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IIASA Working Paper

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Preface

Central and Eastern European countries face rapid and profound economic transition and the need of solving pressing environmental and water pollution problems at the same time. Imposing Western effluent standards would lead to financial consequences which are unrealistic in the short run. For this reason, the development of ambient water quality criteria based, river basin least-cost policies is suggested which can be gradually extended later on. The pre-condition of such a strategy is the usage of water quality models relating emissions and receiving water quality, as well as their respective changes. River water quality models incorporate a number of parameters which should be estimated on the basis of field data, which often is scarce and error corrupted. The data from the regular monitoring cannot be used for this purpose, since it does not incorporate the emission data. Therefore, specially designed experiments are needed. In August 1992 and June 1993 IIASA together the Water Research Institute in Bratislava (VÚVH) and the Váh River Basin Authority performed such experiments in the frame of a policy-oriented study of the Nitra River basin in Slovakia aimed at selecting the most appropriate catchment-wide wastewater treatment strategies. Present work discusses the setting of the water quality profile experiments and the analysis of the obtained data. The Nitra River basin serves as a case study in the context of the ongoing research conducted in the IIASA Water Project, with the broader objective to develop models, methodologies and strategies of interest in the CEE region. This is one of a series of papers that deals with the management of degraded river basins in the CEE region.

Abstract

The Nitra River is one of most polluted rivers in the Slovak Republic, due to numerous industrial and municipal emissions, and low level of wastewater treatment. Policy-oriented water quality management study on the basin was undertaken jointly by IIASA, the Water Research Institute in Bratislava (VÚVH), and the Váh River Basin Authority. One of the components of the research were the water quality profiles experiments incorporating both emission and river water sampling, followed by an analysis with mass balance method. Two experiments were performed in the basin, in August 1992 and June 1993, respectively. The first experiment was focused on the "conventional" water quality parameters affecting dissolved oxygen balance, such as BOD, COD and nitrogen. The second, although limited only to certain regions of the basin, was aimed at understanding more detailed water quality processes in the river such as sedimentation and hydrolysis of organic material. Rough estimates of the process rates were obtained with mass balance method. The results of the work were used for calibration of water quality models essential for the formulation of economically feasible wastewater treatment policy in the basin based on water quality criteria.

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LONGITUDINAL WATER QUALITY PROFILE MEASUREMENTS AND THEIR EVALUATION IN THE NITRA RIVER BASIN (SLOVAKIA)

Masliev, I., Petrovic, P., Kuníková, M., Zajícová, H., and Somlyódy, L.

1 INTRODUCTION

The Nitra River is a tributory of the Váh which enters the Danube in Komárno, downstream of Bratislava. The catchment area is 5140 km^2 and 653 300 inhabitants live there. The length of the river is slightly below 200 km. The mean streamflow near the mouth is 22.5 m^3/s, while a typical August low flow is about 3 m^3/s. The region is highly industrialized with a low level of wastewater treatment. Inadequate and/or partial treatment also characterizes the municipalities. Most of the municipal wastewater treatment plants are overloaded significantly (by 100% or more).

The water quality of the river is one of the poorest in Slovakia. According to the existing evaluation system where Class V indicates the worst quality, the Nitra's water quality is categorized as Class IV-V. As a result, water use is restricted to water abstraction for industrial and irrigation purposes. However, the primary utilization of the river system is actually waste disposal.

A collaborative research aimed at development of water quality management strategies for the Nitra river basin was undertaken in spring of 1992 jointly by IIASA, the Water Research Institute in Bratislava (VÚVH), and the Váh River Basin Authority. The objective was to develop a short-term affordable management policy of wastewater treament which would sufficiently improve present poor water quality of the river. At the same time, the policy solution should provide for subsequent upgrading of the wastewater treatment in the basin to the levels required by the European Community standards.

One of the key elements of the selected methodology (Somlyódy et al, 1994) is intelligent setting of water quality goals: ambient standards, effluent standards or the combination of the two. It was demonstrated that use of effluent-based standards only leads to sufficient overexpenditures, i.e. construction of overly expensive treatment facilities with very little impact on the receiving waters quality. Therefore, for an affordable short-range option one should rely more upon ambient standards, formulating goals directly in terms of receiving water quality. This allows for selection among a variety of upgrading scenarios satisfying the ambient water quality constraints. The criteria for such a selection could be manifold. For instance, it is possible to look for a solution minimizing investment cost, or total annual cost. It is also possible to incorporate into analysis uncertainty issues and check the robustness of the solution. These were key analysis elements of the Nitra study (Somlyódy et al, 1994).

Reliance on ambient water quality standards in policy setting implies use of water quality models. A change in emissions (e.g. due to change in treatment level) results in change in receiving water quality. The model can be used to simulate this effect, providing the basis for comparison of ambient water quality with the desired level (water quality standard, or goal). Furthermore, an optimization routine might be used together with simulation to look for the best solutions according to a given optimization objective. Thus a water quality simulation model is an indispensable tool in policy development on a river basin scale.

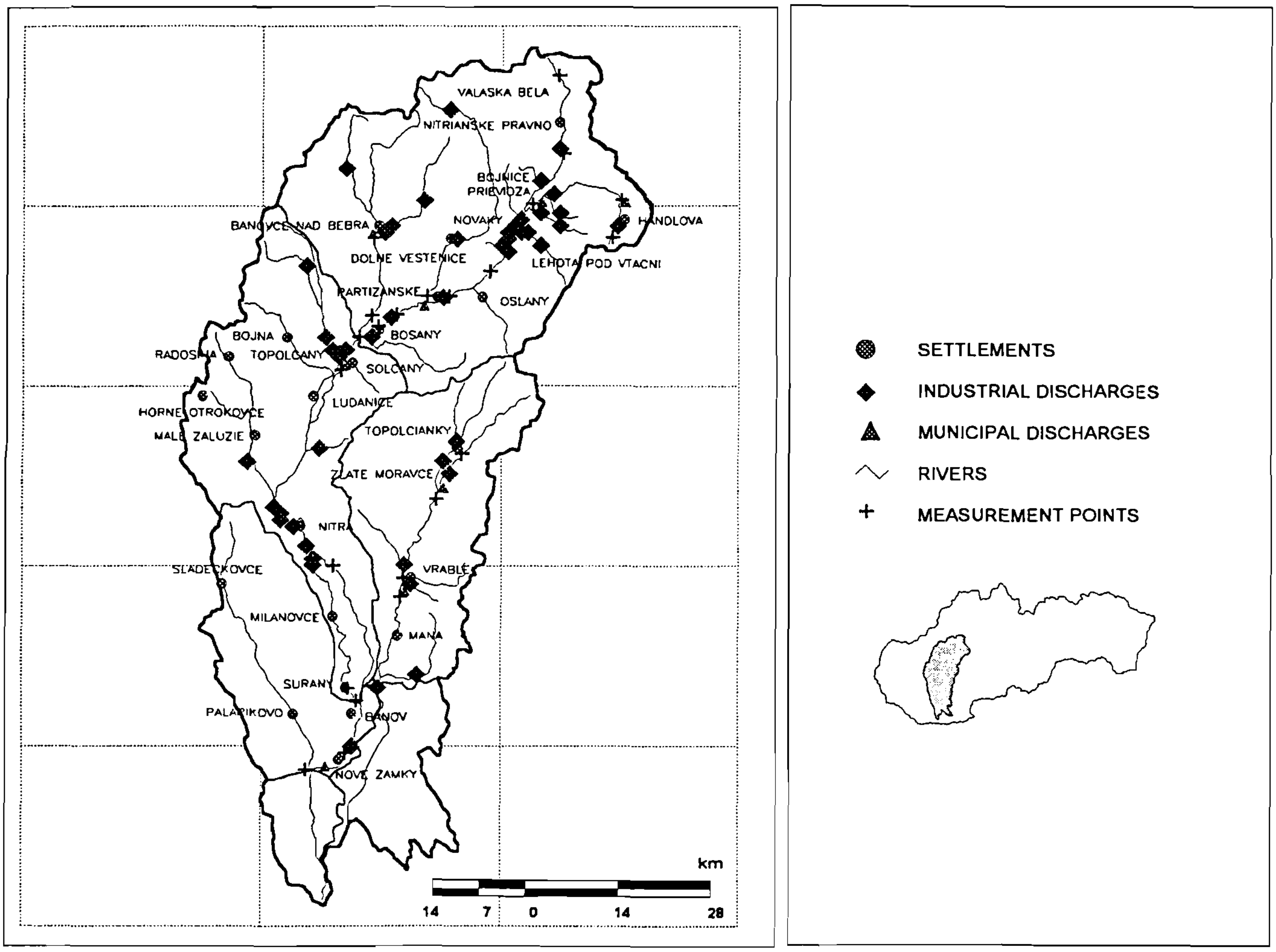


Figure 1.1 The Nitra River basin.

Use of water quality models presumes calibration, or selection of model parameters which would allow the model to adequately describe the modeled object (Jørgensen, 1994). However, it is not an easy process, especially in a situation with a scarcy and unreliable data. In the case of Nitra River basin study, the river water quality monitoring data was relatively good. The monitoring scheme consists of 26 locations (Figure 1.1) where monthly sampling takes place (Somlyódy et al, 1994). However, the data on emissions were very poor and unreliable. For most dischargers only yearly averages were known. Joint analysis of existing unharmonized data sets (monitoring and emissions) in order to calibrate a simple water quality model presented significant difficulties (Koivusalo e.a., 1992). For this reason, it was decided to perform two longitudinal water quality profile observations, monitoring both ambient water quality and emissions. Although the design of the experiments was done jointly by IIASA and VÚVH, the difficult task of the execution relied upon our colleagues from Slovakia.

Present work contains analysis of data obtained in longitudinal water quality profile experiments performed in August 1992 and June 1993. The first measurement program covered the entire river basin, while the second one was focused on three regions for more detailed sampling. The experiments results formed a basis for calibration and validation procedures for the water quality simulation models (Somlyódy et al, 1994). Several model versions were calibrated and applied for simulation of the households of dissolved oxygen and nutrients in the river, both being major regional water quality problems for the Nitra River basin.

The water quality profile experiments were performed jointly by Water Research Institute in Bratislava, the Váh River Authority and IIASA on August 25-26, 1992 and June 7-10, 1993. The June program was designed taking into account the findings of the August 25-26 experiment. Evaluation of both experiments was based on mass balance approach, which served two major goals: identification of water quality processes taking place in the river and rough estimation of the key process parameters. A more refined parameter estimation was made on the basis of the profiles data using probabilistic algorithms (Masliev, Somlyódy, 1993).

Parameter estimation procedure usually consists of two steps: calibration and validation (Beck, 1976). One approach can be to use data collected in one region for calibration and data from another region for validation (validation in space). Another procedure requires samples collected during two (or more) measurement campaigns, in which case the data from the second set of measurements provides the basis for validation in time. Data from the second experiment thus serve as a validation criteria. In the Nitra study, both methods were applied (Somlyódy e.a., 1994).

The material is organized as follows. First, the overall description of the experimental setup is given in Section 2. Comparison between the regular sampling and the experiment data in August 1992 is given to illustrate experimental errors and variability in the measured data (Section 3.1). Next, the longitudinal profiles of major components and the overall water quality situation at the time of experiment is covered for the August 1992 survey (Section 3.2). Mass balances from the August 1992 experiment are discussed in Sections 3.3-3.4. Finally, the analysis and discussion of the water quality profiles and mass balances for the June 1993 experiment is given in Section 4. Conclusions of the study are summarized in Section 5.

2 EXPERIMENTAL SETUP

2.1 August 1992 Experiment

Timing of the first experiment (August 1992) was selected to cover the extreme low-flow event within the year. Under low streamflow conditions diluting of wastewater effluent is minimal, and therefore this event is considered the most critical from the viewpoint of water quality management of source point pollution. The period of low-flow usually is defined as the reference time frame for checking ambient water quality standards (Water Quality Assessment, 1992). The flow exceeding 355 days in an average year (Q_{355}) is used for checking ambient water quality envisaged by the former Slovak Water Law 138/1973 and Governmental Decree 30/1975 from 26 March 1975, as well as in the presently acting Decree 242/1993. The actual stream flow during the August 1992 experiment was less than the Q_{355} value everywhere in the river (Figure 3.5).

All stations of the regular water quality monitoring program on the Nitra River were also sampled during the experiment, and three other sampling sites were added to the scheme. Several tributories which are not regularly monitored were included into the program as well. Altogether, 48 sampling locations were selected. Concurrently, the Váh River Basin Authority carried out its regular monthly sampling, thus providing a possibility for comparison (Section 3.1). At two sampling stations on the Nitra river (ref. to Figure 1.1), namely Nitrianska Streda (river km 91) and Nové Zámky (river km 14), the diurnal changes were monitored for 24 hours (Figure 3.23). The emission data (concentration and flow) on both the industrial and municipal wastewater discharges were registered and stored simultaneously with river water sampling, thus providing the concerted set for further analysis. In order to obtain mass balance estimations, river streamflow was measured at all sampling locations.

The entire watershed was covered by four sampling teams working independently and simultaneously. All selected sites were visited in advance and site photos were taken. At some locations the streamflow was measured in advance in order to save time. Since the weather during the experiment was extremely dry, the streamflow changes were not significant. The work was divided among the participants as follows: the Water Research Institute (VÚVH) was in charge of the streamflow measurements and sampling, the laboratory analyses of samples were done by the River Authority in Piestany, and some of the analyses were also repeated by the VÚVH laboratory for further intercomparisons of the results (Section 3.1).

List of measured parameters was comosed to provide a general idea on the water quality situation in the basin. Both conventional and micropollutants were included, along with basic hydrochemical characteristics. More specifically, the following parameters were measured during the August 1992 profile experiment:

- Basic physical and chemical characteristics (temperature, conductivity, pH, dissolved and suspended solids, dominant anions and cations);
- Oxygen regime parameters (dissolved oxygen, chemical and biological oxygen demand)
- Inorganic nitrogen and phosphorus forms;
- Heavy metals (copper, zinc, cadmium, mercury, arsenic, chromium);
- Industrial organic micropollutants (chloroform, 1,2 dichloroethane, 1,1,1 trichloroethane etc);
- Pesticides (DDT, aldrin, dieldrin, DDE).

The selection of parameters had been dictated by the most serious water quality problems of the region. The major chemical and physical parameters are affected by the effluent of the chemical complex in Novaky, which is also a source of industrial organic micropollutants. Dissolved oxygen problem is caused by the organic pollution coming mostly from municipal wastewater treatment plants. Agriculture provides non-point sources of nitrates and pesticides.

2.2 June 1993 Experiment

The Nitra River water upstream of the confluence with Handlovka (river km 135.7, cf. Figure 1.1) is practically clean. The results of August 1992 experiment show that downstream of Novaky (4 km downstream of the Handlovka confluence, river km 132.5, see Figure 1.1) the

Nitra River could be subdivided to two stretches with respect to water quality. The upstream stretch from Novaky to Nitrianska Streda (river km 91.1, Figure 1.1) is strongly affected by industrial pollution caused by the chemical complex at Novaky and the tannery at Bosany. Smaller municipalities are adding their discharges to this part of the river as well, such as Partizanske WWTP (Figure 1.1). Pollution of the downstream stretch of the river starts from Luzianky (river km 65, Figure 1.1) and is caused mostly by municipal emissions of Topolcany, Nitra and Nove Zamky.

Three regions of the Nitra River were selected for more detailed June 1993 sampling program, two of them in the upstream stretch (Novaky-Nitrianska Streda) and one in the downstream stretch (Nove Zamky-Komoca, cf. Figure 1.1). Several additional locations were included into the sampling program in order to obtain more detailed profiles. Sampling was repeated daily in key locations, providing information on the temporal variability of the water quality parameters and analytical errors.

The set of analyzed parameters for the June 1993 experiment was extended with respect to the August 1992 program. BOD and COD tests with filtered samples water were performed in addition to conventional procedure. This allowed estimation of the particulate and dissolved fractions of the organic material. Total phosphorus and total nitrogen concentrations were determined, and organic fractions were estimated by extraction mineral components concentrations from the total. For the purposes of quantitative evaluation (e.g. mass balances) daily data from the particular location were averaged and the mean value was used for calculations.

