the protozoa density in the lower Rhine does not become as large as in Figure 4.10, so that the degradation ability in the Lower Rhine increases considerably.

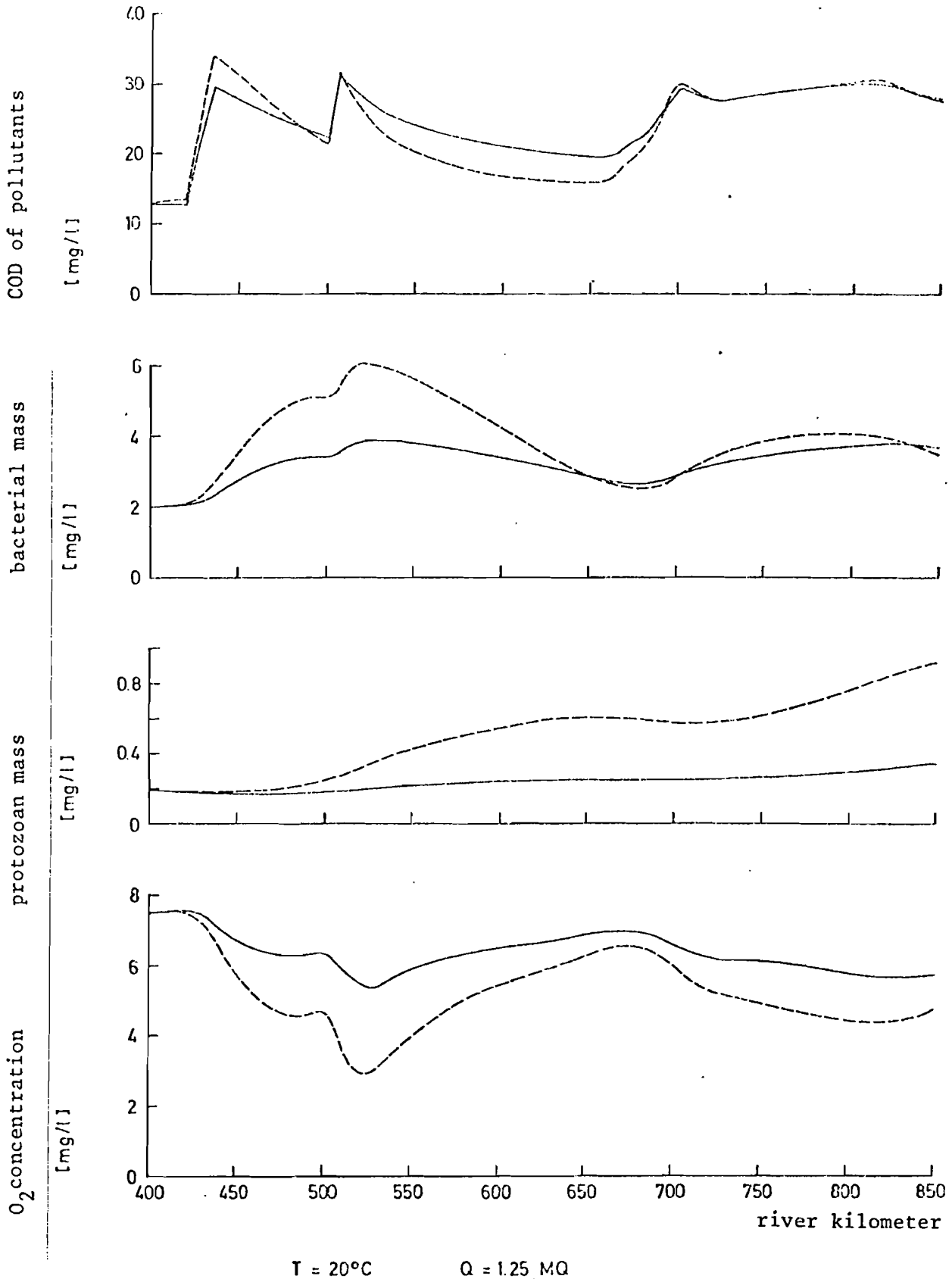


Figure 4.17 Changes in the self-purification behaviour of the Rhine River due to removal of part of the easily degradable component from sewage

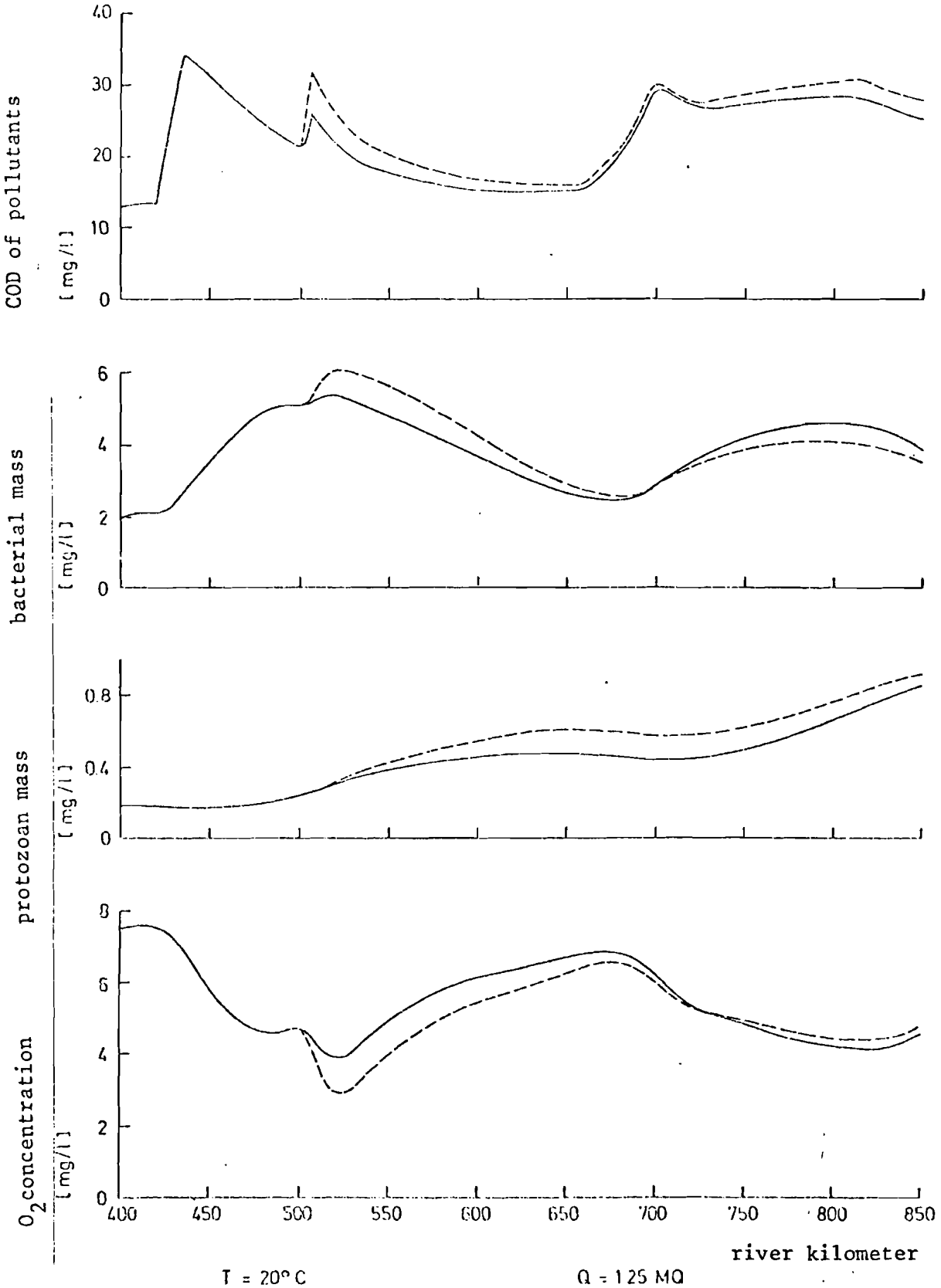


Figure 4.18 Changes in the self-purification behaviour of the Rhine River due to a reduction of the waste introduced by the Main River.

4.4 Sensitivity analysis of the Rhine River model

The results in Section 4.3 are only meaningful if the model behaviour does not change drastically if the parameter values vary within the error bounds. Therefore the sensitivity of the model solution to changes of all parameter and initial values was analysed. In order to avoid as far as possible a wrong estimate of the actual sensitivity, finite sensitivity was calculated rather than differential sensitivity [84]. I.e. sensitivity was estimated from the difference between two solutions of the model with different parameter values rather than from the solution of the sensitivity system. The changes were in all cases 10%, the nominal values for Q and T were 1.25 MQ and 15°C, respectively.

It turned out, that in no case the sensitivity was remarkably high. Figure 4.19 gives, as an example, the sensitivity to changes of the initial value of N_1. The oscillations which can be seen in the figure occur in all other sensitivity functions of that model as well. It is surprising how far downstream the change of the initial value can be felt. (After long flow time the model solution is - independent from the initial values - uniquely determined by the sources along the river, i.e. the model is asymptotically stable. For constant source terms in equations (4.23) - (4.28) and realistic parameter values at least variables B, P, and O reach stable equilibrium values, which can easily be evaluated by solving successively equations (4.27), (4.23), (4.24), (4.26), and (4.28).)

Figure 4.20 gives, as another example, the sensitivity to changes in the maximum bacterial growth rate. The most influential parameter turned out to be the maximum protozoa growth rate. But in all cases the changes of the dependent variables were less than 20%.

The sensitivity to changes of Q and T can be derived from Figures 4.15 and 4.16. If T is changed, the sensitivity is remarkably smaller than if growth rates (which vary with T) are changed separately. It should also be mentioned that for lower Q values the sensitivity of COD to changes of Q might be positive in some places, because, if Q is small, flow time between pollution sources decreases faster as Q increases.

