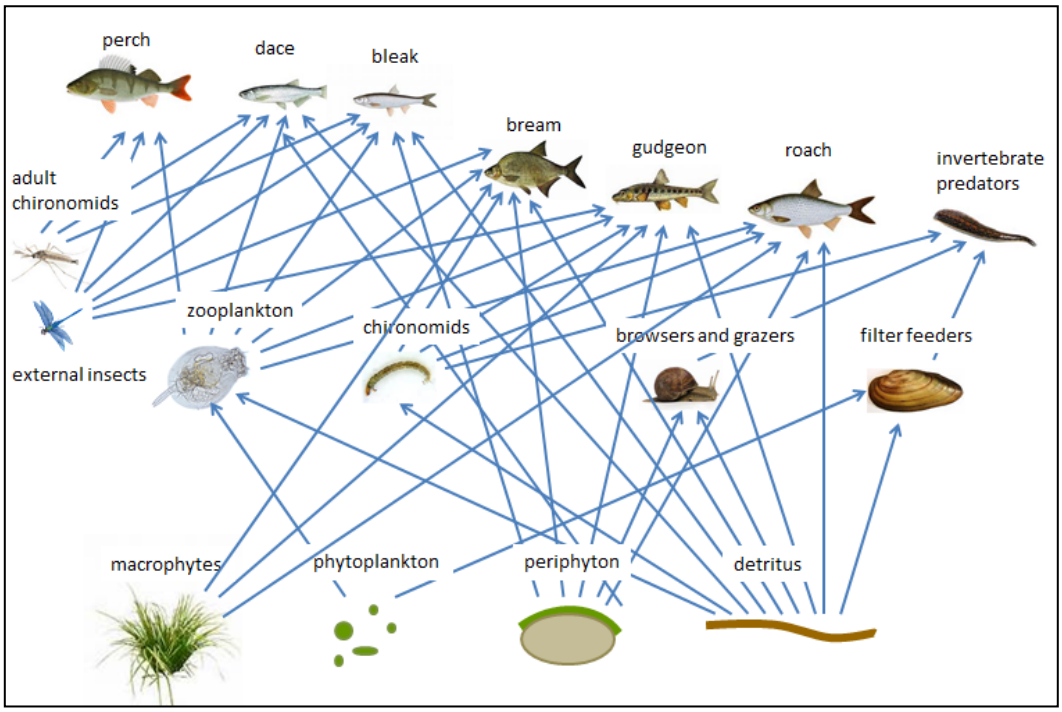
UNIVERSITY OF PADOVA

DEPARTMENT OF INDUSTRIAL ENGINEERING



Master Thesis

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Development of a riverine ecosystem model for use in risk assessment of xenobiotics

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“To halt the decline of an ecosystem it is necessary to think like an ecosystem”

Douglas P. Wheeler

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Abstract

The main aim of this research is to demonstrate the importance of ecosystem modelling used in risk assessment and to estimate the effect of two xenobiotics (Linear Alkylbenzene Sulfonate (LAS) and Triclosan (TCS)) in an aquatic ecosystems.

The River Thames at Reading (UK) between the Coversham and Sonning locks is the aquatic ecosystem chosen for the parameterization of the model. A vast literature is already present about this section of the river; furthermore the presence of the two locks guarantee a simplification of the model.

AQUATOX is the general ecological risk assessment model parameterized to evaluate the effect of the pollutants on the river.

The ecosystem food web has been created considering the different role that organisms have in the trophic network rather than the actual animal taxa present to guarantee a higher grade of generalization of the model.

This ecosystem is formed by fourteen aquatic organisms: three primary producers (Phytoplankton, Periphyton and Macrophytes), five aquatic invertebrates (Zooplankton, Chironomids, Filter Feeders, Browsers and grazers and Invertebrate predators) and six fish (Bleak, Roach, Gudgeon, Dace, Bream, Perch).

The control ecosystem was firstly stabilized over a period of six years of simulation and then a "raw" calibration was done in a way that the average annual biomass of the ecosystem organisms would be equal to the average annual biomass found in the literature study.

Using the acute toxicity parameters (EC_{50}, LC_{50}) AQUATOX simulates the effect of the pollutants on the organisms.