2.3 Summary of the Design of the Two Experiments

Table 2.1 summarizes the design and compares the main features of the two profile experiments.

Table 2.1 Design of longitudinal profile experiments.

Feature	*August 1992 Experiment*	*June 1993 Experiment*
Main objective	Water quality survey; rough mass balance esitmates; initial estimations of processes parameters	Detailed water quality profiles and mass balances; identification of key water quality processes
Spatial extent	Entire watershed	Three selected regions
Duration	Two days	Four days
Number of Samples	One sample for location	Four daily samples at important locations
List of Parameters	Basic water quality parameters and main pollutants	Extended list of parameters allowing to identify water quality processes
Use in water quality modelling	Calibration	Validation

3 AUGUST 1992 EXPERIMENT

3.1 Intercomparison of the Regular Monitoring and Experiment Sampling (August 1992)

During the experiment regular monitoring samples were taken from the river independently by the Vah River Authority. This additional data served as a base for comparison between the two sets of measurements, giving an idea about the experimental errors and data variability. Comparison charts for several water quality parameters are shown in Figures 3.1-3.4.

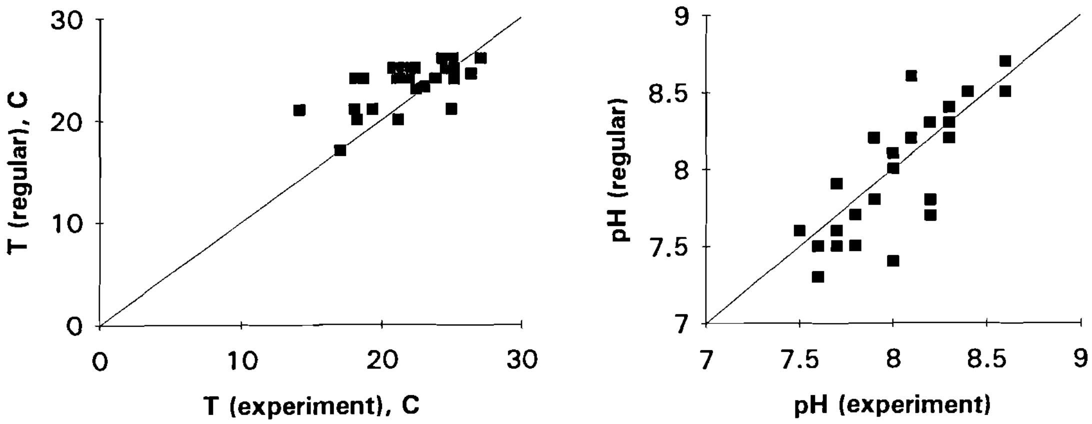


Figure 3.1 A comparison of water temperature and pH measurements for the August 1992 experiment and regular sampling (R=0.62 and 0.84, respectively)

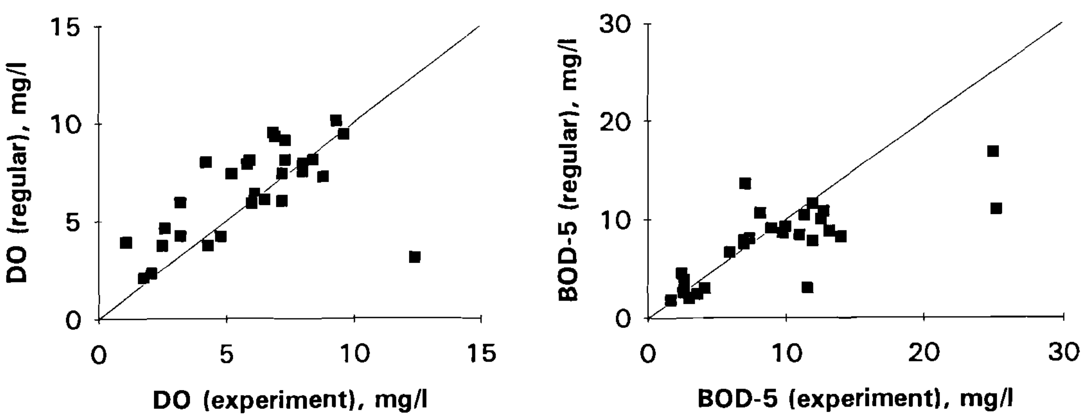


Figure 3.2 A comparison of dissolved oxygen and biological oxygen demand measurements for the August 1992 experiment and regular sampling (R=0.58 and 0.76, respectively)

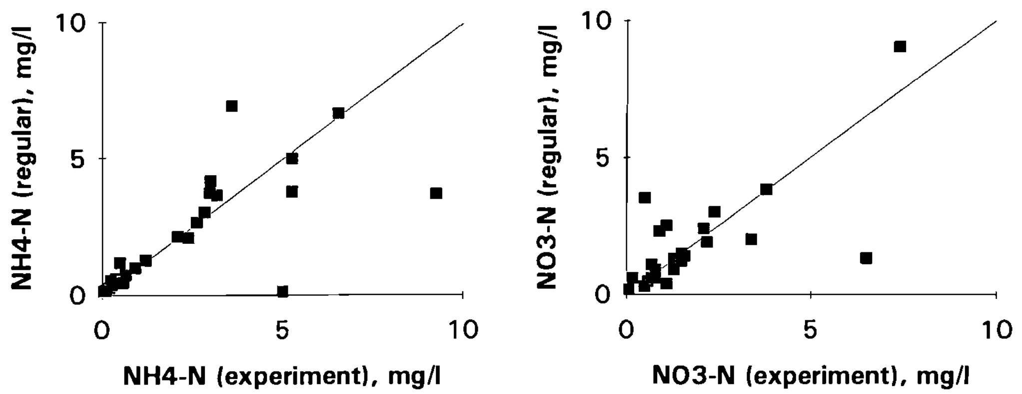


Figure 3.3 A comparison of ammonia and nitrate nitrogen measurements for the August 1992 experiment and regular sampling (R=0.78 and 0.7, respectively)

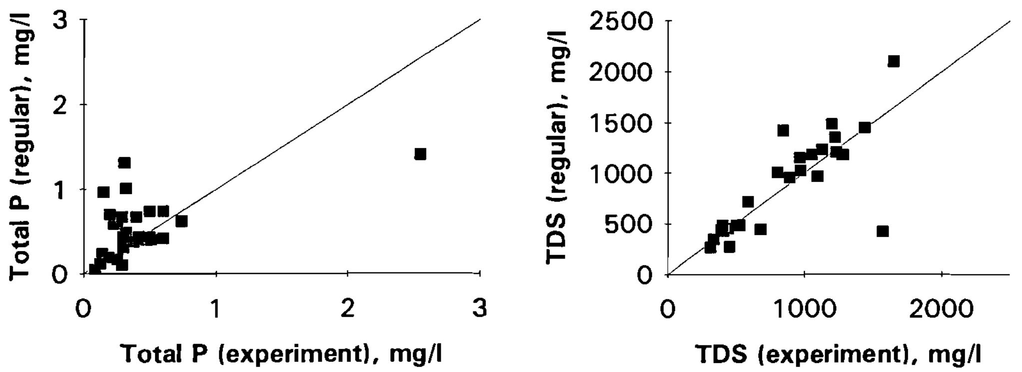


Figure 3.4 A comparison of total phosphorus and total dissolved solids measurements for the August 1992 experiment and regular sampling (R=0.53 and 0.79, respectively)

Water temperature was essentially in the same domain (20-25 ^oC), but correlation is relatively poor (R=0.62, Figure 3.1). Measured pH covers relatively broad range (7.5 - 8.5) and correlate reasonably well (Figure 3.1), although there is some scattering in the plot. Dissolved oxygen measurements show relatively good overall agreement, with the exception of one outlying value (Figure 3.2). BOD-5 and nitrogen forms are generally correlated (Figure 3.2 and 3.3), the same could be said about total dissolved solids (Figure 3.4). However, there are several outlyers, and data is scattered, showing large variations. Phosphorus concentration data are in relatively poor agreement (Figure 3.4). This suggests the need to look into the procedure of phosphorus measurement and to find out the cause of the observed discrepancy. In general, intercomparison plots illustrate the variability and uncertainty in data sets, which cause difficulties in parameter estimation for water quality modelling (Beck, 1987).

3.2 Evaluation of Longitudinal Profiles

The streamflow of the Nitra River is shown in Figure 3.5 The daily flow values exceeded in 355 and 364 days in an average year are plotted along with the actual ones from the experiment. It can be seen that the streamflow in the upper part would be overreached 355 days, in the lower part it is even less than the 364 day limit. The 355 day value is defined as a reference low-flow condition for water quality assessment by the Slovak environmental legislation, as noted before. Thus, the experiment corresponds to the design needs.

The drop in the streamflow between measurement points Nitrianska Streda (river km 91, Figure 1.1) and Luzianky (river km 65, Figure 1.1) is not explained by the known water intakes (Figure 3.5). The most likely cause is the irrigation withdrawal, either the small reservoir at river km 156 (Preselany) or directly from the river. The flow difference was within the range of daily observations performed in 1993 and thus the (not well monitored) reservoir operation gives full evidence for the discrepancy found.

For the above reason the river was subdivided into two stretches (Figure 3.5), both having consistent flow data. These regional subdivision was used for mass balance evaluation (Sections 3.3-3.5) and also for the purpose of calibration and validation in (Somlyódy, et al, 1994).

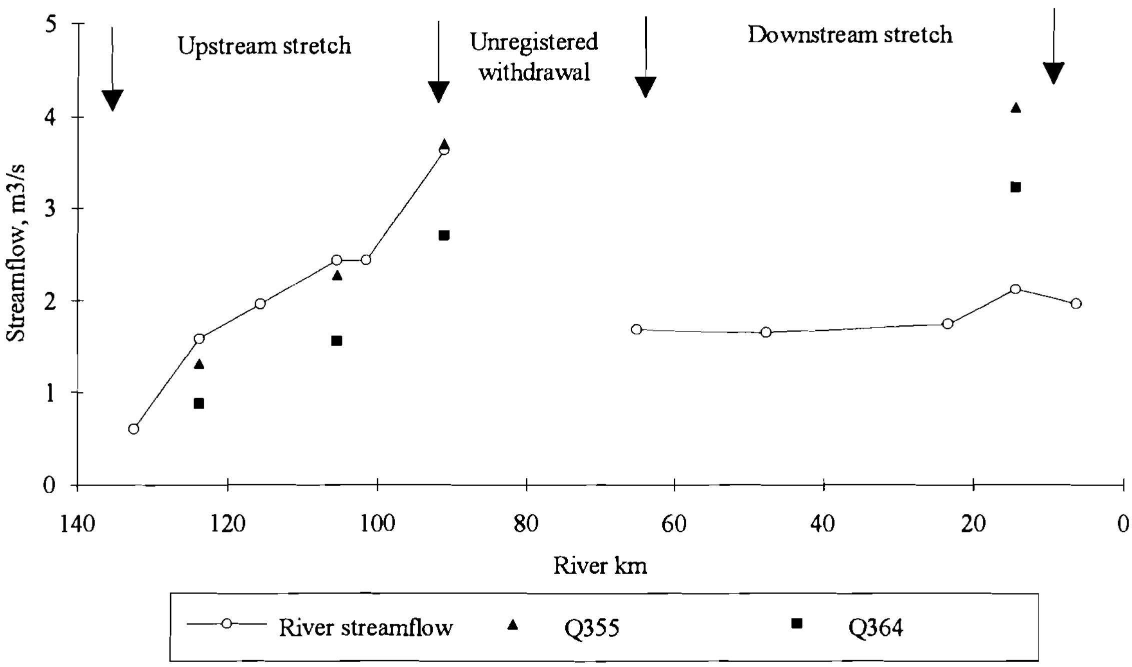
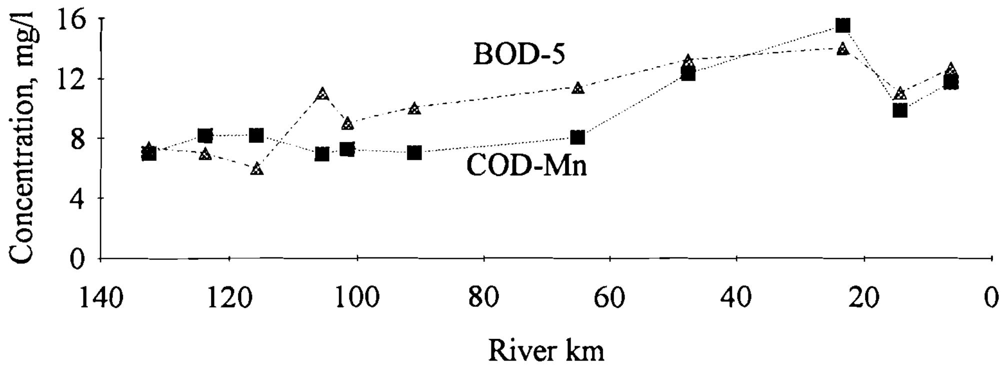


Figure 3.5 Longitudinal profile of the streamflow in the Nitra River (August 1992 experiment)

The longitudinal profile of dissolved oxygen for the whole Nitra River (August 25-26 1992 experiment) is shown in Figure 3.6. In this figure, biological and chemical oxygen demand levels are also given, which influence dissolved oxygen household of the river. In the middle part of the chart, the locations of emissions, tributaries and intakes are indicated with respective symbols. Although at discharge locations the instream concentration should experience an abrupt change (assuming complete mixing), they are not illustrated in the plot. The measured concentrations are connected with lines as if the concentrations were continuous along the course of the river. Subsequent longitudinal profile plots (Figures 3.7-3.8) follow the same fashion. However, the above mentioned concentration changes at the locations of mixing are shown in plots for mass balance evaluation in Section 3.3 (for instance, Figure 3.10, 3.11, etc.)

One can observe that dissolved oxygen drops below 4.0 mg/l at several locations in the profile, sometimes as low as 2.0 mg/l. Simultaneously, high oxygen demand levels indicate that significant amounts of organic material were being discharged into the river (BOD-5 level is above 10 mg/l at most measurement points). According to the Slovak classification of the surface water quality, the river water at most sampling sites corresponds to Class IV (intensely polluted water) for dissolved oxygen related parameters.