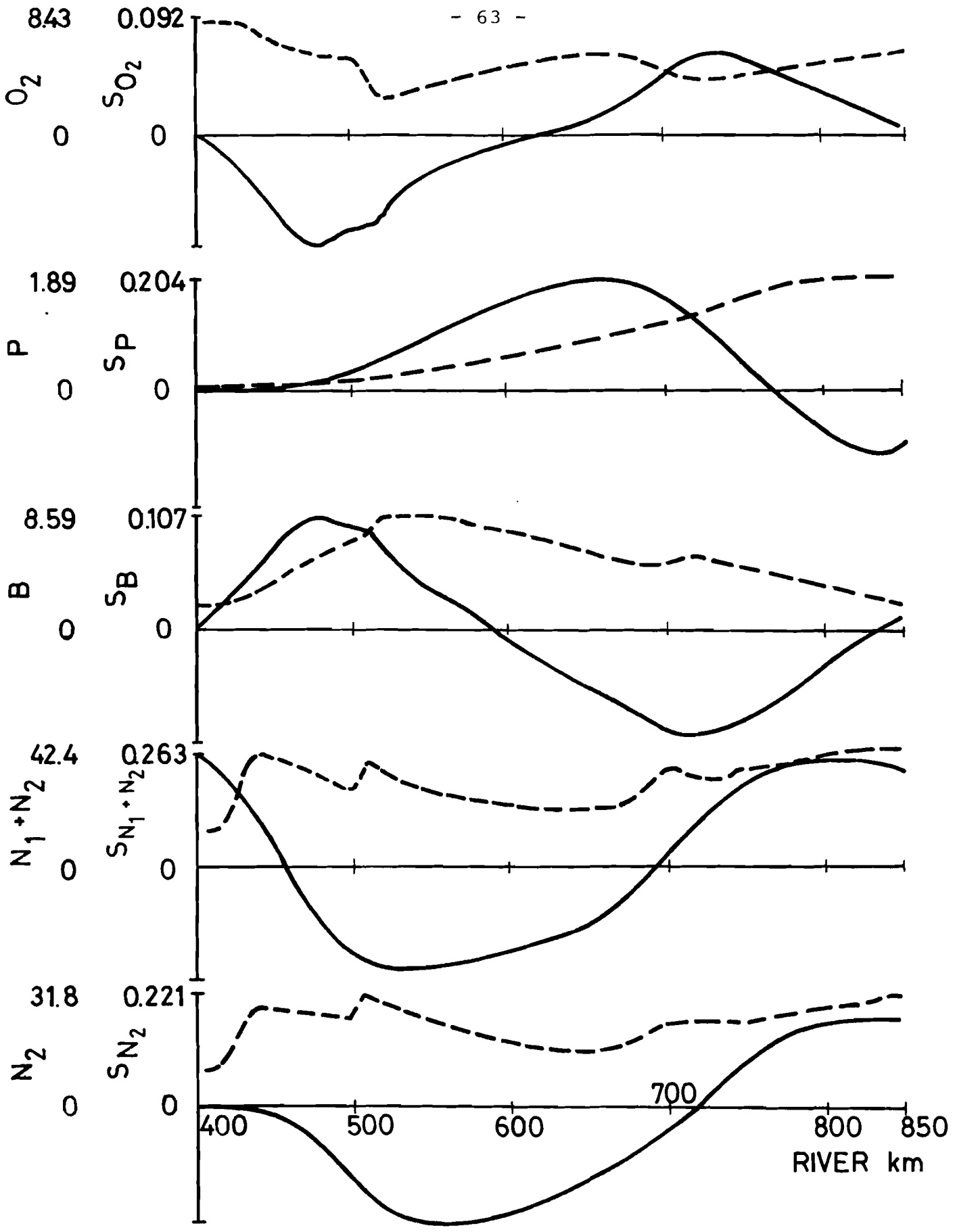


Figure 4.19 Sensitivity of the solution of the Rhine model to changes of the initial value of N_1

- - - Nominal solution of the model (Q=MQ, T=15°C)

——— Sensitivity function (N_1(400) increased by 10%)

All concentrations in [mg/ℓ]

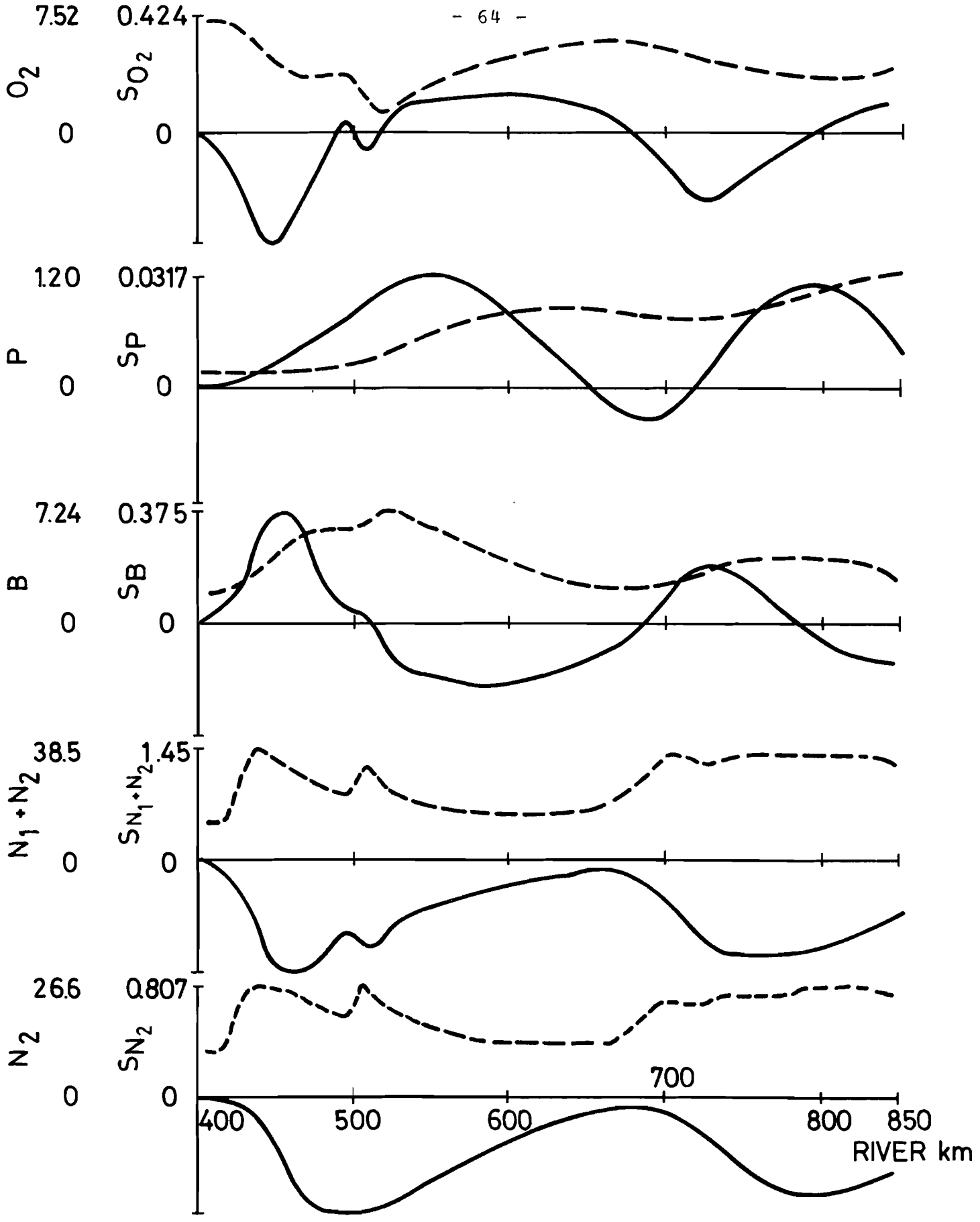


Figure 4.20 Sensitivity of the solution of the Rhine model to changes of the maximum bacterial growth rate

- - - Nominal solution of the model (Q=MQ, T=20°C)
——— Sensitivity function (a_{51} increased by 10%)

All concentrations in [mg/ℓ]

5. Short résumé

The results of the discussions of Sections 2, 3, and 4 may be summarized in the following way:

1. The description of the self-purification processes in rivers through systems of coupled differential equations seems to be possible and useful. In order to determine the model parameters from in-situ measurements (model identification) the quasilinearization technique of Bellmann [8] has proved to be useful. It was used, however, only for models of those rivers in which the benthos was negligible, and which can be considered as being homogeneous in the transverse direction; in these cases the model equations are ordinary differential equations.

2. For benthos-free, homogeneous rivers, a model was suggested which contains the following dependent variables (Section 4.2): chemical oxygen demand (COD) of the easily degradable substances, COD of the slowly degradable substances, bacterial mass density, protozoan mass density, and oxygen concentration. In order to determine the parameters of this model it is sufficient, if one has - apart from bacteria, protozoa, and oxygen values - measured values for the total COD. However, for a few parameters estimates have to be given, which in the process of model identification are treated the same way as the measured values for the dependent variables.

3. In spite of slow transverse mixing, the application of this model to the Rhine River seems to be useful, because the transverse differences of the degradation rate are smaller than the transverse differences of the pollution concentration. After a tentative parameter estimation, based upon very spotty measured values, the model correctly described the self-purification behaviour of the Rhine River between Mannheim and the Dutch-German border. By extrapolating to conditions which differ from those of today the following remarkable changes in the quality of the Rhine River water resulted:

a) an increase of water temperature from 20° to 25°C (which could occur in the future because of waste heat inflows from power plants) causes in the model a decrease of oxygen concentration near Mainz and in the Lower Rhine from approximately 4 mg/l to approximately 2.5 m/l. Thereby a river discharge of 1.25 times the mean discharge has been assumed. (With 0.77 times the mean discharge the oxygen concentration slightly downstream from Mainz sinks to zero even at 20°C.)

b) a decrease of the easily degradable component in the introduced sewage by about 50% (without changing the slowly degradable component) resulted in an increase of the pollution concentration in the Rhine River. This could become reality if in the future only biological sewage treatment plants are built.

c) a uniform decrease of the pollution load of the Main River by 50% resulted in an increase of the self-purification ability of the Lower Rhine.

These findings, in view of the sparse data base, just describe possibilities for future developments, which one has to keep in mind in planning and managing river quality. In order to be able to make more detailed and quantitative forecasts, further measurements on the Rhine River are necessary. Suggestions for this can be found in Sections 4.2 and 4.3. In their planning and implementation, the model developed is an important tool. These further measurements especially will have to clarify to what extent toxic materials which inhibit self-purification have to be explicitly encompassed by the model.

References

[1] Ames, W.F., Numerical Methods for Partial Differential Equations, Thomas Nelson and Sons, London, 1969.

[2] 3. Arbeits- und Erfahrungsbericht der Arbeitsgemeinschaft Rheinwasserwerke e.V. (1953-) 1962-1964, Düsseldorf, 1965.

[3] 24. Bericht der Arbeitsgemeinschaft Rheinwasserwerke e.V., 1967, Karlsruhe, 1969.

[4] 25. Bericht der Arbeitsgemeinschaft Rheinwasserwerke e.V., 1968, Karlsruhe, 1969.

[5] 26. Bericht der Arbeitsgemeinschaft Rheinwasserwerke e.V., 1969, Karlsruhe, 1970.

[6] 27. Bericht der Arbeitsgemeinschaft Rheinwasserwerke e.V., 1970, Karlsruhe, 1971.

[7] 28. Bericht der Arbeitsgemeinschaft Rheinwasserwerke e.V., 1971, Karlsruhe, 1972.