Three perturbed scenarios at different concentrations for LAS and TCS have been designed. A scenario tested the effect of the pollutants with a concentration in water equal to the one actually present in the UK rivers nowadays, while the other two having a characteristic concentration equal to the lowest EC_{50} and LC_{50} of the ecosystem organisms.

The perturbed scenarios confirm that the variations occurring in the ecosystem due to pollutants cannot be explained taking only into consideration ecotoxicological parameters and they reveal the importance of both direct and indirect organism interactions in the ecosystem response to pollution.

Chapter 1

1. Introduction

The “life” of each living being is described by interactions and relationships with the world. Every organism is linked to the others directly or indirectly and also the simple act of breeze produce some sub-products that will disperse in the environment.

The human being is an organism that has to be considered in a different manner from the others because during his everyday life he emits in the environment not only natural organic substances (feces, urine, CO_2, etc.) but also some compounds that are refractory to biodegradation because normally not present in the natural environment (e.g.. Compound coming from the chemical industry).

The continuous increase in the human society progress has brought to an increase in the variety of chemical substances used that could pose a risk to human being and the environment if not well managed. The risk to the environment is also known as ecological risk. “Ecological Risk” is a term referred to risks to nonhuman organisms, population and ecosystem (Suter et al, 2007).

To estimate the ecological risk of an event or a substances there is the need of a risk assessment.

Risk assessment during the last decades started to assume an important role in the environmental regulation of the Europe Union and in the way we decide how to manage a substance from the production to its disposal.

In the Europe Union the instrument used to regulate the chemical production and the chemical use of a substance is the REACH normative (Registration, Evaluation, Authorization, restriction of Chemical Substances).

The aim of REACH is to improve the protection of human health and the environment through the better and earlier identification of the intrinsic properties of chemical substances. The REACH Regulation places greater responsibility on industry to manage the risks from chemicals and to provide safety information on the substances **[I] (the website references are classified with a roman number)**.

A large number of substances have been manufactured and placed on the market in Europe for many years, sometimes in very high amount, and yet there is insufficient information on the hazards they pose to human health and the environment.

There is a need to fill these information gaps to ensure that industry is able to assess hazards and risks of the substances, and to identify and implement the risk management measures to protect humans and the environment.

The Directive 93/67, Regulation 1488/94 and Directive 98/8 require that an environmental risk assessment be carried out on notified new substances, on priority existing substances and active substances and substances of concern in biocidal products, respectively. This risk assessment should proceed in the following sequence (European Chemical Bureau, 2003):

- Hazard identification
- Dose (concentration) – response (effect) assessment
- Exposure assessment
- Risk characterization

Nowadays there are three main approaches to assess the potential impact of individual substances on the environment.

1. A quantitative PEC/PNEC estimation for environmental risk assessment of a substance comparing compartmental concentrations (PEC) with the concentration below which unacceptable effects on organisms will most likely not occur (PNEC). This include also an assessment of food chain accumulation and secondary poisoning (European Chemical Bureau, 2003).
2. A qualitative procedure for the environmental risk assessment of a substance for those cases where a quantitative assessment of the exposure and/or effects is not possible.
3. A PBT (persistant, bioaccumulation and toxicity) assessment of a substance consisting of an identification of the potential of a substance to persist in the environment, accumulate in the biota.

The first method is the most used one. The aim of such this approach is to identify acceptable or unacceptable risks. This method provides the basis for the future regulatory decisions.

The PECs can be derived from available measure data and/or model calculations. The PNEC values are usually determined on the basis of results from single species laboratory test.
Dependent on the PEC/PNEC ratio the decision on whether a substance presents risk to organisms in the environment is taken .
This methodology shows some advantages and disadvantages (Tab 1.1).

Table 1.1 *Description of some advantages and disadvantages of the (PEC/PNEC) method to determine risk assessment*

PEC/PNEC methodology	
Advantages	**Disadvantages**
It is a conservative method. The calculation of PNEC is based on the fact that ecosystem sensitivity depends on the most sensitive species.	It does not take in consideration the role of the species in the ecosystem
It is a rapid way to estimate a risk	It takes in consideration direct effect but not the indirect ones. Secondary pollution is assessed only for top predators. It is not possible to estimate the route of the pollutant in the environment
	It does not consider bioaccumulation