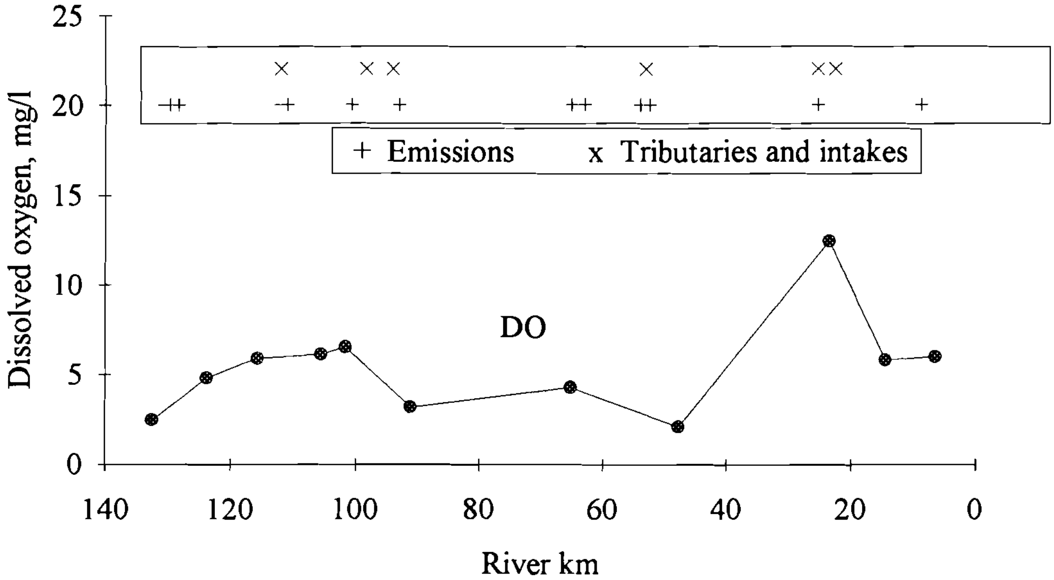
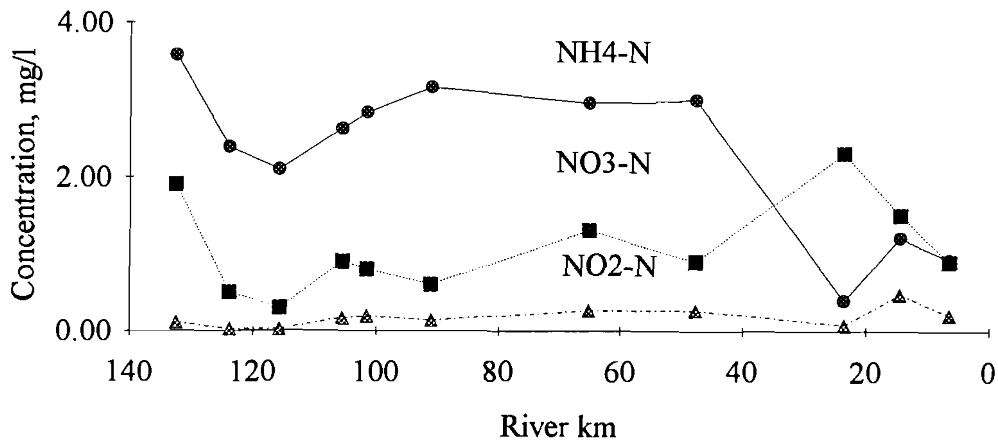


Figure 3.6 Longitudinal profile of the oxygen demands and dissolved oxygen in the Nitra River (August 1992 experiment)

The longitudinal distribution of the nitrogen forms is shown in Figure 3.7. The ammonia nitrogen originates mostly from the effluent of the wastewater treatment plants. The ammonia nitrogen in the lower part of the river is most likely subject to the nitrification process, since the drop in ammonia concentration is accompanied by the simultaneous increase in the nitrate concentration (see also Figure 3.2 and Sections 3.4-3.5).

The longitudinal profile of the phosphorus forms (total and orthophosphate) in the river is shown in Figure 3.7. It can be seen that there were some discrepancies in the analytical procedure, since for some samples the total phosphorus appears to be less than the orthophosphate fraction.



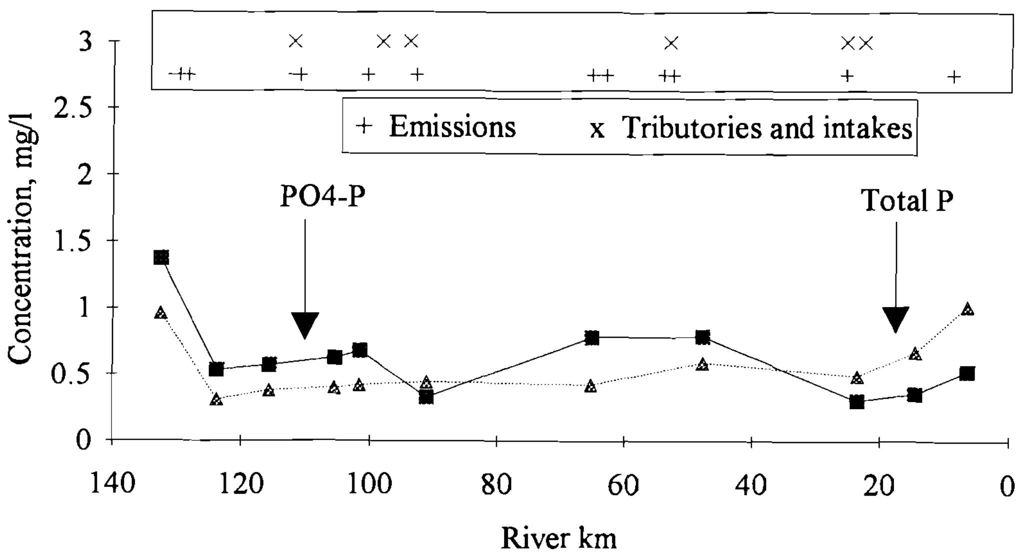


Figure 3.7 Longitudinal profile of the phosphorus and nitrogen forms in the Nitra River (August 1992) experiment

An analysis of chlorophyll "a" was made in several locations in the river (Figure 3.8). It is evident that phytoplankton growth is pronounced; from the upstream to the downstream of the river the concentration is increasing approximately ten times. Considering high level of phosphorus and nitrogen content in the water (Figure 3.7), this is easy to explain. In the course of growth, algae consume phosphorus and nitrogen to build living cells. Algae growth, therefore, causes loss of nitrogen and phosphorus mass from the river (Section 3.4).

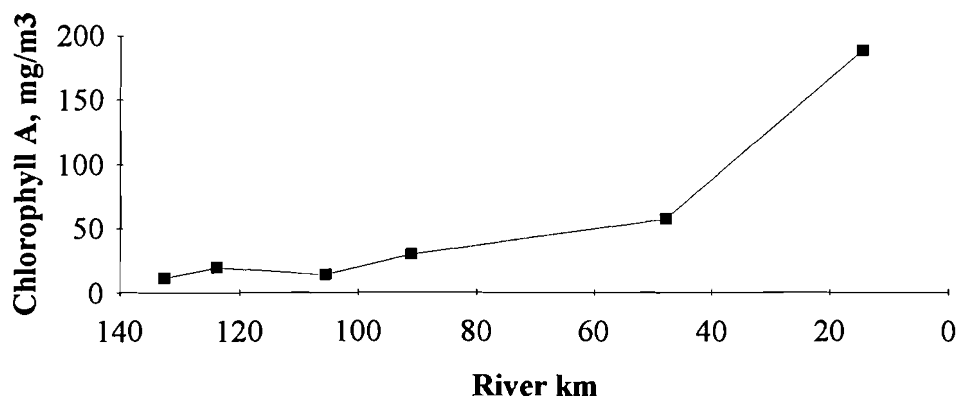


Figure 3.8 Longitudinal profile of chlorophyll "a" in the Nitra River (August 1992 experiment).

Figure 3.9 shows the concentration of the pesticide lindane (hexachlor cyclohexane) in the water of Nitra River during the August 1992 experiment. It is logical to conclude that occurences of the pesticide would be related more to areas of agricultural activity and less to point-sources. The general pattern of the concentration profile in Figure 3.9 confirms this hypothesis, since the areas adjacent to the middle flow of the Nitra River are used for growing irrigated crops. The level of lindane is high enough to cause negative effects on aquatic life (Somlyódy et al, 1994).

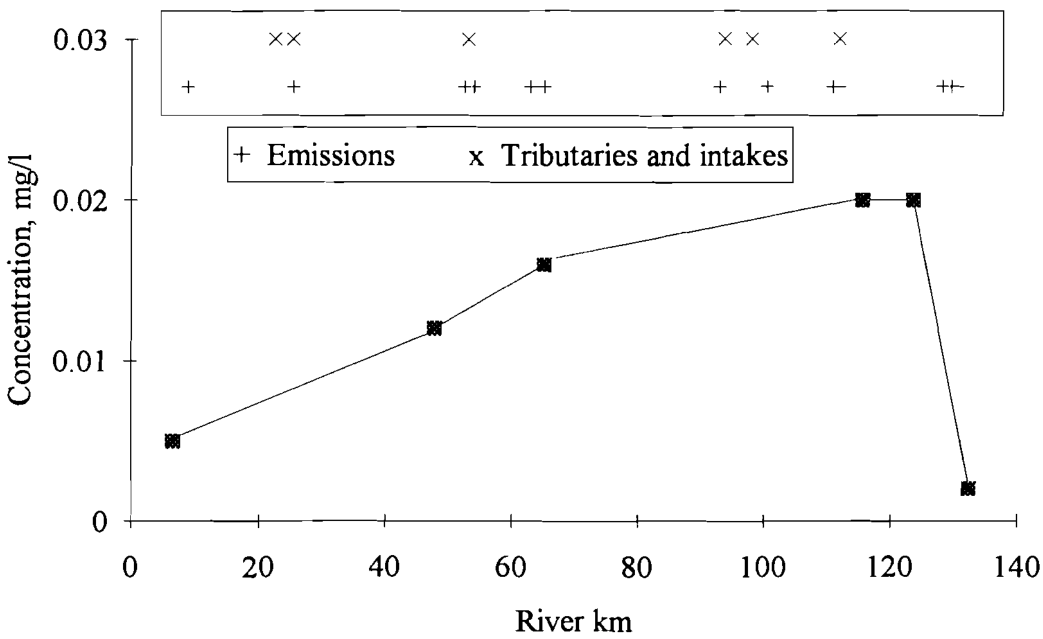


Figure 3.9 Longitudinal profile of lindane concentration in the Nitra River (August 1992 experiment).

The chemical industry complex in Novaky is a source of a number of organic micropollutants. In Table 3.1, the concentrations of seven of them are listed in the following order: concentration upstream of the complex, concentration in the factory effluent, concentration at the sampling point immediately below the discharge and further downstream. The pattern of occurence of these micropollutants is the same in each case: below the sensitivity limit upstream of the complex, significant amount in the effluent and in the river downstream to the discharge and very low further downstream. Therefore, the origin of the micropollutants could be traced, without a doubt, to the chemical factory at Novaky.

Table 3.1 The organic micropollutants impact of the chemical industry in Novaky in August 1992

Location	River km	mg/l Chloroform	mg/l 1,2 Dichloroethane	mg/l 1,1,2 Trichloroethene	mg/l 1,1,2,2 Tetrachl. ethene
Novaky over	132.50	*	*	*	*
Chem. f. Novaky-1	130.60	0.08	16.6	0.056	0.028
Chem. f. Novaky-2	129.70	0.004	0.86	0.060	0.008
Chalmova	123.80	0.004	0.84	0.016	0.021
Partizanske over	115.70	0.001	0.55	0.006	0.008
Praznovce	98.20	*	0.01	*	*

Location	River km	μgl 1,2 Dichlorobenzene	μg/l 1,3 Dichlorobenzene	μg/l Hexachlorobenzene
Novaky over	132.50	*	*	*
Chem. f. Novaky-1	130.60	0.20	16.70	Not measured
Chem. f. Novaky-2	129.70	0.190	9.400	Not measured
Chalmova	123.80	0.013	24.000	0.005
Partizanske over	115.70	0.050	10.300	0.003
Praznovce	98.20	*	0.380	*

Note: * - below the analytically detectable level

3.3 Mass Balances for the Upper Part of the Nitra River

The mass balance procedure accounts for material fluxes within a certain river region. Under presumed conditions, flux of a certain substance at a given location is equal to the flux at the upstream location plus all the emitted loads minus all the losses along the stretch considered. The loads and losses are specific for the substance under consideration, some of them being the result of discharge of the substance at certain emission points, others originate from non-point pollution or from bottom sediment (secondary pollution), and yet others result from various chemical and biological transformation processes in the river water. Thus, by checking the inventory of emitted loads against the longitudinal profile one can gain insight to the water quality processes.

The mass balance calculations were made in the following way. Starting from upstream, the flux of the substance was obtained and at any discharge point, the emitted amount was added. This cumulative mass represents the current flux in the river and was plotted as current mass flow. Mass flux was calculated at measurement points as concentration times the streamflow was substracted from the cumulative mass flow. This difference was plotted as the balance residual which will be indicated by crosses in the accompanying figures.

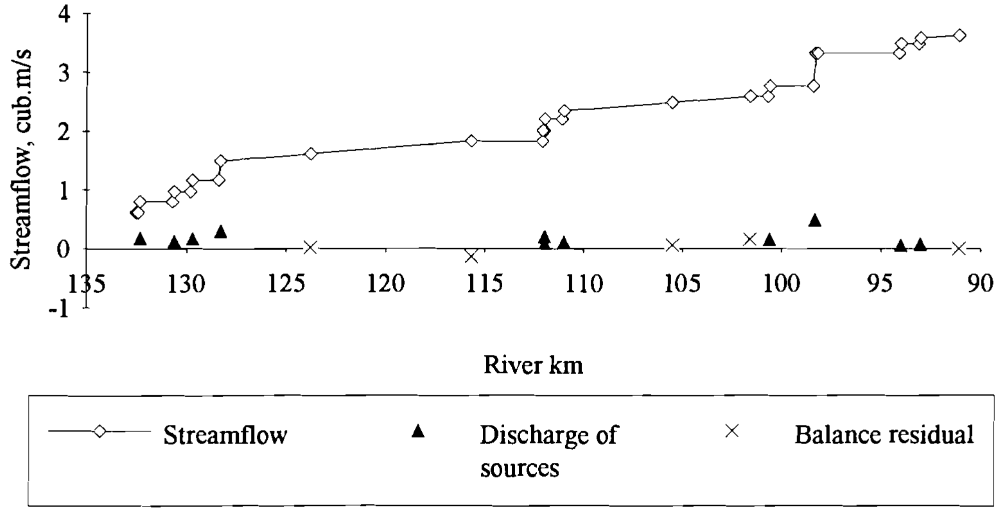


Figure 3.10 Streamflow balance for the upper part of the Nitra River (August 25-26 1992)

A closed balance of water flow is a prerequisite for all subsequent balance calculations, since the flux of any substance is calculated on the basis of the flow measurements. The streamflow balance for the upper part of the Nitra River is shown in Figure 3.10. The cumulative river streamflow is plotted with the line connecting diamonds. The magnitude of the discharges (tributaries or emission points) are shown in filled triangles, and the balance residuals calculated at the measurement points are plotted in crosses. The streamflow showed a systematic increase in balance residuals, and therefore an incremental inflow of 0.027 m^3/ sec per river km was introduced to provide a closed balance. The water quality of the incremental inflow usually is assumed to be close to that of groundwater. Smaller streams are presumed to be in good contact with the groundwater. For subsequent calculations, the concentration of substances in the incremental inflow was taken from the data on the small tributary, Nitrica (Figure 1.1), whose water quality parameters were close to those for other small creeks.

To check the validity of the assumptions used in order to close the streamflow balance (e.g. the amount of introduced lateral inflow), the mass balance of conservative substances (dissolved solids or chloride) can be evaluated. The chloride mass balance is plotted in the Figure 3.11 in a similar fashion as the stream flow balance (Figure 3.10).

The chloride-ion mass balance has some local deviations, but the overall balance error for the entire stretch is less than 10% of the mass flow. Bearing in mind the inherent uncertainties in the measurement procedures and the temporal changes of emissions, the chloride mass balance can be regarded as adequately closed. The streamflow values obtained would be used as a basis for the subsequent estimation of other substance fluxes .

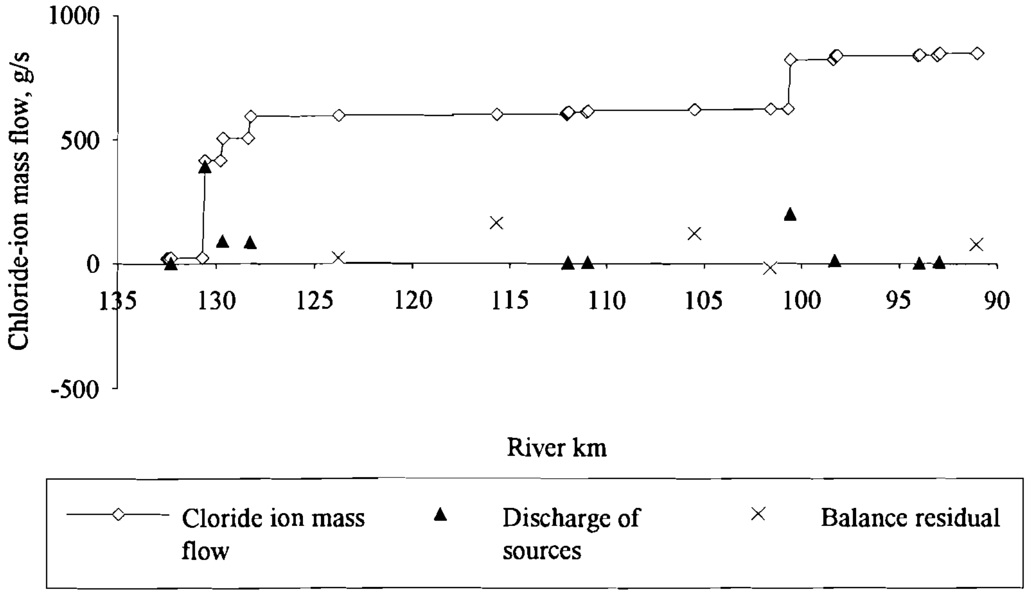


Figure 3.11 Chloride-ion mass balance for the upper part of the Nitra River (August 25-26, 1992 experiment)

With regards to biodegradable organic material, river pollution is characterized by the amount of biological oxygen demand (BOD). The mass balance of BOD-5 (shown in the Figure 3.12) is affected not only by external sources, but also by the instream destruction of organics by heterotrophic bacteria.