[8] Bellman, R.E. and Kalaba, R.E., Quasilinearization and Nonlinear Boundary-Value Problems, American Elsevier Publishing Company, New York, 1965.

[9] Bellman, R.E., Kagiwada, H., and Kalaba, R.E., Inverse Problems in Ecology, J. Theoret. Biol. 11 (1966), 164-167.

[10] Bender, H., Biologie und Biochemie der Mikroorganismen, Verlag Chemie, Weinheim, 1970.

[11] Benedek, P., Farkas, P., and Litheráty, P., Kinetics of Aerobic Sludge Stabilization, Water Research 6 (1972), 91-97.

[12] Bhatla, M.N., and Gaudy, A.F., Role of Protozoa in the Diphasic Exertion of BOD, J. San Engng, Div., Proc. ASCE, 91, (1965), 63-87.

[13] Bick, H., Die Sukzession der Organismen bei der Selbstreinigung von organisch verunreinigtem Wasser unter verschiedenen Milieubedingungen, Düsseldorf, 1964.

[14] Boes, M., Mathematische Analyse der Kinetik des biochemischen Sauerstoffbedarfs (Dissertation), Karlsruhe, 1970.

[15] Bringmann, G., Mikrobiologie des Wassers in: Souci, S.W. and Quentin, K.-E. (ed.), Handbuch der Lebensmittelchemie, Bd. VIII: Wasser und Luft, Teil 1, Springer-Verlag, Berlin-Heidelberg-New York, 1969.

[16] Bringmann, G., Physiologische Verfahren der biologischen Wasseranalyse in: Souci, S.W and Quentin, K.-E. (ed), Handbuch der Lebensmittelchemie, Bd. VIII: Wasser und Luft, Teil 2, Springer-Verlag, Berlin-Heidelberg-New York, 1969.

References (ctd)

[17] Bundesanstalt für Gewässerkunde, Deutsches Gewässerkundliches Jahrbuch: Abflußgebiet Rhein, Abflußjahr 1968, Koblenz, 1970.

[18] Bundesministerium des Innern, Materialien zum Umweltprogramm der Bundesregierung, V. Bericht der Projektgruppe Wasserwirtschaft, Anlage zur Drucksache VI/2710 des Deutschen Bundestages (1971).

[19] Burkhead, C.E. and McKinney, R.E., Energy Concepts of Aerobic Microbial Metabolism, J. Sanit, Engng, Div., Proc. ASCE, 96 (1969), 253-268.

[20] Courant, R. and Hilbert, D., Methods of Mathematical Physics, Vol. II, John Wiley and Sons, New York and London, 1962.

[21] Curds, C.R. and Cockburn, A., Continuous Monoxenic Culture of Tetrahymena pyriformis, J. Gen. Microbiol. 66 (1971), 95-108.

[22] Curds, C.R., A Computer Simulation Study of Predator-Prey Relationships in a Single-Stage Continuous-Culture System, Water Research 5 (1971), 793-812.

[23] Curds, C.R., Computer Simulations of Microbial Population Dynamics in the Activated-Sludge Process, Water Research 5 (1971), 1049-1066.

[24] Dawes, E.A. and Ribbons, D.W., Some Aspects of the Endogenous Metabolism of Bacteria, Bact. Rev. 28, 2 (1964), 126-149.

[25] Dawson, R.N. and Murphy, K.L., The Temperature Dependency of Biological Dentrification, Water Research 6 (1972), 71-83.

[26] Demmerle, S.D., Über die Verschmutzung des Rheins von Schaffhausen bis Kaiserstuhl, Vierteljahresschrift der Naturforschenden Gesellschaft, Zürich III, 2 (1966), 155-224.

[27] Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlammuntersuchung, Verlag Chemie, Weinheim 1960.

[28] Eichelberger, J.W. and Lichtenberg, J.J., Persistence of Pesticides in River Water, Environmental Science and Technology 5, 6 (1971), 541-544.

[29] Fleagle, R.G. and Businger, J.A., Atmospheric Physics, Academic Physics, Academic Press, New York, 1963.

[30] Fraenkel, D.G., The Accumulation of Glucose-6-Phosphate Its Effect in an E. coli Mutant Lacking Phosphoglucose Isomerase and Glucose-6-Phosphate Dehydrogenase, J. Biol. Chem. 243, 24 (1968), 6451-6457.

References (ctd)

[45] Hygiene-Institut des Ruhrgebiets, Biologische Zusatzuntersuchungen 1962-1966, Gelsenkirch.

[46] Jahresberichte des Lehrgebiets Ingenieurbiologie der Universität Karlsruhe, 1968, Karlsruhe, 1969.

[47] Ingraham, J.L., Temperature Relationships, in: Gunsalus, I.C. and Stanier, R.Y. (eds.), The Bacteria, A Treatise on Structure and Function, Vol. IV,Academic Press, New York and London, 1962.

[48] Isaacs, W.P. and Gaudy, A.F., Atmospheric Oxygenation in a Simulated Stream, J. Sanit, Engng. Div., Proc. ASCE, 94 (1968), 319-344.

[49] Jannasch, H.W., New Approaches to Assessment of Microbial Activity in Polluted Waters, in: Mitchell, R. (ed.), Water Pollution Microbiology, John Wiley & Sons, New York-London-Sydney-Toronto, 1972.

[50] Jansen, P.J., Schikarski, W. and Stehfest, H., Beitrag zur Analyse der zulässigen Kraftwerksbelegung des Rheins im Hinblick auf die thermische Belastung, KFK 1511, 1971.

[51] Javornicky, P. and Prokesova, V., The Influence of Protozoa and Bacteria upon the Oxidation of Organic Substances in Water, Int. Revue ges. Hydrobiol. 48,2 (1963), 335-350.

[52] Kelker, N.E. and Anderson, R.L., Sorbitol Metabolism in Aerobacter aerogenes, J. Bacteriol. 105 (1971), 160-164.

[53] Kneese, A.V. and Bower, B.T., Die Wassergütewirtschaft, R. Oldenburg, München, 1972.

[54] Knöpp, H., Untersuchungen über das Sauerstoff-Produktions-Potential von Flußplankton, Schweizerische Zeitschr. f. Hydrologie 22 (1960), 152-166.

[55] Knöpp, H., Der A-Z-Test, ein neues Verfahren zur toxikologischen Prüfung von Abwässern, Deutsche Gewässerkundl. Mitt. 5 (1961).

[56] Knöpp, H., Die "zusätzliche Zehrung" - eine neue biochemische Kennzahl zur Bewertung von Selbstreinigungskraft und Verschmutzung, GWF, Wasser-Abwasser, 105 (1964), 92-97.

[57] Knöpp, H. and Sontheimer, H., Untersuchungen und Überlegungen zur Durchführung einer Rheinwasseraufbereitung im Hessischen Ried, Gutachten im Auftrag des Hessischen Ministers fur Landwirtschaft und Forsten, Wiesbaden, 1969.

[58] Kölle, W., Ruf, H. and Stieglitz, L., Die Belastung des Rheins mit organischen Schadstoffen, Die Naturwissenschaften 59 (1972), 299-305.

References (ctd)

[59] Kölle, W., Private communication.

[60] Kothandaraman, V., Effects of Contaminants on Reaeration Rates in River Water, J. WPCF, 43, 5 (1971), 806-817.

[61] Krampitz, L.O., Cyclic Mechanisms of Terminal Oxidation, in: Gunsalus. I.C. and Stanier, R.Y. (eds.), The Bacteria, A Treatise on Structure and Function, Vol. II, Academic Press, New York and London, 1961.

[62] Krenkel, P.A. and Parker, F.L., Engineering Aspects, Sources, and Magnitude of Thermal Pollution, in: Biological Aspects of Thermal Pollution, Proc. of the Nat. Symp. on Thermal Pollution, Portland, Oregon, June 3-5, 1968. Vanderbilt University Press, Nashville, 1969.

[63] Laideler, K.H., The Chemical Kinetics of Enzyme Action, Oxford University Press, Oxford, 1958.

[64] Leithe, W., Moderne Instrumentation zur analytischen Erfassung organischer Laststoffe in Abwässern, Chemische Rundschau 25 (1972), 978.

[65] Leibmann, H., Handbuch der Frischwasser- und Abwasserbiologie, Vol. I & II, R. Oldenbourg, München, 1962.

[66] McCarthy, P.L., Thermodynamics of Biological Synthesis and Growth, Proc. Second International Conference on Water Pollution Research, Vol. 2 (1964), 169-199.

[67] Monod, J., Zufall und Notwendigkeit, Piper, München, 1970.

[68] Morris, D.L., Quantitative Determination of Carbohydrates with Dreywood's Anthrone Reagent, Science 107 (1948), 254-255.

[69] Müller, D., Private communication, Bundesanstalt für Gewässerkunde, Koblenz.

[70] Münch, F., Der Einfluß der Temperatur auf den Peptonabbau und die damit verknüpfte Organismensukzession unter besonderer Berücksichtigung der Populationsdynamik der Ciliaten, Int. Revue ges. Hydrobiol. 55, 4 (1970), 559-594.

[71] Negulescu, M. and Rojanski, V., Recent Research to Determine Reaeration Coefficient, Water Research 3 (1969), 189-202.

[72] Neubaur, J. and Hollmann, S., Über den Abbau von Sorbit durch Bakterien der Rattenfaeces, Hoppe-Seyler's Z. Physiol. Cehm. 348 (1967), 871-876.

References (ctd)

[31] Frobisher, M., Microbiology, W.B. Saunders, Philadelphia and London, 1957.

[32] Gates, W.E., Pohland, F.G., Mancy, K.G. and Schafie, F.R., A Simplified Physical Model for Studying Assimilative Capacity, Proc. 21st Ind. Waste Conf., Purdue University Extension Service, 1966, 665-687.

[33] Gates, W.E. and Marlar, J.T., Graphical Analysis of Batch Culture Data Using the Monod Expressions, J. WPCF 40 (1968), R469-R476.

[34] Gates, W.E., Marlar, J.T. and Westfield, J.D., The Application of Bacterial Process Kinetics in Stream Simulation and Stream Analysis, Water Research 3 (1969), 663-686.

[35] Gaudy, A.F., Studies of Induction and Repression in Activated Sludge Systems Applied Microbiology 10 (1962), 264-271.

[36] Gaudy, A.F., Komolrit, K. and Bhatla, M.N., Sequential Substrate Removal in Heterogeneous Populations, J. WPCF 35 (1963), 903-922.

[37] Ghosh, S. and Poland, F.G., Kinetics of Assimilation of Multiple Substrates in Dispersed Growth Systems, Water Research 6 (1972), 99-115.

[38] Goering, J.J., The Role of Nitrogen in Eutrophic Processes, in: Mitchell, R.(ed.), Water Pollution Microbiology, John Wiley & Sons, New York-London-Sydney-Toronto, 1972.

[39] Gunslas, I.C. and Shuster, C.W., Energy-Yielding Metabolism in Bacteria, in: Gunsalus, I.C. and Stanier, R.Y. (eds.), The Bacteria, A Treatise on Structure and Function, Vol. II, Academic Press, New York and London, 1961.

[40] Hartmann, L. and Laubenberger, G., Toxicity Measurements in Activated Sludge, J. Sanit. Engng. Div., Proc. ASCE 94 (1968), 247-256.

[41] Hartmann, L. and Laubenberger, G., Discussion of [40], J. Sanit. Engng. Div., Proc. ASCE, 96 (1970), 607-609.

[42] Herrig, H., Untersuchungen an Flußwasser-Inhaltsstoffen, GWF, Wasser-Abwasser, 110 (1969), 1385-1391.

[43] Hopton, J.W., A Survey of some Physiological Characteristics of Stream-Borne Bacteria, Water Research 4 (1970), 493-499.

[44] Huber, L., Stoffwechselphysiologie der Bakterien und biologische Abwasserreinigung, Wasser- und Abwasser-Forschung, Vol. 6 (1968), 240-245.

References (ctd)

[73] O'Connor, D.J., The Temporal and Spatial Distribution of Dissolved Oxygen in Streams, Water Resources Research, 3 (1967), 65-79.

[74] Patterson, C.C. and Gloyna, E.F., Dispersion Measurement in Open Channels, J. Sanit. Engng. Div., Proc. ASCE, 91 (1965), 17-29.

[75] Pirt, S.J., The Maintenance Energy of Bacteria in Growing Culture, Proc. R. Soc., Ser. B., 165 (1965), 224-231.

[76] Pollock, M.R., Exoenzymes, in: Gunsalus, I.C. and Stainer, R.Y. (eds.), The Bacteria, A Treatise on Structure and Function, Vol, IV, Academic Press, New York and London, 1962.

[77] Pomeranz, K.B., Conservation Laws and the Dispersal Equations for Chemical and Thermal Pollution, American Journal of Physics 39 (1971), 1069-1072.

[78] Internationale Kommission zum Schutze des Rheins gegen Verunreinigung, Zahlentafeln der physikalish-chemischen Untersuchungen des Rheins sowie der Mosel/Koblenz, 1969, Koblenz, 1970.

[79] Round, F.E., The Biology of the Algae, Edward Arnold, London, 1965.

[80] Senex, J.C., Some Considerations on the Energetics of Bacterial Growth, Bact. Rev. 26 (1962), 95-107.

[81] Servizi, J.A. and Bogan, R.H., Thermodynamic Aspects of Biological Oxidation and Synthesis, H. WPCF 36, 5 (1964), 607-618.

[82] Sonnichsen, Jr., J.C., Kottwitz, D.A. and Jaske, R.T., Dispersion Characteristics of the Columbia River between River Miles 383 and 355, BNWL 1477, 1970.

[83] Stehfest, H., Definition und Verwirklichung von Qualitätsstandards für Flüsse, in: Gupta, D., Häfele, W., Halbritter, G., Jansen, P., Schikarski, W., Stehfest, H., Wintzer, D. and Zajonc, H., Umweltbilanzen - ein Kernproblem der Umweltschutzpolitik, Beitrag zum 2. internationalen Expertgespräch, "Anwendung des Verursacherprinzips im Gewässerschutz" am 20./21 November 1972 in Karlsruhe, KFK-1804 (1973).

[84] Stehfest, H., Decision Theoretical Remark on Sensitivity Analysis, International Institute for Applied Systems Analysis, RR-75-3, 1975.

[85] Strange, R.E., Dark, F.A. and Ness, A.G., The Survival of Stationary Phase Aerobacter Aerogenes, Stored in Aqueous Suspensions, J. Gen. Microbiol. 25 (1961), 61-76.

References (ctd)

[86] Straskrabová-Prokešová, V. and Legner, M., Interrelations Between Bacteria and Protozoa During Glucose Oxidation in Water, Int. Revue ges. Hydrobiol. 51, 2 (1966), 279-293.

[87] Stumm-Zollinger, E., Effects of Inhibition and Repression on the Utilization of Substrates by Heterogeneous Bacterial Communities, Appl. Microbiol. 14, 4 (1966), 654-664.

[88] Sudo, R. and Aiba, S., "Growth Rate of Aspidiscidae Isolated from Activated Sludge, Water Research 6 (1972), 137-144.

[89] Sutton, O.G., Micrometeorology, McGraw-Hill, New York-Toronto-London, 1953.

[90] Takamatsu, T., Hashimoto, I. and Siova S., Model Identification of Wet Air Oxidation Process Thermal Decompostion, Water Research 4 (1970), 33-59.

[91] van Haaren, F.W.J., Die Qualität des Rheinwassers im Jahre 1969 bei Vreeswijk, Holland, Niederschrift der 1. Arbeitstagung der Internationalen Arbeitsgemeinschaft der Wasserwerke im Rheineinzugsgebiet, 22-24 October 1970, Zürich, 1971.

[92] Wezernak, C.T. and Gannon, J.J. Evaluation of Nitrification in Streams, J. Sanit. Engng. Div., Proc, ASCE, 94 (1970), 883-895.

[93] Wilderer,P. Die Enzymkinetik als Grundlage der BSB-Reaktion, Dissertation, Karlsruhe, 1969.

[94] Wilderer, P. and Hartmann, L., Der Einfluß der Temperatur auf die Lösungsgeschwindigkeit von Sauerstoff in Wasser, GWF, Wasser-Abwasser 110 (1969), 707-711.

[95] Wilderer, P., Hartmann, L. and Janeckova, J., Kritik an der Verwendung des Langzeit-BSB zur Beurteilung von Rohabwasser, Wasser- und Abwasser-Forschung 1 (1970), 7-12.

[96] Wolf, P., Die Berücksichtigung neuerer Erkenntnisse in Sauerstoffhaushaltsberechnungen für Fließgewässer,Teil I und II, GWF, Wasser-Abwasser, 112 (1971), 200-203 u. 250-254.

[97] Wuhrmann, K., Stream Purification, in: Mitchell, R. (ed.) Water Pollution Microbiology, John Wiley & Sons, New York-London-Sydney-Toronto, 1972.

[98] Zurmühl, R., Praktische Mathematik, Springer-Verlag, Berlin-Heidelberg, New York, 1965.

APPENDIX A: DESCRIPTION OF THE RIVER QUALITY MODEL USED FOR THE GENERATION OF MEASUREMENTS (see Sect. 4.2)

The model consists of 39 ordinary differential equations, which are given in Fig. A.1. The meaning of the symbols used in Fig. A.1 is as follows:

N_i = concentration of the i-th pollutant,

E_i = concentration of the i-th exoenzyme,

B = bacterial mass concentration,

P_i = mass concentration of the i-th protozoan species,

O = oxygen concentration,

O_s = oxygen saturation concentration.

The indices are the same as in the computer program given in Appendix B. Most of the parameters a_{ik} are random numbers or are derived from random numbers. In the following, these random numbers are always assumed to be uniformly distributed over the interval specified.

The first 15 pollutants are arranged in 3 groups of 5 each, within which the pollutants inhibit each other competitively (see Sect. 4.1). (These groups may be thought of as representing carbohydrates, proteins, and fats [44].) The parameters a_{ik} in the denominators of these 15 equations were determined according to

$$a_{ik} = \frac{1}{\alpha_{ik}} \quad , \tag{A.1}$$

where α_{ik} are random numbers from the interval (0.1, 20). (This means, if the expressions degenerate into simple Michaelis-Menten expressions, their saturation constants are equally distributed over the range (0.1, 20). On the basis of these values, the parameters $a_{36,1}$, i=1 ... 15, in the 36-th equation were calculated according to

$$a_{36,i} = \phi_i \cdot a_{5k+1,i-5k+1}, \quad k=0,1,2 \; . \tag{A.2}$$

The index k denotes the pollutants group to which the i-th pollutant belongs, ϕ_i is a random number from the interval $(0,v_k)$ and v_k is the maximum rate at which bacteria can grow if they live on pollutants of group k exclusively. The maximum growth rates v_k were chosen in such a way that they add up to 1 and that their expectation is 1/3. (Two random

$$\dot{N}_1 = - \frac{a_{1,1} N_1}{1 + \sum_{i=1}^{5} a_{1,i+1} N_i} B$$

$$\vdots$$

$$\dot{N}_5 = - \frac{a_{5,1} N_5}{1 + \sum_{i=1}^{5} a_{1,i+1} N_i} B$$

$$\dot{N}_6 = \ldots\ldots$$

$$\vdots$$

$$\dot{N}_{10} = \ldots\ldots$$

$$\dot{N}_{11} = \ldots\ldots$$

$$\vdots$$

$$\dot{N}_{15} = \frac{a_{15,1} N_{15}}{1 + \sum_{i=11}^{15} a_{11,i+1} N_i} B$$

$$\dot{N}_{16} = - \frac{a_{16,1} N_{16}}{1 + a_{16,2} N_{16} + \sum_{i=1}^{15} a_{16,i+2} N_i} B$$

$$\vdots$$

$$\dot{N}_{20} = \ldots\ldots$$

$$\dot{N}_{21} = - \frac{a_{21,1} N_{21}}{(1 + a_{21,2} N_{21})(1 + a_{21,3} N_{\xi 21})} B$$

$$\vdots$$

$$\dot{N}_{25} = \ldots\ldots$$

$$\dot{N}_{26} = - \frac{a_{26,1} N_{26}}{1 + a_{26,2} N_{26}} E_1$$

$$\vdots$$

$$\dot{N}_{30} = \ldots\ldots$$

$$\dot{E}_1 = \frac{a_{31,1} N_{26}}{(1 + a_{31,2} N_{26})(1 + \sum_{i=1}^{15} a_{31,i+2} N_i)} B$$

$$\vdots$$

$$\dot{E}_5 = \ldots\ldots$$

$$\dot{B} = - \sum_{i=1}^{30} a_{36,i} \frac{\dot{N}_i}{a_{i,1}} - a_{36,31} B - \frac{a_{36,32} B}{1 + a_{36,33} B} P_1 - \frac{a_{36,34} B}{1 + a_{36,35} B} P_2$$

$$\dot{P}_1 = \frac{a_{37,1} B}{1 + a_{36,33} B} P_1 - a_{37,2} P_1$$

$$\dot{P}_2 = \ldots\ldots$$

$$\dot{O} = \sum_{i=1}^{30} a_{39,i} \frac{\dot{N}_i}{a_{i,1}} - a_{39,31} B - \frac{a_{39,32} B}{1 + a_{36,33} B} P_1 - \frac{a_{39,33} B}{1 + a_{36,35} B} P_2 - a_{39,34} P_1$$

$$- a_{39,35} P_2 + a_{39,36} (O_S - O)$$

Figure A.1: Equations of the model used for generating river quality "measurements"

numbers ξ_1 and ξ_2 were drawn from the interval (0,1) and v_k, k=0,1,2 was calculated according to

$$v_o = \text{Min}\{\xi_1, \xi_2\},\ v_1 = |\xi_2 - \xi_1|,\ v_2 = 1 - \text{Max}\{\xi_1, \xi_2\}.)$$

This means that the maximum possible growth rate of the bacteria is 1 if they live on the first 15 pollutants; this corresponds to a generation time of about 20 minutes. The actual maximum of the bacterial growth rate is the sum of the three maxima of y_i over the three groups of pollutants, because

$$\text{Max}\left\{ \sum_{i=1}^{I} \frac{c_i N_i}{1 + \sum_{i=1}^{I} d_i N_i} \;\middle|\; N_i \geq 0 \right\} = \text{Max}\left\{ \frac{c_1}{d_1}, \frac{c_2}{d_2}, \ldots \frac{c_I}{d_I} \right\} .$$

The parameters $a_{i,1}$ were determined by multiplying the corresponding $a_{36,i}$ by a random number η_i from the interval (2, 6):

$$a_{i,1} = a_{36,i} \cdot \eta_i \,. \tag{A.3}$$

The parameter $a_{39,i}$ were fixed in an analogous way:

$$a_{39,i} = a_{36,i} \cdot \zeta_i \,, \tag{A.4}$$

where ζ_i is a random number from the interval (1,4).