As the organic material undergoes microbial decomposition, the balance residual in the mass flow is systematically decreasing, indicating a (instream) loss of mass. From the beginning to the end of the upper stretch of the river, the loss in mass flow is 40% of the total emitted amount. Assuming that the loss in mass flow can be explained by the first-order decay, we can write

$$F(t) = F(0) \exp(-k\, t), \qquad (1)$$

where F(t) - mass flow at the end of the stretch,
F(0) - mass flow at the beginning of the stretch,
t - travel time for the stretch (days),
and k is the decay rate (1/d).

From (1) it is easy to estimate decay rate k:

$$k = -\frac{1}{t}\ln\frac{F(t)}{F(0)} \qquad (2)$$

The pollution sources are distributed along the stretch, so for pollution entering the stretch closer to the downstream end travel time is less. If we roughly estimate the average travel time for pollution discharged in this stretch as 13 hours (half of the travel time of 26 hours for the whole stretch), the corresponding decay rate computed from (2) will be 1.0 1/day. This is close to the value 1.1 1/day obtained from the same data with the help of more sophisticated parameter estimation technique (Somlyódy et al, 1994).

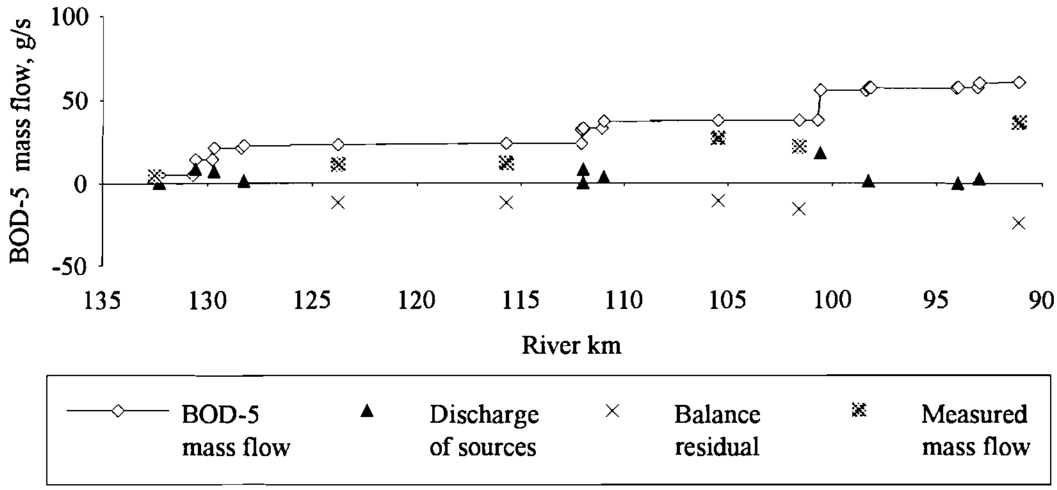


Figure 3.12 BOD-5 mass balance for the upper part of the Nitra River (August 25-26, 1992 experiment)

The major emitters of BOD-5 and, consequently, organic material in this stretch of the Nitra River are (from the upstream to the downstream) chemical industries in Novaky, municipal sewage works at Partizanske, the tannery factory in Bosany and the municipal wastewater treatment plant in Topolcany. Of the total emitted mass of BOD-5 effluent, the tannery factory accounts for 35% of the emission, (the most intensive single polluter), the municipalities, together, account for 30% of total BOD emission and other industries comprise the rest.

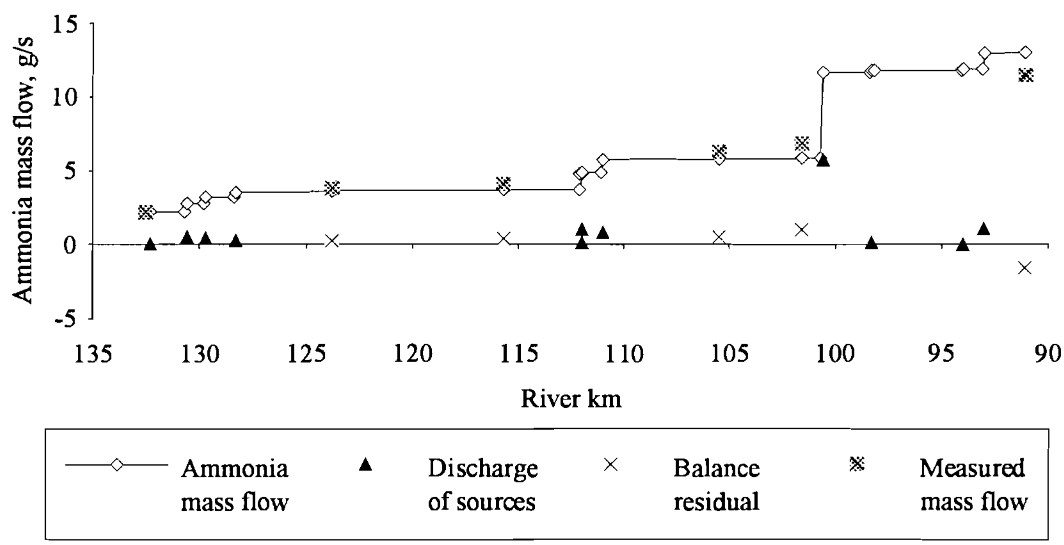


Figure 3.13 Ammonia nitrogen mass balance for the upper part of the Nitra River (August 25-26, 1992 experiment)

The ammonia nitrogen mass balance is shown in Figure 3.13. One can see that the balance residuals are sometimes positive, indicating the presence of unaccounted-for sources of ammonia. These discrepancies are relatively small and could be caused by significant diurnal changes of emission intensity. The overall loss of ammonia mass constitutes 14% of the emitted amount, which leads to a 0.25 1/day estimation of the removal rate . The estimation from (Masliev, Somlyódy, 1994), for which Monte-Carlo methodology was used, is 0.24 1/day.

The distribution of the load between the emitters is as follows: the tannery factory in Bosany provides 55% of the emitted mass, municipalities accounte for 30% of pollution and other industrial emitters comprise the rest of the mass.

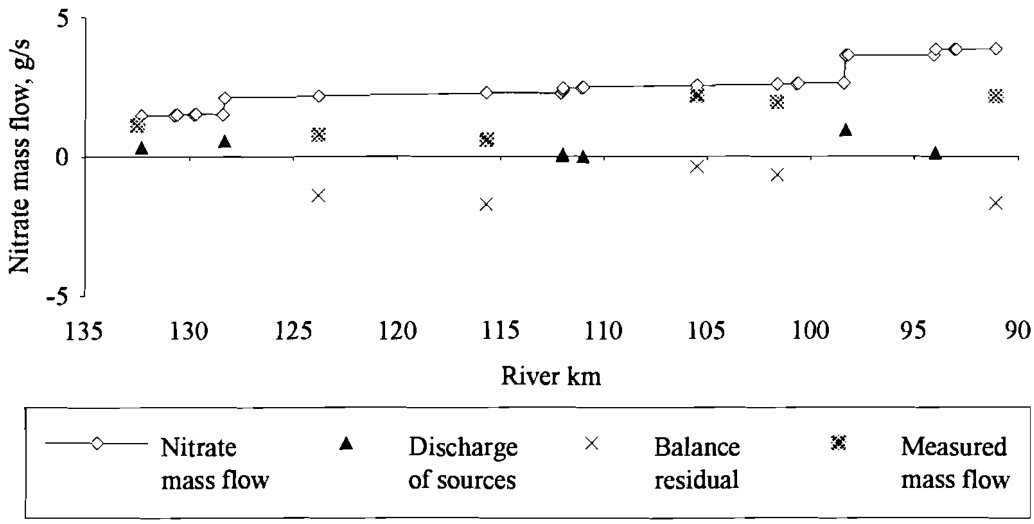


Figure 3.14 Nitrate nitrogen mass balance for the upper part of the Nitra River for the August 25-26, 1992 experiment

The nitrate mass balance is shown in Figure 3.14. The residual analysis suggests that the nitrate nitrogen is removed from the system. Since the dissolved oxygen concentration in the river is low, it is possible that the process of denitrification is taking place, being favored by anaerobic conditions. This process is typical for water polluted with organic materials during low-flow conditions (Water Quality Assessment, 1992). This hypothesis can be further verified if microbiological analysis would reveal the presence of the denitrifying microorganisms in the river and interstitial waters of the sediment. The estimated removal rate of the nitrate nitrogen is about 1.0 1/day.

The total phosphorus mass balance for the upper part of the Nitra River, shown in Figure 3.15, indicates loss of mass from the system. The loss can be explained with consumption of reactive phosphorus by aquatic biota (e.g. phytoplankton, see Figure 3.7) and sedimentation of the particulate phosphorus to the river bed. The ortophosphate phosphorus mass balance, shown in Figure 3.16, indicates a certain loss of reactive phosphorus from the river. The rest of the total phosphorus loss is likely to be explained by the sedimentation process. The estimations for the removal rates (1.3 1/day and 1.7 1/day for the total phosphorus and for the ortophosphate fraction, respectively) are unrealistically high. In this case, Monte Carlo parameter estimation process could be used to obtain more realistic rate, like in (Masliev, Somlyódy, 1994). Another possibility is to assume that some portion of emitted load is very quickly removed from the system immediately after entering the river.

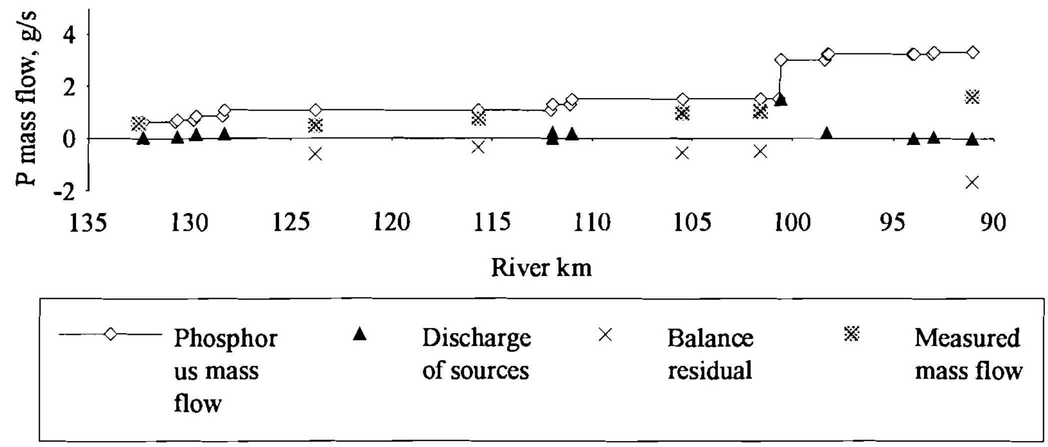


Figure 3.15 Total phosphorus mass balance for the upper part of the Nitra River (August 25-26, 1992 experiment)

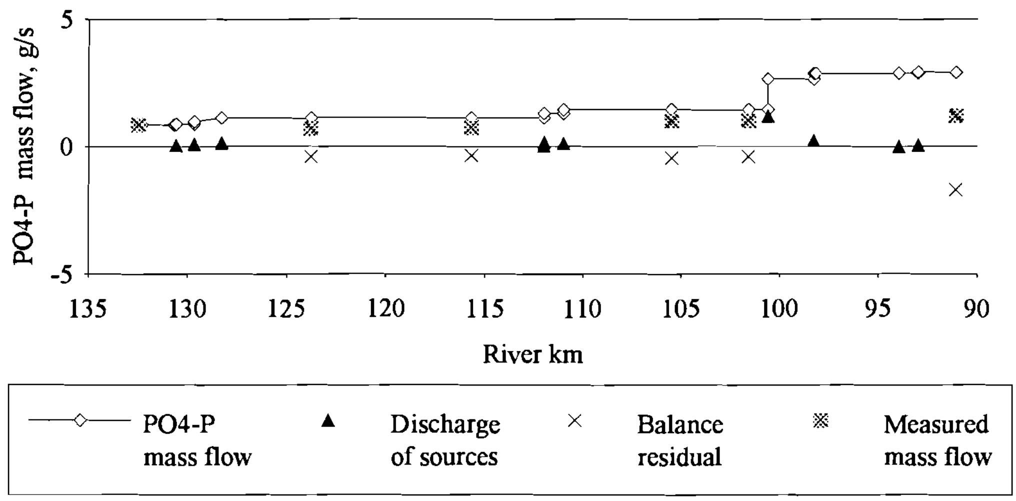


Figure 3.16 Ortophosphate phosphorus mass balance for the upper part of the Nitra River (August 25-26, 1992 experiment)

The distribution of the phosphorus load into the upper part of the river is as follows: 20% from the industrial complex at Novaky, 60% from the tannery in Bosany, and the rest (20%) from municipalities. The principal input of phosphorus into the river is provided by industrial emissions, although municipalities also play a role. It is unclear how much phosphorus is bound within the river sediment, but if this amount is significant, then there will no be immediate effect on the instream phosphorus concentration if emissions are reduced.

3.4 Mass Balances for the Lower Part of the Nitra River

The river streamflow mass balance does not show any major discrepancies (Figure 3.17). By observing the chloride-ion mass balance (Figure 3.18) one can verify that the mass balance is closed.