For the pollutants N_{16} through N_{20} a competitive inhibition by N_1 through N_{15} was assumed. The constants $a_{i,k}$, $16 \leq i \leq 20$, $2 \leq k \leq 17$ were again determined according to (A.1); for k=2 even the interval from which the $\alpha_{i,k}$ were drawn was the same as above, while for the remaining $a_{i,k}$ the interval (0.5, 50) was used. The parameters $a_{36,i}$ for $16 \leq i \leq 20$ were determined according to

$$a_{36,i} = a_{i,2} \cdot \nu_i \,, \tag{A.5}$$

whereby ν_i are random numbers from the interval (0, 0.06).

(i.e. the maximum bacterial growth rate on the basis of N_{16} through N_{20} is, on the average, smaller than for the three groups of pollutants mentioned above.) The values of $a_{i,1}$ and $a_{39,i}$ for $16 \leq i \leq 20$ were determined in the same manner as for $1 \leq i \leq 15$. However, η_i in Eq. (A.3) was chosen from the interval (2,9), so that for pollutants N_{16} through N_{20} the transformation into bacterial mass is, on the average, less efficient.

For pollutants N_{21} through N_{25} an allosteric inhibition through one of pollutants N_1 through N_{15} was assumed, the inhibiting pollutants (N_{ξ_i}, $21 \leq i \leq 25$ in Fig. A.1) also being selected randomly. The values of $a_{i,2}$, $a_{36,i}$, $a_{i,1}$, and $a_{39,i}$ for $21 \leq i \leq 25$ were determined in the same way as for $16 \leq i \leq 20$, the constants $a_{i,3}$ are random numbers from the interval (0.1, 10).

The degradation of pollutants N_{26} through N_{30} is assumed to be catalyzed by exoenzymes and to follow the Michaelis-Menten law. All pertinent parameter values were calculated analogous to the parameters for N_{16} through N_{20}, only the ν_i in (A.5) are now drawn from the interval (0, 0.2).

The equations describing the dynamics of the exoenzyme concentration are certainly only a rough description of the processes of enzyme formation. However, they reflect the reasonable assumptions that enzyme synthesis does not take place if the concentration of N_1 through N_{15} is high, and that the enzyme production rate is proportional to the substrate concentration if the latter is low, while the production rate becomes constant for high substrate concentrations. The values of $a_{i,2}$ $31 \leq i \leq 35$ were determined in the same way as the corresponding values in the previous equations. The values of $a_{i,1}$ were obtained from them through multiplication by a random number from the interval (0, 0.5), the remaining $a_{i,k}$ being random numbers from the interval (0,1). (The constants $a_{i,1}$ ought to be much greater for $26 \leq i \leq 30$ than for $1 \leq i \leq 25$, and much smaller for $31 \leq i \leq 35$, because the concentrations E_i are smaller than bacterial mass concentrations by orders of magnitude. Constants of the magnitude indicated above are obtained, however, if the E_i's are understood to be exoenzyme concentrations times some suitable, large constant.)

The constants $a_{36,31}$ and $a_{39,31}$ were fixed at 0.05 for all computations. Likewise, parameters $a_{37,2}$, $a_{38,2}$, $a_{39,34}$, and $a_{39,35}$ were given the value 0.04, while $a_{39,36}$ was fixed at 1.

The saturation constants $1/a_{36,33}$ and $1/a_{36,35}$ for the feeding activity of the two protozoan species were drawn from the interval (5,25), the maximum feeding rates $a_{37,1}/a_{36,33}$ and $a_{38,1}/a_{36,35}$ are random numbers from the

interval (0.1, 0.5). The efficiency of the transformation of bacteria into protozoan mass was chosen randomly from the interval (0.3, 0.6), the specific oxygen consumption for this process is a random number between 0.8 and 1.2.

Finally, it should be emphasized again that the purpose of the model was mainly to generate a large variety of possible "measurements" as bases for the system identification described in Sect. 4.2. The detailed description of every single process was not intended. The ranges given for the values of the numerous parameters can be seen to be realistic by going through the corresponding discussion in Sect. 4.3.

APPENDIX B: COMPUTER PROGRAM FOR SYSTEM IDENTIFICATION THROUGH QUASILINEARIZATION

This is a description of a PL/I computer program which calculates the "measured values" of Fig. 4.6b, and determines the parameters of Eqs. (4.16-20) such that those "measured values" are fitted well in the least square sense. The "measured values" are calculated on the basis of the model described in Appendix A, and the parameter estimation for Eqs. (4.16-20) is carried out according to the quasilinearization technique outlined in Sect. 3.2. Since the program structure is essentially linear, no flow diagram is presented. Instead , the program statements are commented on sequentially:

Statement Number	
3	The meaning of the most important variables is as follows:
	T = time
	MW = "measurements" generated by the complex river quality model
	HW = weights according to Eq. (3.2.1)
	GX, PR, X = variables $X_r; p_r; c_o, c_1, \ldots c_{10}$, respectively, in equations (3.15) and (3.17)
	DGX, DPR, DX = derivations of the preceding variables
	JM = Jacobian matrix of system (4.16-20) with the parameters interpreted as dependent variables (see Eq. (3.14)).
	A,B = homogeneous and inhomogeneous part of the matrix of the linear algebraic system (3.20)
	C = solution of system (3.20)
	G = right hand side of system (4.16-20) written in the form (3.14)
	CO = parameters of the complex river quality model (denoted by $a_{i,k}$ in Appendix A)
	FH = array to specify the parameters of model (4.16-20) for which a priori estimates ("measurements") are given. The first element gives the total number of these parameters, the following elements indicate the position of each of them within the vector $\vec{c}$ of Eq. (3.14).

Statement Number	
3(ctd)	GH = weights for the parameter specified by FH R = index n in Eq. (3.15) N = number of dependent variables of model (4.16-20) (including the parameters to be estimated. It is equal to 23.)
4-52	Calculation of the right hand side of the complex river quality model (see Fig. A.1)
53-81	Calculation of the right hand sides of system (3.18) and of the systems for $\vec{p}_r(t)$, $\vec{c}_o(t)$, $\vec{c}_1(t)$, ... $\vec{c}_{r-1}(t)$
82-110	Performance of one Runge-Kutta integration step for the differential equation system whose right hand side is calculated by the subroutine Fl. Equations in which the right hand side is zero are ignored.
111-169	Calculation of the Jacobian matrix JM
170-181	Calculation of the right hand side of Eq. (3.14) as derived from the model (4.16-20)
182-188	Multiplication of a matrix by a vector
189-201	Multiplication of a matrix A having NV rows and N columns by an NxN matrix B whose elements in columns NV+1 through N are all zero except for the diagonal elements which are equal to one.
202-207	Random number generator. The multiplicative congruential technique is used. The psuedo random numbers are uniformly distributed over the interval (u,0)
213-271	Determination of the parameter values for the complex river quality model (see Appendix A)
272-284	Determination of the initial values for the complex river quality model
285-286	Printing out of the parameter and initial values of the complex river quality model
287-315	Integration of the model equations of Fig. A.1 and calculation of the noise-free measurements for Fig. 4.6b. Element MW(2,0) is equal to the sum of all N_i at time T = 145h. This value

Statement Number	
287-315 (ctd)	is considered to be a measure of the pollutants which are non-degradable in view of a flow time of 20 hours. This value is subtracted from MW(1,*). The values of all dependent variables at T=20 and T=145 are printed out.
316-332	Determination of the weights according to Eq. (3.21) and addition of random errors to the values of MW. The errors are normally distributed, the variance being 7.5% of the maximum value of each variable.
333-360	Fixing of those parameters which are to be considered as a priori estimates and determination of their weights. Specification of N and of some auxiliary variables.
361-390	Assignment of the initial values of $\vec{c}_o$, X_i, and $\vec{p}_i$ (see Eqs. (3.17,18)).
391-436	Calculation of the $\vec{c}_n(0)$, n=1,2,3, ..., according to the procedure described in Sect. 3.2. The coefficients of system (3.20) are built up successively as integration proceeds from measurement point to measurement point. The contribution of the a priori parameter estimates to the coefficients is calculated through statements 424-427. The external subroutine MINV inverts matrix A; it is the double-precision version of a subroutine from the "System / 360 Scientific Subroutines Package (PL/I)" of IBM.

The computing time of the program on an IBM / 370-165 computer is several minutes. (A more precise statement cannot be made, since the computing time (CPU-time!) depends strongly on the other programs being executed at the same time.) After 10 iterations the components of $\vec{c}_n(0)$ vary by less than 5% during further iterations.

SOURCE LISTING

```
STMT LEV NT

   1          (NOUNDERFLOW):
              VS: PROC OPTIONS(MAIN);
   2    1     OPEN FILE(SYSPRINT) LINESIZE(132);
   3    1     DCL (H,EPS,T,OS,MW(5,0:40),HW(5),(YH,Y)(810),YO(810) INITIAL((810)0),
                H1,H2,Z,(JM,A)(23,23),(B,C,G,GH)(23),CO(39,39),D,VM(3),R1,R2,
                GX(23,23) BASED(QP),        DGX(23,23) BASED(DQP),
                PR(23) BASED(RP),           DPR(23) BASED(DRP),
                X(0:10,23) BASED(SP),       DX(0:10,23) BASED(DSP)  ) FLOAT(15),
                (I,J,K,L,M,N,NM,NQ,NQN,NV,(NU,NO)(13),R,FH(0:23),
                XI(21:25)) FIXED BINARY,
               IR INITIAL (3111693) FIXED BINARY(31,0),
               MINV ENTRY;

   4    1     FO: PROCEDURE(T,Y,DY);
   5    2     DCL (T,Y(*),DY(*),H,H1,H2) FLOAT(15),
                (I,NH) FIXED BINARY;
   6    2     H1=Y(36)*Y(37)/(1+CO(36,33)*Y(36));
   7    2     H2=Y(36)*Y(38)/(1+CO(36,35)*Y(36));
   8    2     DY(36)=-CO(36,31)*Y(36)-CO(36,32)*H1-CO(36,34)*H2;
   9    2     DY(37)=CO(37,1)*H1-CO(37,2)*Y(37);
  10    2     DY(38)=CO(38,1)*H2-CO(38,2)*Y(38);
  11    2     DY(39)=-CO(39,31)*Y(36)-CO(39,32)*H1-CO(39,33)*H2-CO(39,34)*Y(37)
                   -CO(39,35)*Y(38)+CO(39,36)*(OS-Y(39));
  12    2     DO I=1 TO 11 BY 5;
  13    2  1   H=1;
  14    2  1   DO K=1 TO 5;
  15    2  2    H=H+CO(I,K+1)*Y(I+K-1);
  16    2  2   END;
  17    2  1   H=1/H;
  18    2  1   DO K=1 TO 5;
  19    2  2    NH=I+K-1;
  20    2  2    DY(NH)=-CO(NH,1)*Y(NH)*Y(36)*H;
  21    2  2    DY(36)=DY(36)-CO(36,NH)*DY(NH)/CO(NH,1);
  22    2  2    DY(39)=DY(39)+CO(39,NH)*DY(NH)/CO(NH,1);
  23    2  2   END;
  24    2  1  END;
  25    2     DO I=16 TO 20;
  26    2  1   H=1+CO(I,2)*Y(I);
  27    2  1   DO K=1 TO 15;
  28    2  2    H=H+CO(I,2+K)*Y(K);
  29    2  2   END;
  30    2  1   DY(I)=-CO(I,1)*Y(I)*Y(36)/H;
  31    2  1   DY(36)=DY(36)-CO(36,I)*DY(I)/CO(I,1);
  32    2  1   DY(39)=DY(39)+CO(39,I)*DY(I)/CO(I,1);
  33    2  1  END;
  34    2     DO I=21 TO 25;
```

```
STMT LEV NT

  35    2  1  DY(I)=-CO(I,1)*Y(I)*Y(36)/((1+CO(I,2)*Y(I))*(1+CO(I,3)*Y(XI(I))));
  36    2  1  DY(36)=DY(36)-CO(36,I)*DY(I)/CO(I,1);
  37    2  1  DY(39)=DY(39)+CO(39,I)*DY(I)/CO(I,1);
  38    2  1 END;
  39    2    DO I=26 TO 30;
  40    2  1  DY(I)=-CO(I,1)*Y(I)*Y(I+5)/(1+CO(I,2)*Y(I));
  41    2  1  DY(36)=DY(36)-CO(36,I)*DY(I)/CO(I,1);
  42    2  1  DY(39)=DY(39)+CO(39,I)*DY(I)/CO(I,1);
  43    2  1 END;
  44    2    DO I=31 TO 35;
  45    2  1  H=1;
  46    2  1  DO K=1 TO 15;
  47    2  2   H=H+CO(I,K+2)*Y(K);
  48    2  2  END;
  49    2  1  DY(I)=CO(I,1)*Y(I-5)/(1+CO(I,2)*Y(I-5))/H*Y(36);
  50    2  1 END;
  51    2    RETURN;
  52    2    END;

  53    1    F1: PROCEDURE (T,Y,DY);
  54    2    DCL (T,Y(*),DY(*)) FLOAT (15),
                (I,K) FIXED BINARY;
  55    2    OP=ADDR(Y(1));          DOP=ADDR(DY(1));
  57    2    RP=ADDR(Y(NQ));         DRP=ADDR(DY(NQ));
  59    2    SP=ADDR(Y(NQN));        DSP=ADDR(DY(NQN));
  61    2    CALL JACOBI (X(R-1,*),JM);
  62    2    CALL MMSS (JM,GX,N,NV,DGX);
  63    2    CALL RS (X(R-1,*),G);
  64    2    CALL MMGV (JM,PR-X(R-1,*),NV,DPR);
  65    2    DO I=1 TO NV; DPR(I)=DPR(I)+ G(I); END;
  68    2    IF R>1 THEN CALL RS(X(0,*),G);
  69    2    DO I=1 TO NV; DX(0,I)=G(I); END;
  72    2    DO K=1 TO R-1;
  73    2  1  CALL JACOBI (X(K-1,*),JM);
  74    2  1  IF K>1 THEN CALL RS(X(K-1,*),G);
  75    2  1  CALL MMGV(JM,X(K,*)-X(K-1,*),NV,DX(K,*));
  76    2  1  DO I=1 TO NV; DX(K,I)=DX(K,I)+G(I); END;
  79    2  1 END;
  80    2    RETURN;
  81    2    END;

  82    1    RK: PROCEDURE (T,H,Y,N,FKT);
  83    2    DCL FKT ENTRY,
             (T,H,Y(*),HH,(DY1,DY2,DY3,DY4)(N))   FLOAT(15),
             (N,I,K)FIXED BINARY;
  84    2    HH=H/2;
  85    2    CALL FKT(T,Y,DY1);
  86    2    DO I=1 TO NM;
  87    2  1  DO K=NU(I) TO NO(I);
```

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  88    2  2    YH(K)=Y(K)+HH*DY1(K);
  89    2  2   END;
  90    2  1 END;
  91    2     CALL FKT(T,YH,DY2);
  92    2     DO I=1 TO NM;
  93    2  1   DO K=NU(I) TO NO(I);
  94    2  2    YH(K)=Y(K)+HH*DY2(K);
  95    2  2   END;
  96    2  1 END;
  97    2     CALL FKT(T,YH,DY3);
  98    2     DO I=1 TO NM;
  99    2  1   DO K=NU(I) TO NO(I);
 100    2  2    YH(K)=Y(K)+H*DY3(K);
 101    2  2   END;
 102    2  1 END;
 103    2     CALL FKT(T,YH,DY4);
 104    2     DO I=1 TO NM;
 105    2  1   DO K=NU(I) TO NO(I);
 106    2  2    Y(K)=Y(K)+H*(DY1(K)+2*(DY2(K)+DY3(K))+DY4(K))/6;
 107    2  2   END;
 108    2  1 END;
 109    2     RETURN;
 110    2     END;

 111    1     JACOBI: PROCEDURE (X,J);
 112    2     DCL (X(*),J(*,*),H1,H2,H3,H4,H5) FLOAT(15);
 113    2     H1=1/(X(7)+X(1));
 114    2     H2=1/(X(9)+X(2)+X(23)*X(1));
 115    2     H3=1/(X(13)+X(3));
 116    2     H4=X(17)/X(6);
 117    2     H5=X(18)/X(8);
 118    2     J(1,1)=-X(6)*X(10)*X(3)*X(7)*H1*H1;
 119    2     J(1,3)=-X(6)*X(10)*X(1)*H1;
 120    2     J(1,6)=-X(10)*X(1)*X(3)*H1;
 121    2     J(1,7)=-J(1,1)*X(1)/X(7);
 122    2     J(1,10)=J(1,6)*X(6)/X(10);
 123    2     J(2,1)=X(8)*X(11)*X(2)*X(3)*H2*H2*X(23);
 124    2     J(2,2)=-J(2,1)*(X(9)+X(23)*X(1))/(X(2)*X(23));
 125    2     J(2,3)=-X(8)*X(11)*X(2)*H2;
 126    2     J(2,8)=J(2,3)*X(3)/X(8);
 127    2     J(2,9)=J(2,1)/X(23);
 128    2     J(2,11)=J(2,8)*X(8)/X(11);
 129    2     J(2,23)=J(2,9)*X(1);
 130    2     J(3,1)=-J(1,1)/X(6)-J(2,1)/X(8);
 131    2     J(3,2)=-J(2,2)/X(8);
 132    2     J(3,3)=-J(1,3)/X(6)-J(2,3)/X(8)-X(12)*X(15)*X(4)*X(13)*H3*H3-X(14);
 133    2     J(3,4)=-X(12)*X(15)*X(3)*H3;
 134    2     J(3,7)=-J(1,7)/X(6);
 135    2     J(3,9)=-J(2,9)/X(8);
```

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 136   2     J(3,10)=-J(1,10)/X(6);
 137   2     J(3,11)=-J(2,11)/X(8);
 138   2     J(3,12)=J(3,4)*X(4)/X(12);
 139   2     J(3,13)=-J(3,4)*X(4)*H3;
 140   2     J(3,14)=-X(3);
 141   2     J(3,15)=J(3,12)*X(12)/X(15);
 142   2     J(3,23)=-J(2,23)/X(8);
 143   2     J(4,3)=X(15)*X(4)*X(13)*H3*H3;
 144   2     J(4,4)=-J(3,4)/X(12)-X(16);
 145   2     J(4,13)=-J(4,3)*X(3)/X(13);
 146   2     J(4,15)=-J(3,12)/X(15);
 147   2     J(4,16)=-X(4);
 148   2     J(5,1)=J(1,1)*H4+J(2,1)*H5;
 149   2     J(5,2)=J(2,2)*H5;
 150   2     J(5,3)=J(1,3)*H4+J(2,3)*H5-J(4,3)*X(19)-X(20)*X(14);
 151   2     J(5,4)=J(3,12)*X(19)/X(4)-X(21)*X(16);
 152   2     J(5,5)=-X(22);
 153   2     J(5,7)=J(1,7)*H4;
 154   2     J(5,9)=J(2,9)*H5;
 155   2     J(5,10)=J(1,10)*H4;
 156   2     J(5,11)=J(2,11)*H5;
 157   2     J(5,13)=-J(4,13)*X(19);
 158   2     J(5,14)=-X(20)*X(3);
 159   2     J(5,15)=-J(4,15)*X(19);
 160   2     J(5,16)=-X(21)*X(4);
 161   2     J(5,17)=J(1,6);
 162   2     J(5,18)=J(2,8);
 163   2     J(5,19)=J(3,12);
 164   2     J(5,20)=-X(14)*X(3);
 165   2     J(5,21)=-X(16)*X(4);
 166   2     J(5,22)=DS-X(5);
 167   2     J(5,23)=J(2,23)*H5;
 168   2     RETURN;
 169   2     END;

 170   1     PS: PROCEDURE (X,G);
 171   2     DCL (X(*),G(*),H1,H2,H3) FLOAT(15);
 172   2     H1=X(10)*X(1)*X(3)/(X(7)+X(1));
 173   2     H2=X(11)*X(2)*X(3)/(X(9)+X(2)+X(23)*X(1));
 174   2     H3=X(15)*X(3)*X(4)/(X(13)+X(3));
 175   2     G(1)=-X(6)*H1;
 176   2     G(2)=-X(8)*H2;
 177   2     G(3)=H1+H2-X(12)*H3-X(14)*X(3);
 178   2     G(4)=H3-X(16)*X(4);
 179   2     G(5)=-X(17)*H1-X(18)*H2-X(19)*H3-X(20)*X(14)*X(3)-X(21)*X(16)*X(4)
                   +X(22)*(DS-X(5));
 180   2     RETURN;
 181   2     END;
```