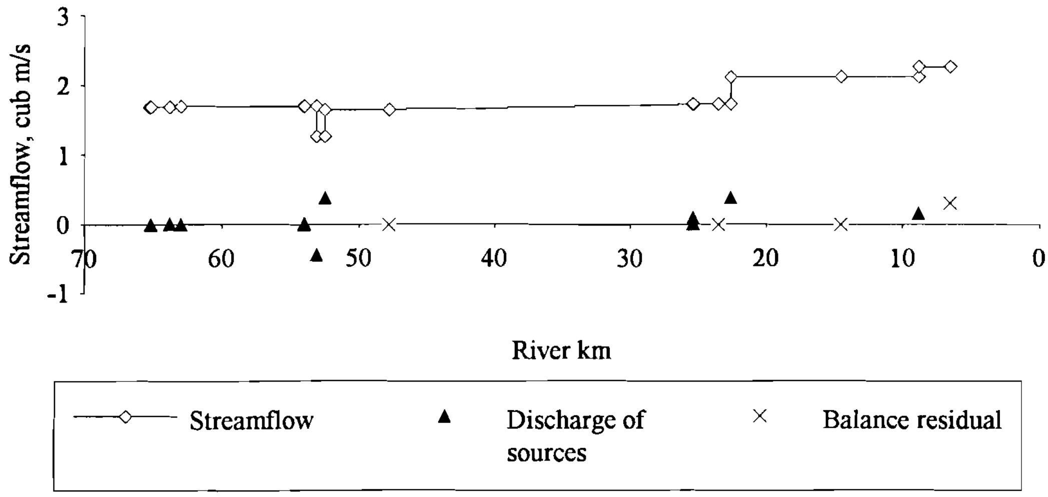


Figure 3.17 Streamflow balance for the lower part of the Nitra River (August 25-26, 1992 experiment)

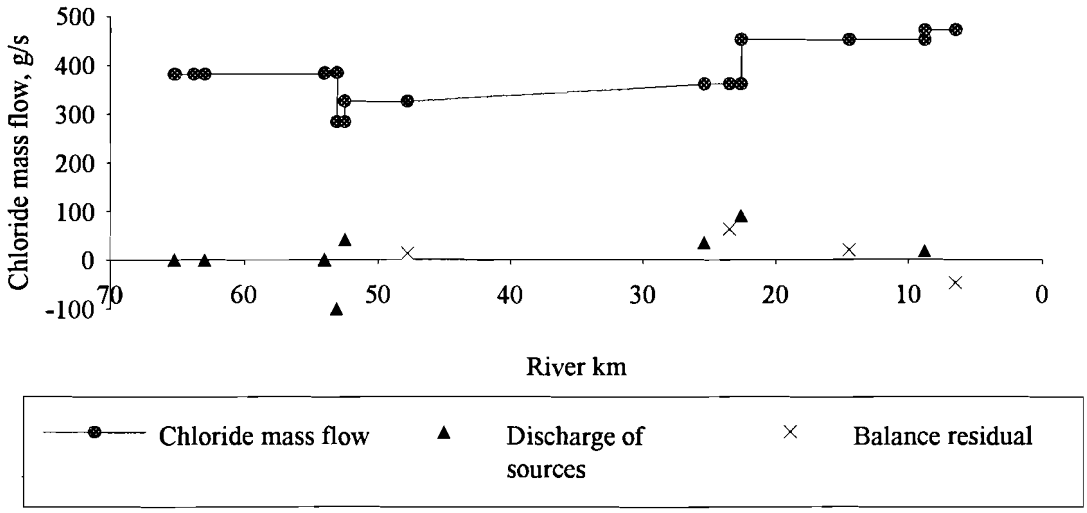


Figure 3.18 Chloride-ion mass balance for the lower part of the Nitra River (August 25-26, 1992 experiment)

The mass balance of BOD is shown in Figure 3.19. Two major emitters are providing nearly all (92%) of the organic material load to the river, namely the Nitra and Nove Zamky sewage treatment plants; the rest is emitted by industrial enterprises. The balance residuals are systematically more and more negative, indicating progressive destruction of the waste material in the river water. Of all the organic material flowing into the river at the lower stretch (flow from the upstream, emissions and tributaries) only 60% reaches the mouth of Nitra River, and 40% is destroyed in the river by heterotrophic bacteria. This indicates high microbiological activity in this river stretch, caused by high levels of pollution. This river stretch, in fact, serves as a secondary treatment facility by stabilizing waste material which was not oxidized during the initial municipal treatment process. This can be also observed by high in-stream BOD concentrations (exceeding 10 mg/l), providing the necessary food source for the heterotrophs. The saprobic index of water in this stretch (measured in June 1993) exceeds 2.5, characterizing an abundance of waste-stabilizing microorganisms. The rough estimation for the BOD removal rate is 1.4 1/day. This is two times more than the value obtained in the Monte-Carlo procedure (Somlyódy et al, 1994). In this case the rough estimation procedure does not provide realistic parameter value.

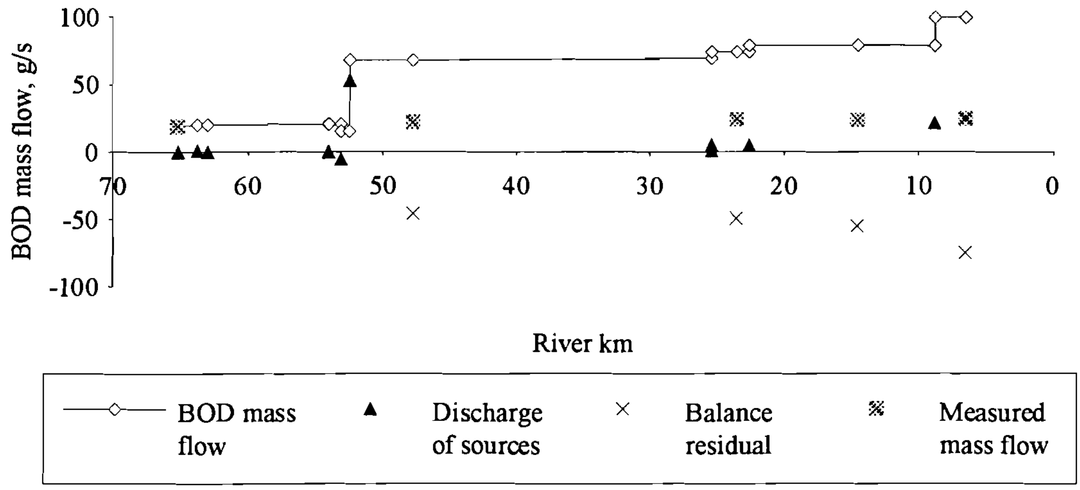


Figure 3.19 BOD-5 mass balance for the lower part of the Nitra River (August 25-26, 1992 experiment)

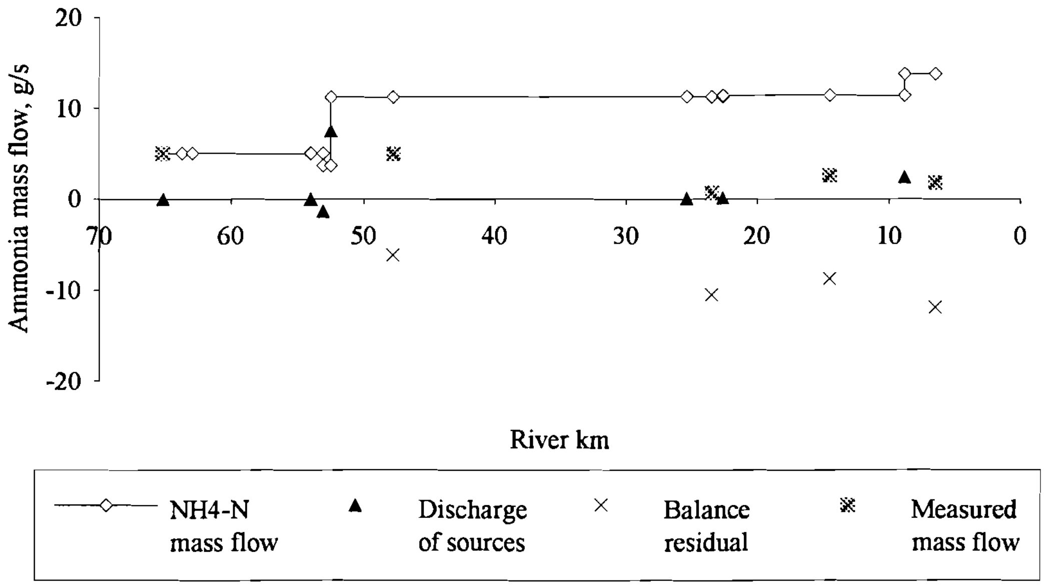


Figure 3.20 Ammonia nitrogen mass balance for the lower part of the Nitra River (August 1992 experiment)

The ammonia nitrogen mass balance (shown in Figure 3.20) exhibits significant losses in the emitted amount along the course of the river. The estimation for the loss rate is 2.0 1/day. This can signify, again, increased microbiological activity in this stretch, namely proliferation of nitrifiers (Nitrosomonas and Nitrobacter). This conclusion can be further verified by the analysis of nitrate nitrogen (Figure 3.21). The positive mass balance at the Nitriansky Hrádok location (river km 25) signals an unaccounted for nitrate source. This source can be related to nitrate release as the result of nitrification process. Further downstream, the nitrate content in the river again diminishes, possibly due to the phytoplanktonic uptakes (Figure 3.7) or denitrification processes.

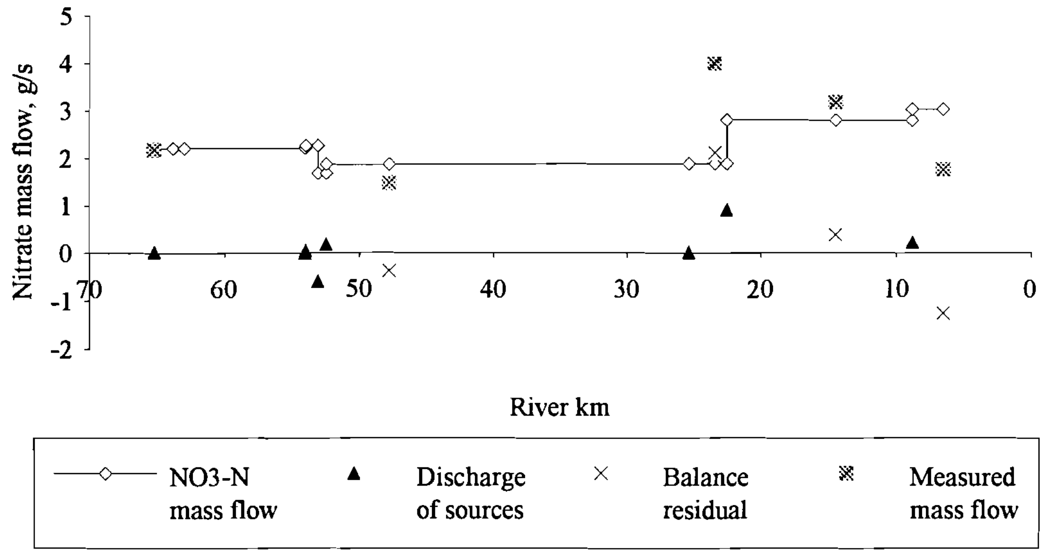


Figure 3.21 Nitrate nitrogen mass balance for the lower part of the Nitra River (August 25-26, 1992 experiment)

The total phosphorus mass balance can be analysed on the basis of Figure 3.22 and the ortophosphate phosphorus mass balance is shown in Figure 3.23. The principal input of phosphorus into the river comes from two municipal treatment plants, Nitra and Nove Zamky, while industry provides about 5% of the load. It can be inferred that the losses of total phosphorus mass flow, as in the case of the upper stretch, are caused by the uptake of aquatic plants and sedimentation. The estimated removal rate is 0.12 1/day. The loss in ortophosphate phosphorus mass from the lower stretch of the river (Figure 3.23; estimated removal rate is 0.7 1/day) can be explained by development of aquatic plants in the lower stretch with slow water movement.

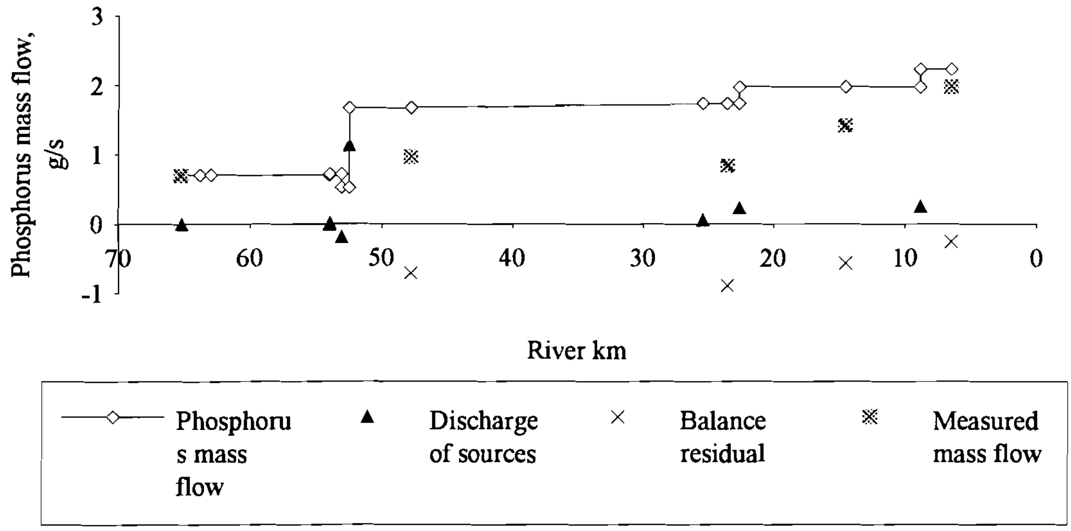


Figure 3.22 Total phosphorus mass balance for the lower part of the Nitra River (August 1992 experiment)

Relatively high chlorophyll-a concentrations in the lower stretch (in the range 100-150 µg/l, cf. Figure 3.7), further support this conclusion. High diurnal variations of dissolved oxygen concentrations (from 3 to 9 mg/l with afternoon maximum), observed during the August 1992 experiment at Nove Zamky (river km 14.5), also speaks in favor of photosynthetic algae activity in the lower stretch of the Nitra River (Figure 3.24).

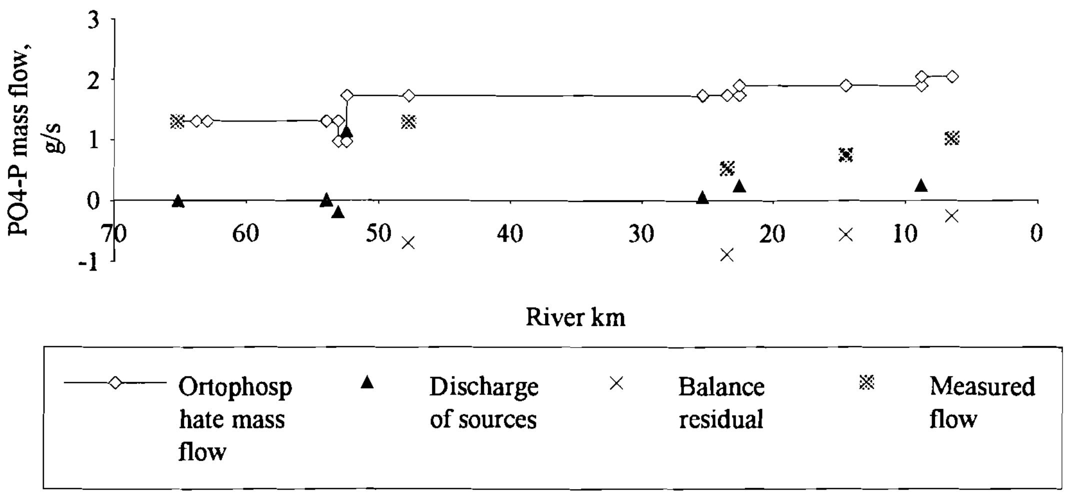


Figure 3.23 Ortophosphate phosphorus mass balance for the lower part of the Nitra River (August 25-26, 1992 experiment)

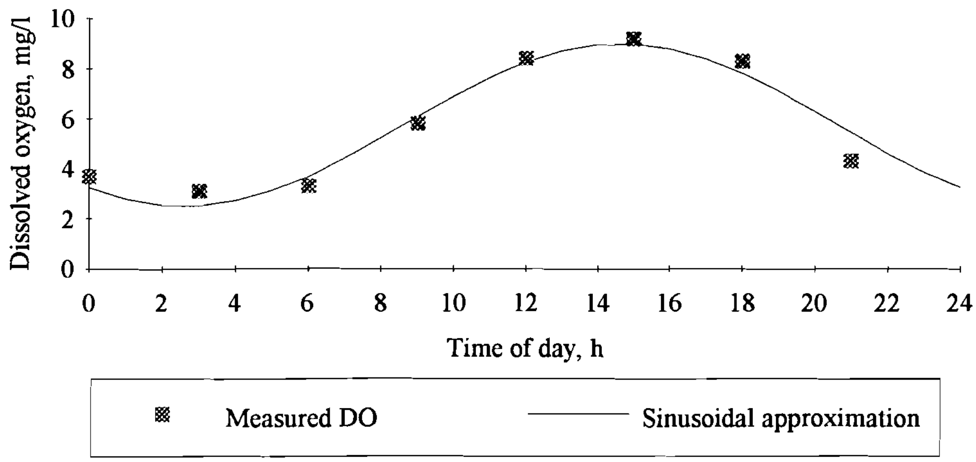


Figure 3.24 Diurnal variations in dissolved oxygen at the measurement point Nitrianska Streda (river km 91.1) during August 25-26, 1992

3.5 Distribution of the emitted load between polluters

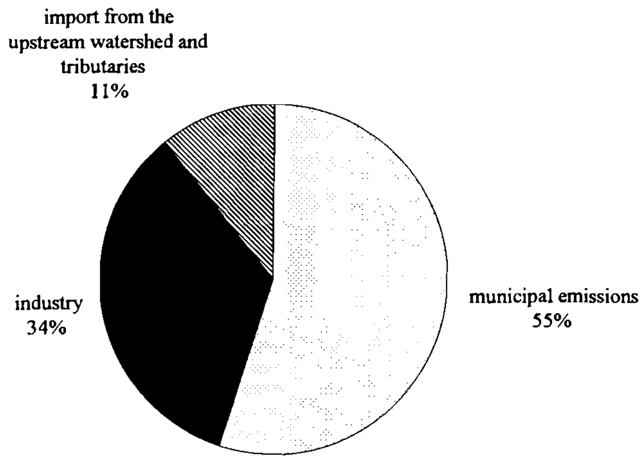
Figure 3.25 and Table 3.2 summarize the balance of organic material in the Nitra River on the basis of the August 1992 experiment. It is important to note that the majority of the organic material is discharged into the river by municipal wastewater treatment plants, while industry accounts for 34% of the load. Tributories and upstream stretches contribute an order of magnitude less. Most part of the emitted organic material (60%) is decomposed in the river by microorganisms, and only 17% of the emitted organic reaches the mouth of Nitra. This indicates that current wastewater treatment does not provide sufficient removal of organic material, and heterotrophic organisms in the river have enough substrate for growth.