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 182   1     MMGV: PROCEDURE (A,B,N,C);
 183   2     DCL (A(*,*),B(*),C(*)) FLOAT(15),
                 (N,I) FIXED BINARY;
 184   2     DO I=1 TO N;
 185   2  1   C(I)=SUM(A(I,*)*B);
 186   2  1  END;
 187   2     RETURN;
 188   2     END;

 189   1     MMSS: PROC (A,B,N,NV,C);
 190   2     DCL (A(*,*),B(*,*),C(*,*),S) FLOAT(15),
                 (I,K,L,N,NV) BINARY FIXED;
 191   2     DO I=1 TO NV;
 192   2  1   DO K=1 TO N;
 193   2  2     S=0;
 194   2  2     DO L=1 TO NV;
 195   2  3       S=S+A(I,L)*B(L,K);
 196   2  3     END;
 197   2  2     IF K>NV THEN S=S+A(I,K);
 198   2  2     C(I,K)=S;
 199   2  2   END;
 200   2  1  END;
 201   2     END;

 202   1     (NOFIXEDOVERFLOW):
             ZUFL: PROCEDURE (U,O) RETURNS(FLOAT(15));
 203   2     DCL (U,O) FLOAT(15);
 204   2     IR=IR*65539;
 205   2     IF IR<0 THEN IR=IR+2147483647+1;
 206   2     RETURN(U+IR*0.4656613E-9*(O-U));
 207   2     END;

 208   1     ON ERROR SNAP BEGIN; PUT LIST (D,R,T,Y); GO TO ENDE; END;
 212   1     CO=0;
 213   1     OS=8.0;
 214   1     R1=ZUFL(0,1);  R2=ZUFL(0,1);
 216   1     VM(1)=MIN(R1,R2);  VM(2)=ABS(R2-R1);  VM(3)=1-MAX(R1,R2);
 219   1     DO I=1 TO 11 BY 5;
 220   1  1   DO K=1 TO 5;
 221   1  2     CO(I,K+1)=1/ZUFL(0.1,20);
 222   1  2     CO(36,I+K-1)=ZUFL(0,VM(I/5+1))*CO(I,K+1);
 223   1  2     CO(39,I+K-1)=ZUFL(1,4)*CO(36,I+K-1);
 224   1  2     CO(I+K-1,1)=ZUFL(2,6)*CO(36,I+K-1);
 225   1  2   END;
 226   1  1  END;
 227   1     DO I=16 TO 20;
 228   1  1   CO(I,2)=1/ZUFL(0.1,20);
 229   1  1   CO(36,I)=ZUFL(0,0.06)*CO(I,2);
 230   1  1   CO(39,I)=ZUFL(1,4)*CO(36,I);
```

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231    1  1  C0(I,1)=ZUFL(2,9)*C0(36,I);
232    1  1  DO K=1 TO 15;
233    1  2   C0(I,K+2)=1/ZUFL(0.5,50);
234    1  2  END;
235    1  1 END;
236    1     DO I=21 TO 25;
237    1  1  C0(I,2)=1/ZUFL(0.1,20);
238    1  1  C0(36,I)=ZUFL(0,0.06)*C0(I,2);
239    1  1  C0(39,I)=ZUFL(1,4)*C0(36,I);
240    1  1  C0(I,1)=ZUFL(2,9)*C0(36,I);
241    1  1  C0(I,3)=ZUFL(0.1,10);
242    1  1  XI(I)=ZUFL(1,16);
243    1  1 END;
244    1     DO I=26 TO 30;
245    1  1  C0(I,2)=1/ZUFL(0.1,20);
246    1  1  C0(36,I)=ZUFL(0,0.2)*C0(I,2);
247    1  1  C0(39,I)=ZUFL(1,4)*C0(36,I);
248    1  1  C0(I,1)=ZUFL(2,9)*C0(36,I);
249    1  1 END;
250    1     DO I=31 TO 35;
251    1  1  C0(I,2)=1/ZUFL(0.1,20);
252    1  1  C0(I,1)=ZUFL(0,0.5)*C0(I,2);
253    1  1  DO K=1 TO 15;
254    1  2   C0(I,K+2)=ZUFL(0,1);
255    1  2  END;
256    1  1 END;
257    1     C0(36,31)=0.05;
258    1     C0(36,33)=1/ZUFL(5,25);  C0(36,32)=ZUFL(0.10,0.50)*C0(36,33);
260    1     C0(36,35)=1/ZUFL(5,25);  C0(36,34)=ZUFL(0.10,0.50)*C0(36,35);
262    1     C0(37,1)=ZUFL(0.3,0.6)*C0(36,32); C0(37,2)=0.04;
264    1     C0(38,1)=ZUFL(0.3,0.6)*C0(36,34); C0(38,2)=0.04;
266    1     C0(39,31)=0.05;  C0(39,32)=ZUFL(0.8,1.2)*C0(36,32); C0(39,34)=0.04;
269    1     C0(39,33)=ZUFL(0.8,1.2)*C0(36,34);  C0(39,35)=0.04;  C0(39,36)=1.0;
272    1     MW(1,0)=0;
273    1     DO I=1 TO 30;
274    1  1  Y(I)=ZUFL(0,6);
275    1  1  MW(1,0)=MW(1,0)+Y(I);
276    1  1 END;
277    1     DO I=31 TO 35; Y(I)=0; END;
280    1     MW(3,0),Y(36)=5.0;
281    1     Y(37)=ZUFL(0,0.5); Y(38)=0.5-Y(37); MW(4,0)=0.5;
284    1     MW(5,0),Y(39)=05;
285    1     PUT EDIT ((Y(I),C0(I,*) DO I=1 TO 39)) (F(9,3),SKIP,3 (13 F(9,3),SKIP),
                                                                    SKIP);
286    1     PUT EDIT ((Y(I) DO I=1 TO 39)) (SKIP,3 (13 F(9,3),SKIP),SKIP);
287    1     T=0;   H=0.05;  NM=1;  NU(1)=1;  M,ND(1)=39;
292    1     DO I=1 TO 20;
293    1  1  DO J=1 TO 20;
294    1  2   CALL RK(T,H,Y,M,F0);
```

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STMT LEV NT

 295    1  2    T=T+H;
 296    1  2   END;
 297    1  1   MW(1,I)=0;
 298    1  1   DO J=1 TO 30;
 299    1  2    MW(1,I)=MW(1,I)+Y(J);
 300    1  2   END;
 301    1  1   MW(3,I)=Y(36); MW(4,I)=Y(37)+Y(38); MW(5,I)=Y(39);
 304    1  1  END;
 305    1     PUT EDIT ((Y(I) DO I=1 TO 39)) (SKIP,3 (13 F(9,3),SKIP),SKIP);
 306    1     DO I=1 TO 2500;
 307    1  1   CALL RK(T,H,Y,M,F0);
 308    1  1   T=T+H;
 309    1  1  END;
 310    1     PUT EDIT ((Y(I) DO I=1 TO 39)) (SKIP,3 (13 F(9,3),SKIP),SKIP);
 311    1     MW(2,*)=0;
 312    1     DO I=1 TO 30;
 313    1  1   MW(2,0)=MW(2,0)+Y(I);
 314    1  1  END;
 315    1     MW(1,*)=MW(1,*)-MW(2,0);
 316    1     DO I=1,3,4,5;
 317    1  1   HW(I)=MW(I,0);
 318    1  1   DO K=1 TO 20;
 319    1  2    IF MW(I,K)>HW(I) THEN HW(I)=MW(I,K);
 320    1  2   END;
 321    1  1   H1=HW(I)*0.15; H2=0.797884/H1;
 323    1  1   DO K=0 TO 20;
 324    1  2    ZV:
                 Z=ZUFL(-H1,H1);
 325    1  2     IF H2*EXP(-2*(Z/H1)**2)<ZUFL(0,H2) THEN GOTO ZV;
 326    1  2   MW(I,K)=MW(I,K)+Z;
 327    1  2   END;
 328    1  1   HW(I)=1/HW(I)**2;
 329    1  1  END;
 330    1     DO I=0 TO 20; PUT LIST (MW(*,I)) SKIP; END;
 333    1     FH(0)=11; FH(1)=10; FH(2)=9;  FH(3)=12;  FH(4)=14;  FH(5)=13;
 339    1     FH(6)=19;  FH(7)=20;  FH(8)=21;  FH(9)=22;  FH(10)=15;   FH(11)=23;
 345    1     GH=0.003;
 346    1     EPS=1E-50;  H=0.05;
 348    1     Y=0;     C=0;  JM=0;
 351    1     N=23;    NQ=N*N+1;   NQN=NQ+N;
 354    1     NV=5;  NU(1)=1;  NO(1)=N*NV;
 357    1     DO I=2 TO 13;
 358    1  1   NU(I)=NQ+N*(I-2);  NO(I)=NU(I)+NV-1;
 360    1  1  END;
 361    1     YO(NQN)=MW(1,0)*0.45;     YO(NQN+1)=MW(1,0)*0.55;
 363    1     YO(NQN+2)=MW(3,0);        YO(NQN+3)=MW(4,0);
 365    1     YO(NQN+4)=MW(5,0);  YO(NQN+5)=2.0;       YO(NQN+6)=2.00;
 368    1     YO(NQN+7)=2.0;      YO(NQN+8)=20.0;      YO(NQN+9)=0.5;
 371    1     YO(NQN+10)=0.07;    YO(NQN+11)=2.0;      YO(NQN+12)=15.0;
```

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STMT LEV NT

 374    1     YO(NQN+13)=0.04;     YO(NQN+14)=0.135;    YO(NQN+15)=0.04;
 377    1     YO(NQN+16)=4.0;      YO(NQN+17)=1.0;      YO(NQN+18)=1.0;
 380    1     YO(NQN+19)=1.0;      YO(NQN+20)=1.0;      YO(NQN+21)=1.0;
 383    1     YO(NQN+22)=1.0;
 384    1     L=0;
 385    1     DO I=1 TO N;
 386    1  1   DO K=1 TO N;
 387    1  2    L=L+1;
 388    1  2    IF I=K THEN YO(L)=1;
 389    1  2   END;
 390    1  1  END;
 391    1     DO R=1 TO 10;
 392    1  1   NM=R+2;
 393    1  1   M=N*(N+R+1);    T=0;    A=0;    B=0;
 397    1  1   B(1),B(2)=MW(1,0)*HW(1);  B(3)=MW(3,0)*HW(3);
 399    1  1   B(4)=MW(4,0)*HW(4);  B(5)=MW(5,0)*HW(5);
 401    1  1   A(1,1),A(1,2),A(2,1),A(2,2)=HW(1);  A(3,3)=HW(3);
 403    1  1   A(4,4)=HW(4);  A(5,5)=HW(5);
 405    1  1   DO I=1 TO M;
 406    1  2    YH(I),Y(I)=YO(I);
 407    1  2   END;
 408    1  1   DO I=1 TO 20;
 409    1  2    DO K = 1 TO 20;
 410    1  3     CALL RK(T,H,Y,M,F1)    ;
 411    1  3     T=T+H ;
 412    1  3    END;
 413    1  2    QP=ADDR(Y(1));    RP=ADDR(Y(NQ));    SP=ADDR(Y(NQN));
 416    1  2    PUT EDIT(T,(X(R-1,L) DO L=1 TO 5)) (SKIP, 6 E(11,3));
 417    1  2    DO J=1 TO N;
 418    1  3     B(J)=B(J)+(GX(1,J)+GX(2,J))*(MW(1,I)-PP(1)-PR(2))*HW(1)+GX(3,J)*
                    (MW(3,I)-PP(3))*HW(3)+GX(4,J)*(MW(4,I)-PR(4))*HW(4)+
                    GX(5,J)*(MW(5,I)-PR(5))*HW(5);
 419    1  3     DO K=1 TO N;
 420    1  4      A(J,K)=A(J,K)+(GX(1,J)+GX(2,J))*(GX(1,K)+GX(2,K))*HW(1)+
                       GX(3,J)*GX(3,K)*HW(3)+GX(4,J)*GX(4,K)*HW(4)+
                       GX(5,J)*GX(5,K)*HW(5);
 421    1  4     END;
 422    1  3    END;
 423    1  2   END;
 424    1  1   DO I=1 TO FH(0);
 425    1  2    A(FH(I),FH(I))=A(FH(I),FH(I))+GH(I)/YO(NQN+FH(I)-1)**2;
 426    1  2    B(FH(I))=B(FH(I))+GH(I)/YO(NQN+FH(I)-1);
 427    1  2   END;
 428    1  1   CALL MINV (A,N,D,EPS);
 429    1  1   CALL MMGV (A,B,N,C);
 430    1  1   PUT SKIP;
 431    1  1   PUT LIST (C);
 432    1  1   DO I=1 TO N;
 433    1  2    YO(M+I)=C(I);

 434    1  2   END;
 435    1  1  END;
 436    1     ENDE:
             END;
```

APPENDIX C: COMPUTER PROGRAM FOR THE SELF-PURIFICATION MODEL OF THE RHINE RIVER

A PL/I computer program which solves Eqs. (4.23-28) is given below. The results correspond to the curves of Fig. 4.10. Only a few explanations seem necessary to understand the very simple program:

Statement Number	
2	The meaning of the most important variables is as follows: T = time WFV= ratio between river discharge Q and mean discharge MQ WT = water temperature OM = oxygen saturation concentration O_s Y = state vector of model (4.23-28) A = array containing the parameter values for model (4.23-28) DC,V,W,DK,SV = arrays giving, for each of the twelve reaches, influx of degradable pollutants (see Fig. 4.11a), velocity, mean discharge, reaeration rate (for 20°C), and proportion of the degradable pollutants which is easily degradable. UG = array specifying the boundaries of the 12 reaches
3-16	Calculation of the right hand side of system (4.23-28)
17-37	Performance of one Runge-Kutta step on system (4.23-28)
38-48	Reading in and printing out of input data. Modification of the reaeration rates according to the temperature chosen (statement 43).
49-73	Integration of system (4.23-28) from river-km 400 to 850. Printing out of river-km, sum of pollutants, and all dependent variables every second kilometer.

SOURCE LISTING

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STMT LEV NT

   1          RH: PROC OPTIONS (MAIN);
   2    1     DCL (H,HH,T,WFV,WT,OM,Y(6),A(6,7),(DC,V,W,DK,SV)(12),KM,KMN) FLOAT(15),
                (UG(13),I,J,M) FIXED BINARY;

   3    1     FO: PROC (T,Y,DY);
   4    2     DCL (T,Y(*),DY(*),H1,H2,H3) FLOAT (15);
   5    2     H1=A(4,1)*Y(1)*Y(4)/(A(4,2)+Y(1));
   6    2     H2=A(4,3)*Y(2)*Y(4)/(A(4,4)+Y(2)+A(4,5)*Y(1));
   7    2     H3=A(5,1)*Y(4)*Y(5)/(A(5,2)+Y(4));
   8    2     IF Y(6)<0.1 THEN H1,H2,H3=0;
   9    2     DY(1)=-A(1,1)*H1+A(1,2)*A(1,3);
  10    2     DY(2)=-A(2,1)*H2+(1-A(1,2))*A(1,3);
  11    2     DY(3)=A(3,1)*A(1,3);
  12    2     DY(4)=H1+H2-A(4,6)*H3-A(4,7)*Y(4);
  13    2     DY(5)=H3-A(5,3)*Y(5);
  14    2     DY(6)=A(6,1)*(OM-Y(6))-A(6,2)*H1-A(6,3)*H2-A(6,4)*A(6,7)*Y(4)-A(6,5)*H3
                  -A(6,6)*A(5,3)*Y(5)+A(6,7);
  15    2     RETURN;
  16    2     END;

  17    1     RK: PROCEDURE (T,H,Y,N,FKT);
  18    2     DCL FKT ENTRY,
              (T,H,Y(*),HH,(YO,DY1,DY2,DY3,DY4)(N))   FLOAT(15),
              (N,I,K)FIXED BINARY;
  19    2     HH=H/2;
  20    2     CALL FKT(T,Y,DY1);
  21    2     DO I=1 TO N;   YO(I)=Y(I)+HH*DY1(I);   END;
  24    2     CALL FKT(T,YO,DY2);
  25    2     DO I=1 TO N;   YO(I)=Y(I)+HH*DY2(I);   END;
  28    2     CALL FKT(T,YO,DY3);
  29    2     DO I=1 TO N;   YO(I)=Y(I)+H*DY3(I);   END;
  32    2     CALL FKT(T,YO,DY4);
  33    2     DO I=1 TO N;
  34    2   1  Y(I)=Y(I)+H*(DY1(I)+2*(DY2(I)+DY3(I))+DY4(I))/6;
  35    2   1 END;
  36    2     RETURN;
  37    2     END;

  38    1     GET LIST (A);  PUT EDIT ('PARAMETER',A) (X(25),A,SKIP(2),6(SKIP,
                                                      7 F(10,3)));
  40    1     PUT EDIT ('KM','A(1,3)','A(1,2)','V','MQ','A(6,1)')
                       (SKIP(4),A,X(8),A,X(9),A,X(11),A,X(14),A,X(11),A);
  41    1     GET LIST (UG,DC,W,SV,DK,V);
  42    1     GET LIST (WFV,WT,OM);
  43    1     DK=DK*1.2*1.0241**(WT-20);
  44    1     DO I=1 TO 12;
```

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STMT LEV NT

 45   1  1  PUT EDIT (UG(I),DC(I),SV(I),V(I),W(I),DK(I)) (SKIP,F(3,0),5 E(15,3));
 46   1  1 END;
 47   1    PUT EDIT ('Q/MQ','T','OS') (SKIP(3),X(10),A,X(5),A,X(7),A);
 48   1    PUT EDIT (WFV,WT,OM) (SKIP,X(9),F(5,2),2 F(8,2));
 49   1    KM=400.00;  T=0;  H=0.05;  M=6;  J=1;
 54   1    GET LIST (Y); HH=Y(1)+Y(2)+Y(3);
 56   1    PUT EDIT (KM,HH,Y) (SKIP(20),F(6,0),7 E(15,5));
 57   1    DO WHILE (KM<850);
 58   1  1  IF (KM>=UG(J)) THEN DO;
 59   1  2   A(1,3)=DC(J)*V(J)/(WFV*W(J))*277.778;
 60   1  2   A(1,2)=SV(J);
 61   1  2   A(6,1)=DK(J);
 62   1  2   J=J+1;
 63   1  2  END;
 64   1  1  CALL RK(T,H,Y,M,FO);
 65   1  1  T=T+H;  KMN=KM+V(J-1)*H;
 67   1  1  IF (TRUNC(KM/2)<TRUNC(KMN/2)) THEN DO;
 68   1  2   HH=Y(1)+Y(2)+Y(3);
 69   1  2   PUT EDIT (KMN,HH,Y) (SKIP,F(6,0),7 E(15,5));
 70   1  2  END;
 71   1  1  KM=KMN;
 72   1  1 END;
 73   1    END;
```

PARAMETERS

2.600	0.000	0.000	0.000	0.000	0.000	0.000
3.400	0.000	0.000	0.000	0.000	0.000	0.000
0.050	0.000	0.000	0.000	0.000	0.000	0.000
0.480	20.000	0.100	20.000	3.000	3.000	0.060
0.360	12.000	0.070	0.000	0.000	0.000	0.000
0.000	1.600	2.400	1.000	2.000	1.000	0.070

KM	A	A(1,2)	V	MQ	A(6,1)
400	6.250E-01	5.000E-01	5.000E+00	1.200E+03	2.520E-01
420	8.750E+00	4.000E-01	5.000E+00	1.300E+03	2.520E-01
435	5.000E-01	5.000E-01	5.000E+00	1.300E+03	2.520E-01
500	1.375E+01	4.000E-01	4.000E+00	1.500E+03	2.280E-01
506	6.250E-01	5.000E-01	3.500E+00	1.500E+03	2.160E-01
530	3.750E-01	5.000E-01	6.500E+00	1.600E+03	2.640E-01
590	7.500E-01	5.000E-01	6.000E+00	1.900E+03	2.400E-01
660	3.125E+00	5.000E-01	5.000E+00	2.000E+03	2.400E-01
680	5.625E+00	5.000E-01	5.000E+00	2.000E+03	2.400E-01
700	1.250E+00	5.000E-01	5.000E+00	2.000E+03	2.400E-01
725	2.500E+00	5.000E-01	5.000E+00	2.000E+03	2.520E-01
815	1.250E+00	5.000E-01	5.000E+00	2.100E+03	2.400E-01

Q/MQ	T	OS
1.25	20.00	9.20