Table 3.2 The overall balance of BOD-5 mass flows in the Nitra River

Load	kg/day	Removal	kg/day
total emitted load	11 280	export from the mouth	2 134
of that:		removed from the river	10 493
municipal emissions	6 953	of that:	
industry	4 327	abstracted for river branches (sanitary discharge)	646
import from the upstream catchment and tributaries	1 347	*abstracted for agriculture	2 090
		assimilated by microorganisms	7 757

* assuming the loss of mass between P15 and P16 to be caused by irrigation abstraction

Sources of BOD-5 loads to the Nitra River



Outflows of BOD-5 from the Nitra River

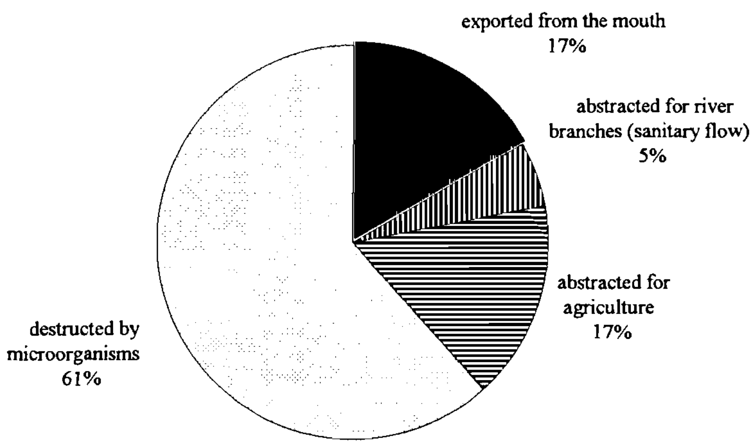


Figure 3.25 The overall balance of BOD-5 mass flows in the Nitra River (August 1992 experiment).

3.6 Summary of the August 1992 measurement program

On the basis of the above analysis of water quality longitudinal profile data from August 1992 experiment, the following conclusions could be made:

- During summer low-flow period oxygen deficit in the Nitra River exceeds both national and international standards.
- Dissolved oxygen problem is caused by exceptionally heavy conventional pollution of the river water with organic material, both from municipalities and from the industry.
- Mass balance analysis and estimations of process rates indicate intensive microbiological activity in the river water (stabilization of organic waste material). This fact is confirmed also by microbiological test (saprobity index).
- Level of phosphorus and nitrogen concentrations is high enough to cause intensive development of phytoplankton (river eutrophication). Mass balances indicate loss of both mineral nitrogen and phosphorus from the river water, accompanied by development of aquatic plants (chlorophyll "a").
- Intercomparison of regular monitoring data and experiment results indicate large variabilities/uncertainties in data; process rates estimates on the basis of mass balances often are unrealistic. This calls for application of more advanced parameter estimates techniques to account for uncertainty in data.
- Second experiment is desirable for detailing important water quality processes (e.g. sedimentation/hydrolysis), resolving components of organic matter and nutrients (particulate organic matter, organic phosphorus and nitrogen), and verification of rate estimates.

4 JUNE 1993 EXPERIMENT

4.1 Longitudinal profiles

Figure 4.1 shows the longitudinal profile of the river streamflow and the dissolved oxygen based on the results of the June 1993 experiment. It can be seen that the streamflow is significantly higher than during the August 1992 (cf. Figure 3.5). This period is usually associated with summer precipitation, producing surface runoff which contributes to an increase in streamflow.

The higher streamflow increases dilution of the wastewater, consequently, the concentrations of the pollutants are lower than during the low-flow (cf. Figures 3.6 and 4.2). Therefore it is not surprising that there are no sites with major dissolved oxygen reductions (Figure 4.1). As mentioned earlier, the higher streamflows during the June experiment allowed for the checking of the parameter estimation under different hydraulic conditions, therefore providing validation in time.

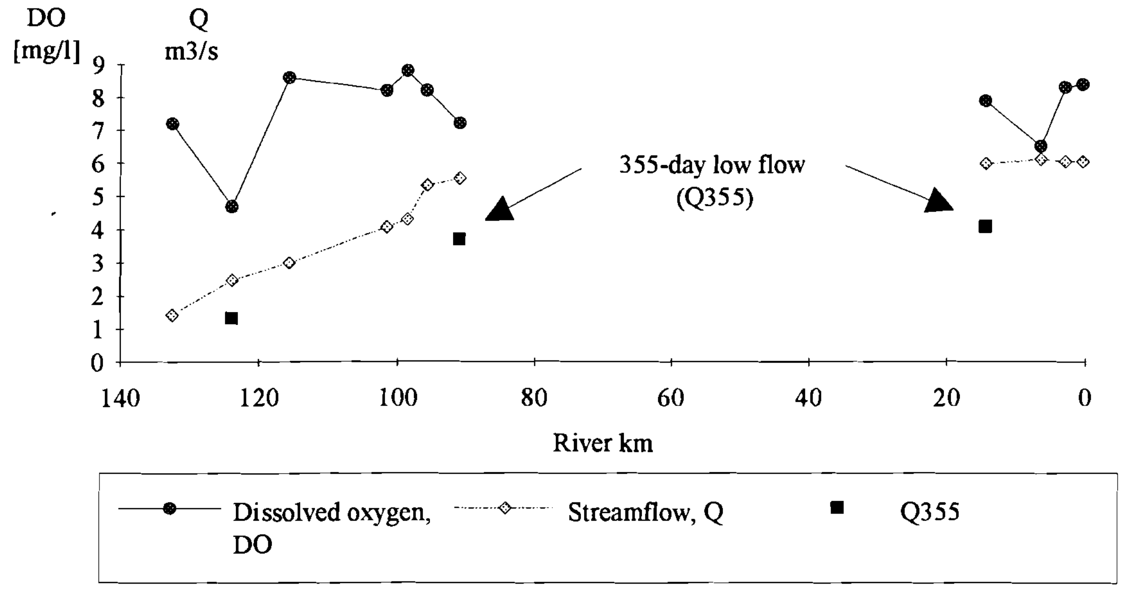


Figure 4.1 Longitudinal profile (partial) of the streamflow and dissolved oxygen in the Nitra River (June 1993 experiment)

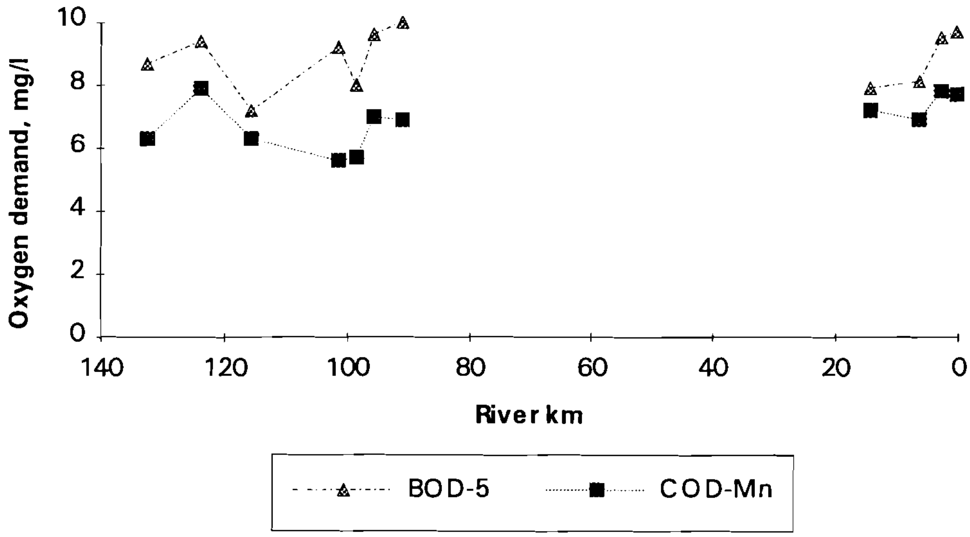
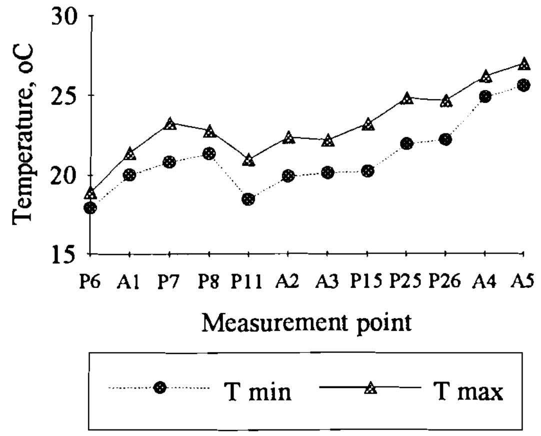


Figure 4.2 Longitudinal profile (partial) of the biological and chemical oxygen demand in the Nitra River (June 1993 experiment)

Finally, Figures 4.3-4.5 illustrate the range of the temporal changes registered during the 4-day sampling program in June 1993. The minimum and maximum registered values are presented on the plots. For temperature, dissolved oxygen, chemical and biological oxygen demand the ranges of extreme values margins are narrow, i.e. the changes were not profound. However, for nitrogen and phosphorus (Figure 4.5) the changes are significant. The difference between the oxygen demand and the nitrogen-phosphorus data can be partially explained by variations in the phytoplankton uptakes subject to diurnal changes (cf. Figure 3.24 and 3.7).



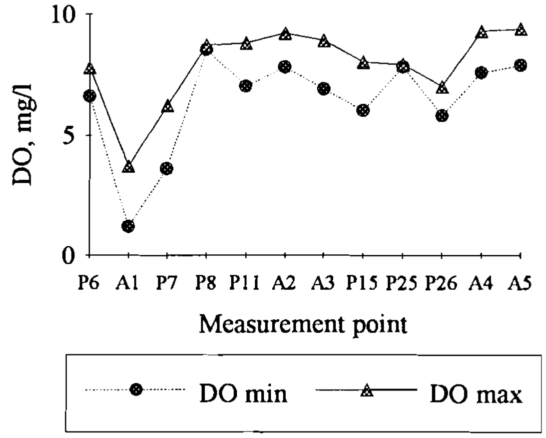
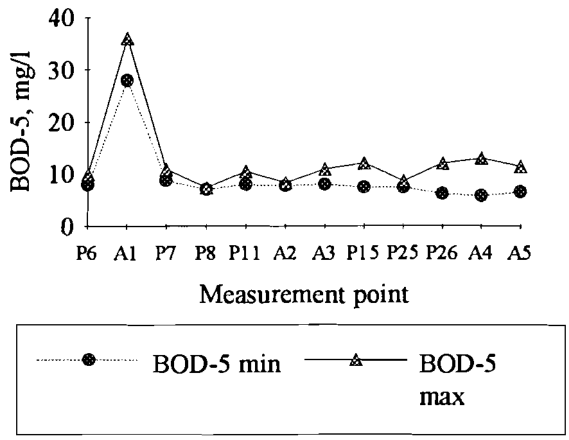


Figure 4.3 Range of the temporal changes in the water temperature and dissolved oxygen (June 1993 experiment)



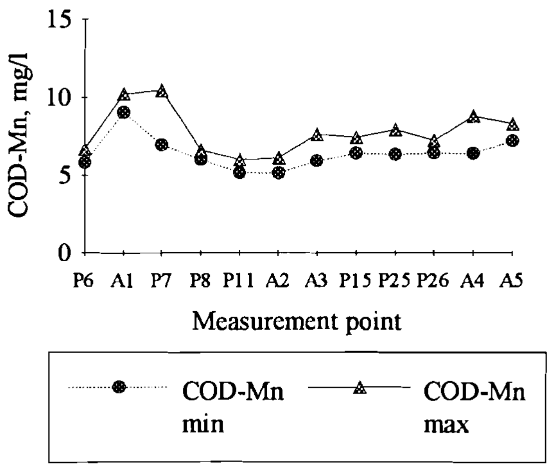
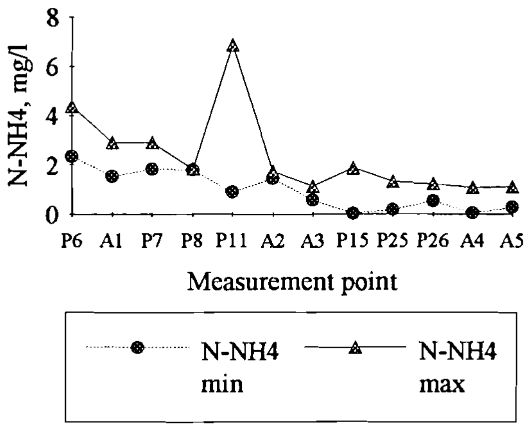


Figure 4.4 Range of the temporal changes in the biological and chemical oxygen demand (June 1993 experiment)



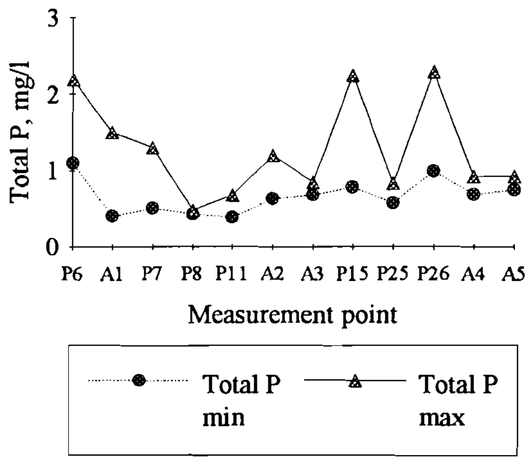


Figure 4.5 Range of the temporal changes in the ammonia nitrogen and total phosphorus (June 1993 experiment)

4.2 Composition of organic material in the effluent and river water

The June 1993 experiment was designed with the aim to get an idea on some details of water quality processes in the river, including finer fractioning of the organic pollution, its relation to the nutrients balance and sediment processes. Therefore, the list of measured parameters for June 1993 experiment was prepared with the aim to resolve suspended and dissolved fractions of organic material. For this purpose, two tests of BOD-5 were prepared, one with initial sample and the other with the sample filtered through 0.45 μm filter. The particulate organic material was detained by the filter, therefore its oxygen demand was not registered by the second test. Similar procedure was also performed for chemical demand measurements. Both effluent and river water samples were processed in this manner.

By substracting the oxygen demand of the filtered water from that of the original sample, it is possible to estimate the oxygen demand of particulate organic material. The amount of particulate organic material in the sample was measured by heating the filtrate (suspended solids) at 600°C and evaluating the loss of mass. The relationship between particulate organic matter and its oxygen demand indicates the ratio of (easily) destructible organic matter in suspended form. This is an important characteristic of both effluent and river water which should be known for application of water quality models describing sedimentation and processes in the river bottom layer, since only the particulate organic material is subject to sedimentation.

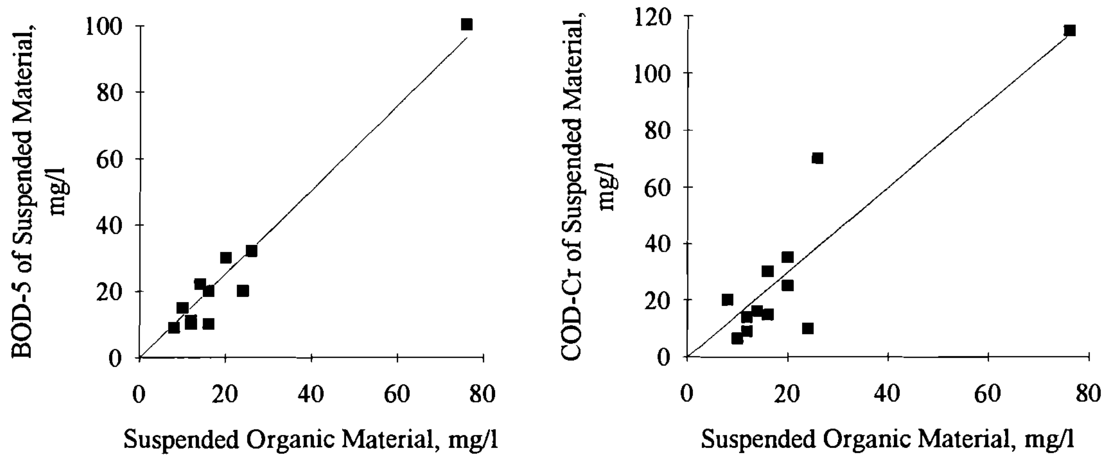


Figure 4.6 Relationship of suspended organic material and BOD-5 and COD-Cr of suspended material for biologically treated effluent in Nitra basin (June 1993 experiment).

For biologically treated effluent water this relationship turned out to be fairly stable (1 mg of particulate organic material corresponds to 1.5 mg chemical oxygen demand and 1.26 mg of BOD-5, Figure 4.6). The linear regression for 12 samples explains this relationship with square of correlation coefficient $R^2 = 0.95$ and 0.9 for BOD-5 and COD-Cr, respectively. This means that significant part of the particulate organic matter in the effluent of treatment facilities is easily destructible, i.e. not stabilized. In part this reflects low level of (partial) biological treatment typical for Nitra River basin, where the majority of plants are overloaded and treatment efficiency is low.

Samples from the river water (Figure 4.7) show more diversified ratios of oxygen demand and particulate organic material. It is the consequence of several factors such as variation of in-river dilution ratio for emissions and difference in river stabilization times for effluent particles. Moreover, part of organic material is not of the sewage origin, which leads to increased variation. In general, the ratio of oxygen demand to the particulate matter is significantly lower in river water (0.08 for BOD-5 and 0.24 for COD-Cr). The proportion of BOD-5 versus COD-Cr is also much smaller. This indicates progress in the degree of stabilization of effluent organic matter in the river water. It is a result of two simultaneous processes: hydrolysis and heterotrophic destruction (Rinaldi et al, 1979). As a result of hydrolysis, there is an increase in concentration of dissolved organic material and, therefore, increase in its oxygen demand. As contrasted to the first process, the oxidation of organic matter by heterotrophic bacteria does not give rise to oxygen demand of filtered sample. For water quality models dealing with sedimentation of organic material it is important to know (at least approximately) the rates of both processes. Rough estimates of the process rates were made using the mass balance method (Section 4.3).

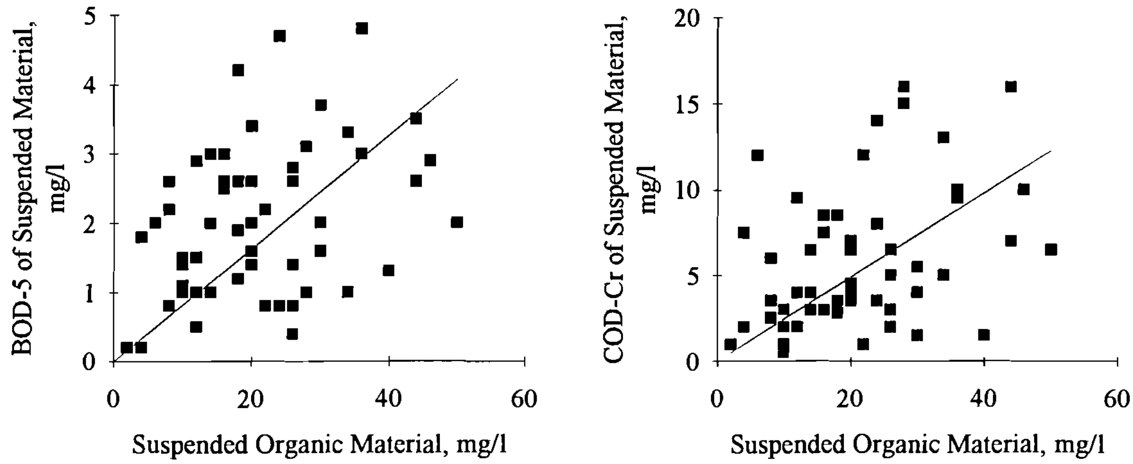


Figure 4.7 Relationship of suspended organic material and BOD-5 and COD-Cr of suspended material for river water in Nitra basin (June 1993 experiment). $R^2 = 0.735$ and 0.689, resp.

4.3 Mass balances

Mass balances were analyzed in more detail for the upper section of the river (Novaky-Partizanske, cf. Figure 1.1), where numerous pollution sources of different origin are found.

The water balance for this section of the river is shown in the Figure 4.8. It can be seen that the discrepancies are not significant.

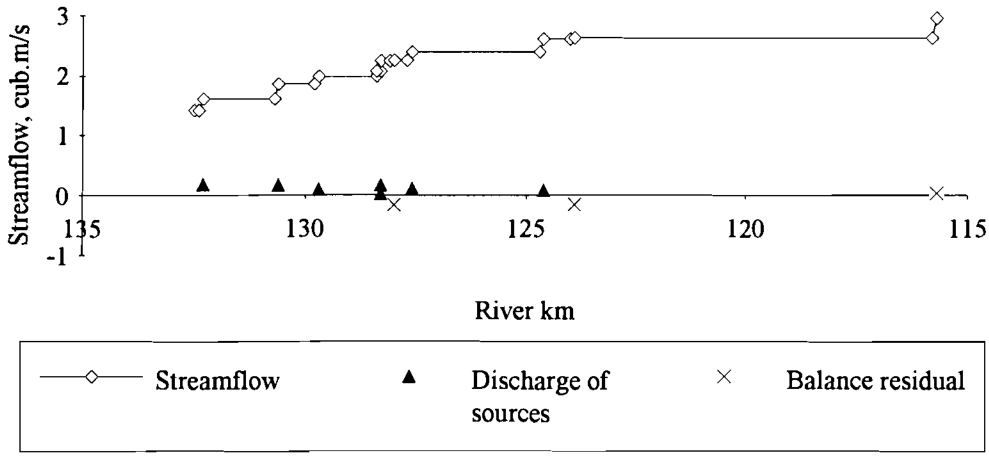


Figure 4.8 Streamflow balance for the upper part of the Nitra River (June 1993 experiment).

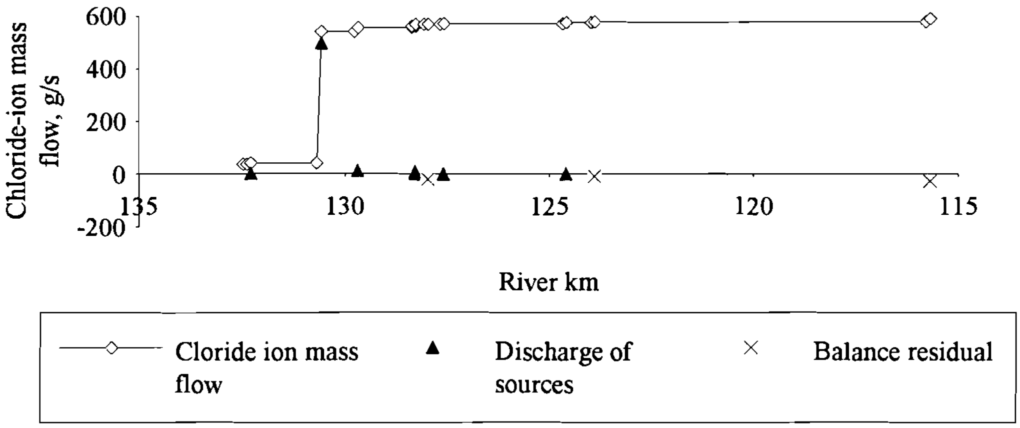


Figure 4.9 Chloride mass balance for the upper part of the Nitra River (June 1993 experiment)

The mass balance of chloride ion, which is conservative material, is shown in Figure 4.9. The balance residuals are small as compared to the mass flow of chloride in the river.

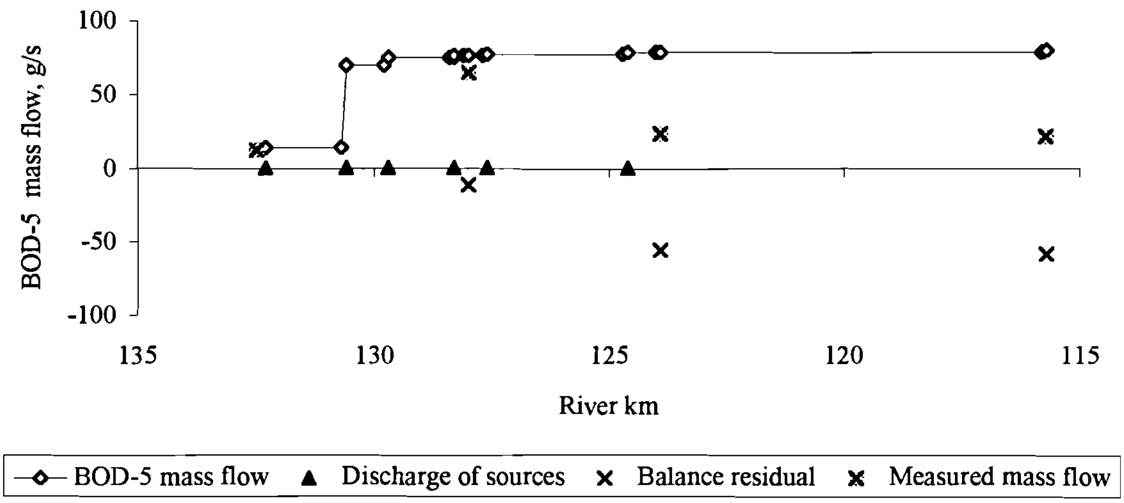


Figure 4.10 BOD-5 mass balance for the upper part of the Nitra River (June 1993 experiment)

BOD-5 mass balance is shown in Figure 4.10. It indicates progressive removal of organic material from river water by heterotrophic bacteria which use it as energy source (Rinaldi et al, 1979). BOD-5 removal rate can be estimated on the basis of travel time for this reach (about 9 hours) and percent material removed. For this reach it is 0.95 1/day, close to the previous estimate (Section 3).

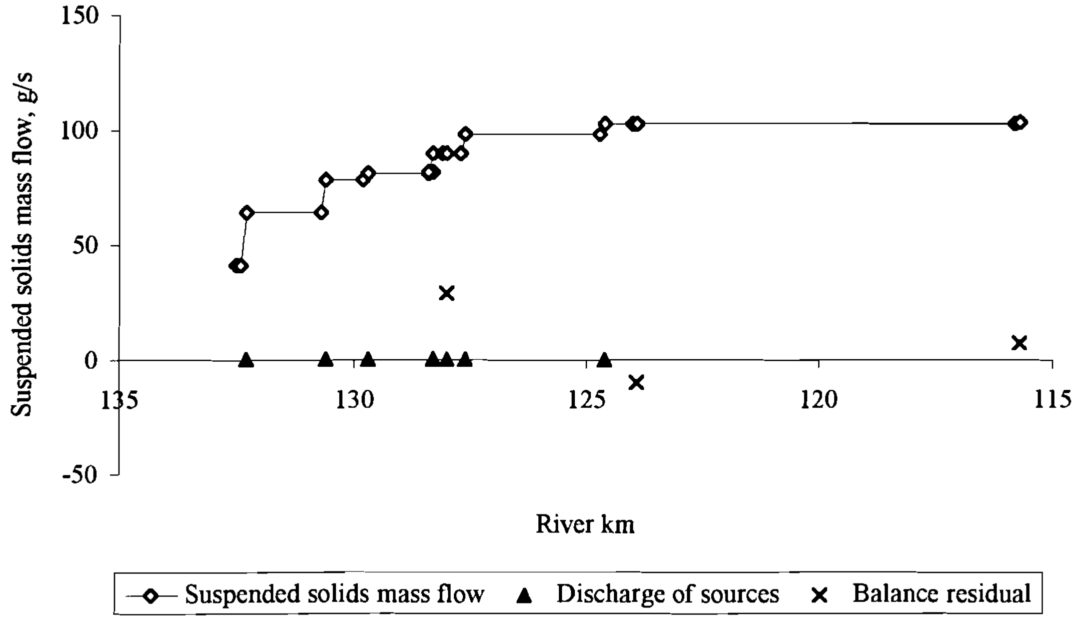


Figure 4.11 Suspended solids mass balance for the upper part of the Nitra River (June 1993 experiment)

Suspended solids mass balance (Figure 4.11) does not indicate significant removal of mass from the river (the balance residual at measurement point A1, river km 128, is caused by incomplete mixing of tributory Lazny P. at this cross section). It shows that sedimentation processes are not intensive in this part of the river. This is justifiable, considering relatively high slopes of river bottom (0.002 - 0.004) in this mountaineous part of the basin.

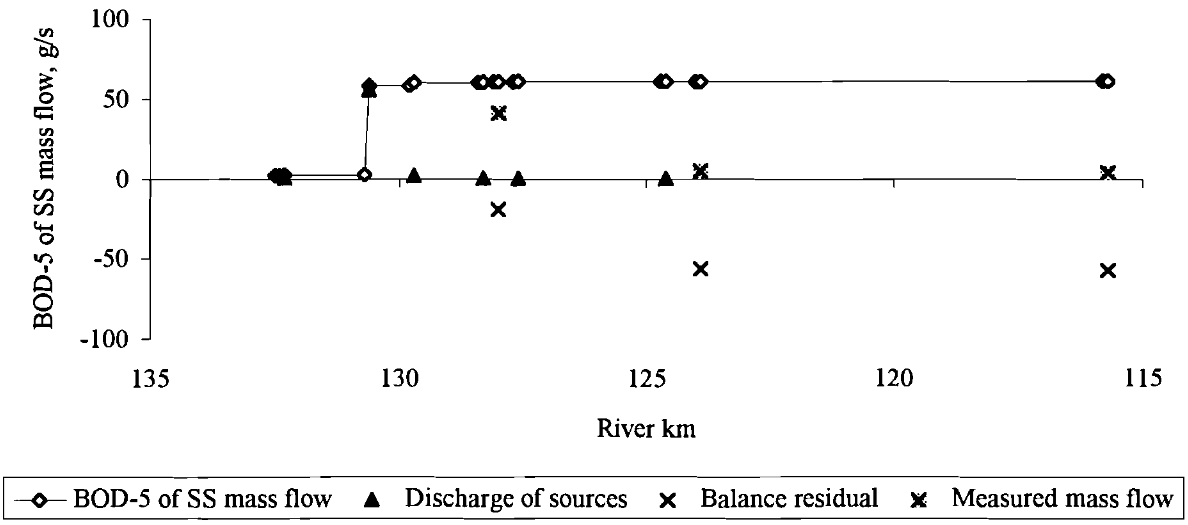


Figure 4.12 Particulate BOD-5 mass balance for the upper part of the Nitra River (June 1993 experiment)

Mass balance of BOD-5 of suspended material (Figure 4.12) demonstrates rapid removal of material from the river (removal rate estimate is 4.0 1/day). As was discussed in Section 3.2, it is combined rate of two processes: hydrolysis and bacterial stabilization. The removal rate of 4.0 1/day significantly exceeds typical overall decomposition rates (0.2-0.5 1/day, depending on the level of wastewater treatment). Since the particluate and dissolved fractions of BOD are of the same order of magnitude, the rate of about 3-4 1/day should be ascribed to the process of hydrolysis of particulate organic material in the river. Overall decomposition rate can be somewhat higher in this case, considering small water depth in this stretch (~ 0.5 m) and better contact of organic material with benthic microorganisms.

Hydrolysis converts particulate organic material into dissolved form, therefore acting as an "internal source" of dissolved oxygen demand. The mass balance of dissolved BOD-5 (Figure 4.13) properly reflects this fact. Although biological decomposition should remove dissolved organic matter and cause loss of mass from the system, the balance does not show this removal. Apparently, bacterial decomposition of dissolved organic is offset by addition of dissolved fraction from hydrolysis.

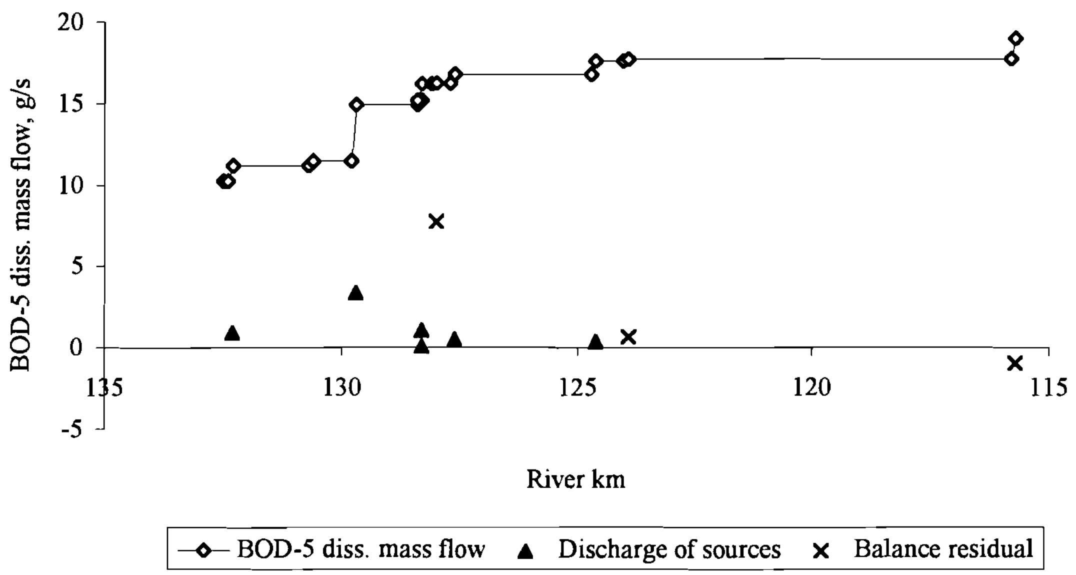


Figure 4.13 Dissolved BOD-5 mass balance for the upper part of the Nitra River (June 1993 experiment)

Organic forms of phosphorus and nitrogen were calculated as the difference between the total concentration and concentration of the mineral forms. Mass balance of the organic nitrogen is shown in Figure 4.14. There is rapid loss of mass from the river at a rate close to that of hydrolysis (~ 5 1/day). It can be surmised that most of organic nitrogen appears in the effluent in particulate form, and it is rapidly utilized when converted to dissolved form by hydrolysis. According to recent models of organic oxidation (Henze e.a., 1987), rates of hydrolysis of carbonaceous organic materials and of particulate organic nitrogen are close to each other. The hydrolysis of organic nitrogen should give rise to mineral nitrogen (dissolved fraction) minus uptake from the aquatic organisms. Figure 4.15 indicates that there is indeed some increase of mineral nitrogen in the system.

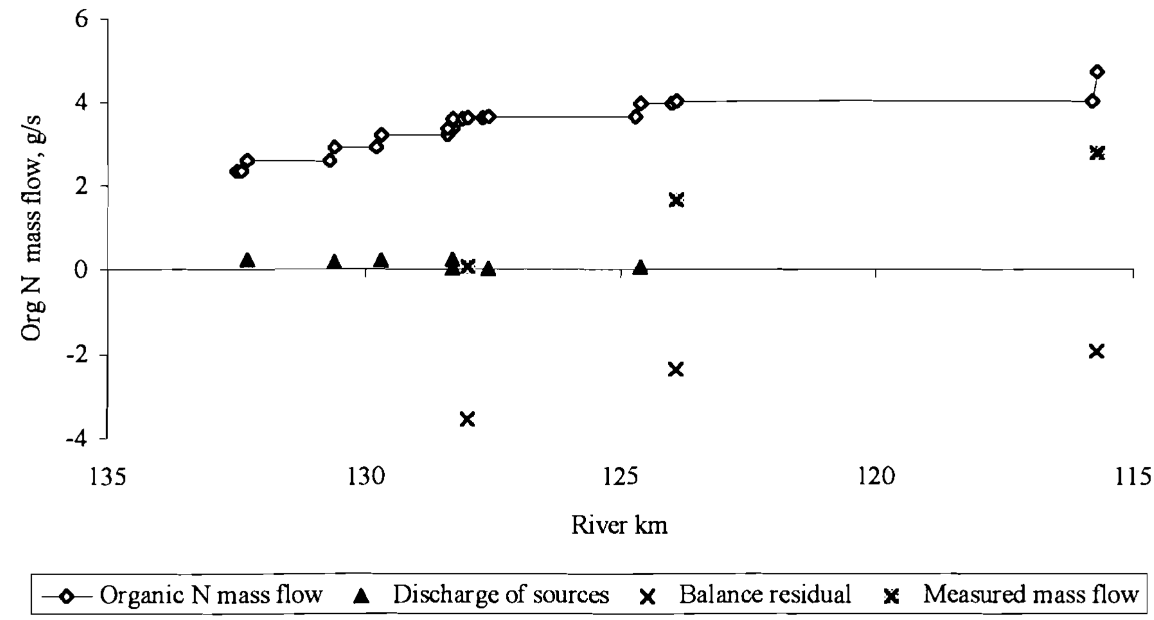


Figure 4.14 Organic nitrogen mass balance for the upper part of the Nitra River (June 1993 experiment)

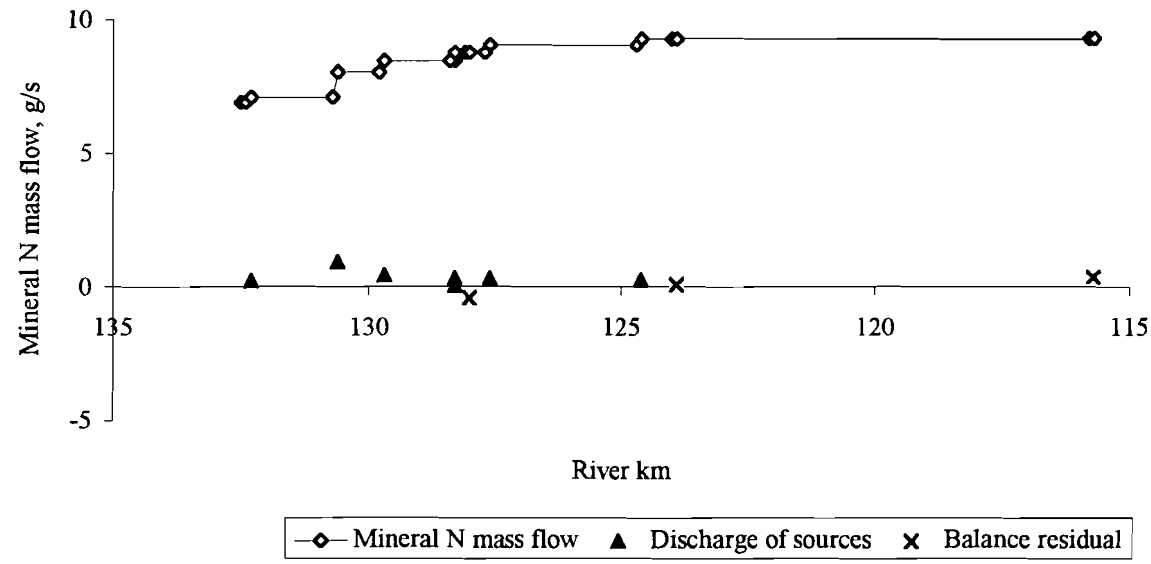


Figure 4.15 Mineral N mass balance for the upper part of the Nitra River (June 1993 experiment)

The situation is different with organic phosphorus (Figure 4.16). Removal rate of organic phosphorus (~ 1.0 1/day) resembles that of overall BOD removal rate. The hypothesis can be that phosphorus is released from the bound to organic when organic carbon (responsible for most of the oxygen demand) is fully decomposed. Rapid removal of mineral phosphorus (Figure 4.17) indicates possible nutrient uptake by algae.

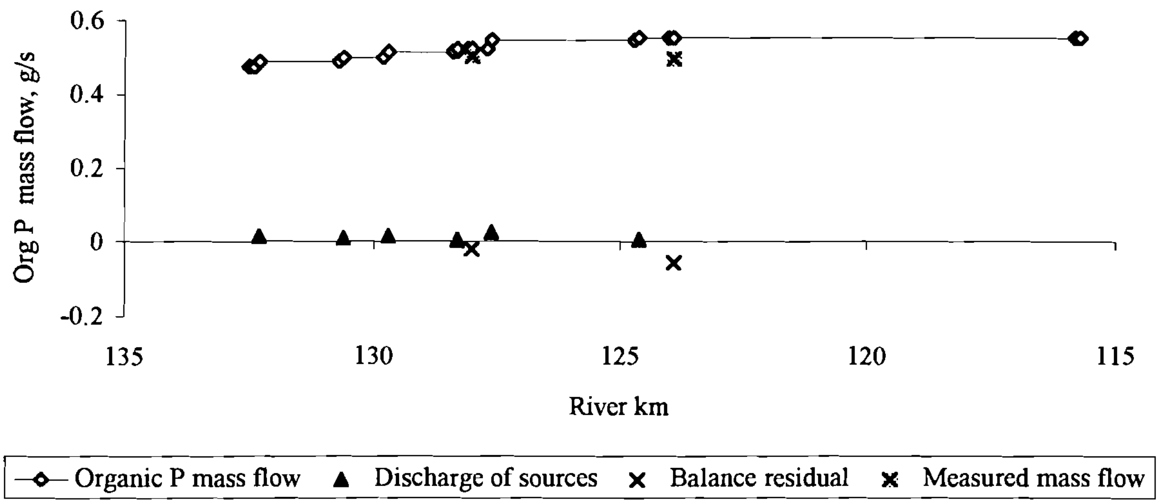


Figure 4.16 Organic phosphorus mass balance for the upper part of the Nitra River (June 1993 experiment)

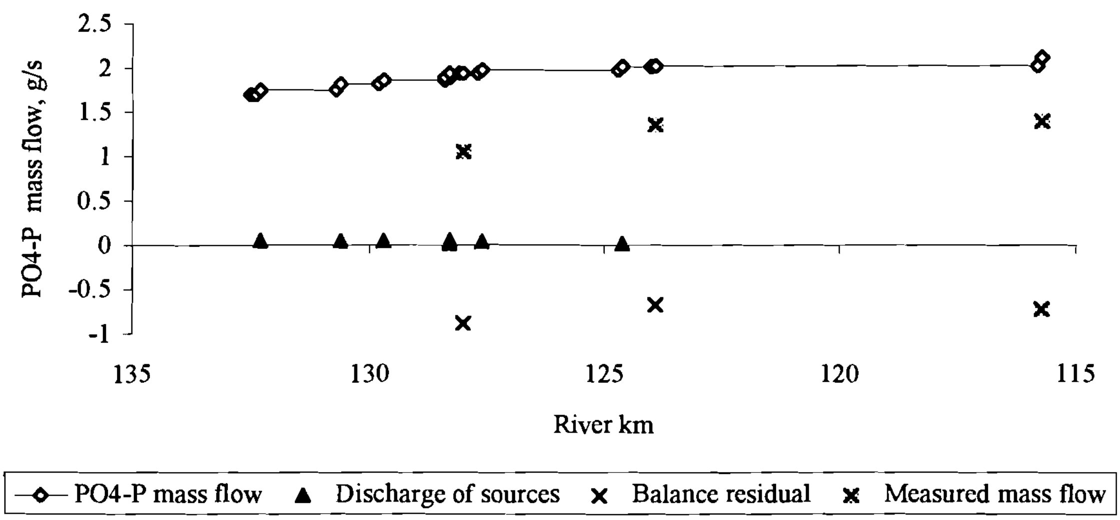


Figure 4.17 Ortophosphate phosphorus mass balance for the upper part of the Nitra River (June 1993 experiment)

4.4 Conclusions from 1993 water quality profile experiments

The detailed water quality profile experiment of June 1993 allowed to resolve particulate and dissolved fractions of organic material in Nitra River and to look in more detail into behavior of nutrient fractions (phosphorus and nitrogen). This analysis should help in the model selection and calibration procedure when a model of more complex type will be applied.

In particular, the following conclusions can be drawn from the analysis of 1993 water quality profile data:

- Biologically treated effluent water in Nitra River basin contain significant amounts of particulate easily destructible organic material.

- The amount of particulate organic material subject to decomposition is reduced in the river water. This indicates intensive stabilization processes in the river.

- The analysis of suspended solids profile does not show significant sedimentation. The sedimentation process can be neglected in the model at least for the upper river reaches.

- Rate of hydrolysis of particulate organic material is rather high. This suggests again exclusion of model for sedimentation processes, the main removal mechanism of organic material being bacterial decomposition.

- Removal rate of organic nitrogen is close to that of hydrolysis, indicating rapid consumption of dissolved organic nitrogen fraction of bacteria and possibly algae. Removal rate of organic phosphorus is closer to that of organic carbon (or biological oxygen demand). Mineral phosphorus also is subject to rapid removal from the river water, indicating possible algae uptake. This shows the need of including algae submodel into the more complex model to be applied in future Nitra studies.

5 CONCLUSIONS FROM THE STUDY

Two longitudinal profile experiments were performed in the Nitra River catchment, focusing mostly on conventional pollutants. The first experiment covered low-flow period which is often critical from the water quality point of view. It was designed as a survey of the whole region. The second experiment was planned on the basis of the first, focusing on the most sensitive areas of the basin and on the processes which govern the behaviour of the polluters in question. Mass balance approach was

The following overall conclusions can be drawn from the analysis of the experiments data:

- Untreated and partially biologically treated effluents in Nitra River basin contain large amounts of easily destructible organic material, most of it in particulate form. It is decomposed subsequently by bacteria, giving rise to intensive microbiological activity in the river water. In the course of in-river stabilisation of organic materials, dissolved oxygen is depleted. During summer low-flow period oxygen deficits in the Nitra River can exceed both national and international standards.

- Phosphorus and nitrogen load to the river is high enough to cause intensive development of phytoplankton (river eutrophication), which is increasing from the upstream to the downstream. Mineral nitrogen and phosphorus fractions are removed from the river water, this process is accompanied by intensive development of aquatic plants (indicated by high levels of chlorophyll "a").

- Intercomparison of regular monitoring data and experiment results indicate large variabilities/uncertainties in data. Approximate process rates estimates based on mass balances calculations give wide range of values and sometimes are unrealistic. This calls for application of more advanced parameter estimates techniques to account for uncertainty in data, such as Monte-Carlo technique used in later studies of Nitra River (Somlyódy e.a., 1994). For comparison, estimations of BOD removal rate were grouped together in Table 5.1 . It can be seen that estimations of the BOD removal rate fall within 0.5-1.1 1/day range. The final value selected for the use with models (0.8 1/day) is in the middle of this interval; cf. Table 5.1).

Table 5.1 Estimations of BOD removal rate for the upper stretch of Nitra River (Novaky-Luzianky, cf. Figure 1.1).

Mass balance August 1992	*Mass balance June 1993*	*Monte-Carlo estimation, August 1992*	*Monte-Carlo estimation, June 1993*	*Parameter value used in the model*
1.0 1/day	1.1 1/day	0.95 1/day	0.5 1/day	0.8 1/day

ACKNOWLEDGEMENTS

Authors would like to express their gratitude to the personnel of the Water Research Institute in Bratislava (VÚVH) and the Váh River Basin Authority, who participated in data collection and processing for the experiment programs. Without their dedicated efforts this study could not be conducted.

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