It is easy to understand that PEC/PNEC ratio is a simple indicator that is not able to describe in a global way the risk posed by a substance for an ecosystem.
This is because the processes and the ecological dynamics that takes place in an ecosystem depend mainly on the kind of ecosystem and its chemical and physical conditions. The number of uncertainties and limits inherent to the current approach to assess risk reveal the need to face the risk assessment issue in a different way. In the last decades the ecological modelling is continuously developing and it seems to be a great tool to improve risk assessment efficiency. A number of ecological models have been developed and reviewed for potential use in the ecological risk assessment of chemicals (Campbell & Bartell, 1998) (Naito et al, 2002).
One of the main aspects of this innovative approach for risk assessment is the recognition of important biotic-abiotic feedback loops that determines the dynamics of ecosystem structure and function.
That is, abiotic factors can dictate the nature of organisms that can live in a determine area or volume and, in turn, the presence of animal and the production of sub-products due to their metabolisms can change the abiotic property of the system and open the area for new inhabitants (Suter et al, 2007).

Another conceptual contribution of the ecosystem approach is the recognition of the significance of the "asymmetry" of the ecosystem: the presence of an organism within an ecosystem depends on many biotic factors (competition, grazing, predation, metabolism etc.) that are continuously in relation with abiotic factors but not all processes and interactions are of equal importance at all times and all locations.

The characterization of ecosystem asymmetry can provide insights into the selection of endpoints of risk assessment and suggest relevant scales in time and space.

There are four main ecological effects that can be observed in the ecosystem models but not in other kind of models such as population one and organisms dynamics (Suter et al, 2007):

1. the effect of an agent on the nature of ecological interactions among residents populations;
2. indirect effects that propagates through organism sensitive to the agent and subsequently impact organisms not directly affected;
3. alteration in the trophic structure or number of species;
4. alterations in the ecosystem structure;

As highlighted in point 3 and 4, food web has a central role in the ecosystem model including ecotoxicological ones, because it takes into account the transport of the pollutants through the trophic network.

Changes in the trophic network causes indirectly a variation in abiotic-biotic feedback mechanisms. Large changes in these processes could pose serious threats to ecosystem integrity.

Using Ecological modelling is possible to create scenarios that analyze the effect of a pollutant on the ecosystem for a chosen period of time while PEC/PNEC approach measures the immediate risk of the environment to a pollutant exposure but some effects can be visible only after years or decades of exposure.

This thesis work takes up in this context and reveal the importance of a new way to estimate the environmental risk assessment of substances. The aim of this work is to carry out the risk assessment of two micro-pollutants (Linear Alkylbenzene Sulfonate and Triclosan) discharged into an aquatic ecosystem using an ecosystem model and to identify some environmental indicators that can describes the changes occurred in the ecosystem due to the pollutant. The case study selected in this work is the River Thames ecosystem.

The use of various indicators can give to the modeler different point of views on the environmental variations occurred in the ecosystem due to the chemical perturbation and help him/her to have a more comprehensive idea of the ecosystem status.

The study is divided in three main chapters. In the Chapter 2 the materials and methods utilized are shown. This chapter gives an overview on the choice of the aquatic ecosystem (river, lake, reservoir etc.) and the main abiotic and biotic variables and processes that belong to the system.

The relationship between the populations of the ecosystem are described by the trophic network. In the Chapter 2 is explained how the model food web has been constructed.

The last part of the chapter is dedicated to describe the ecotoxicological parameters for the two chemicals and the indicators of the environmental status.

In the third Chapter the results of the two constructed ecosystem simulations are described: one simulation portrays a stabilized control ecosystem where the two chemicals are not present; the other describes an ecosystem perturbed by the two substances. In the perturbed ecosystem paragraph the effects of the pollutant on single organisms and ecosystem are described. Furthermore the level of ecosystem perturbation is assessed with objective, biological and ecosystem service indicators. The last chapter is dedicated to discuss the obtained results underlining the fragile equilibrium that exist between organisms.

Chapter 2

2. Materials and methods

In the beginning the key point was to choose the most representative scenario that could fit with the research purpose.

The first decision to be taken was to choose the type of the aquatic ecosystem to be modelled. The most interesting ones from an ecotoxicological point of view were the lake and the river. Both of them had some advantages and disadvantages.

Literature on lake studies is wider than the river one, that means that it would have been easier to find data in the literature about fauna and flora biology and ecology; furthermore lakes can be modelled as closed systems as far as it concerns organisms fluxes and this can simplify the model equations and its data requirements.

On the contrary the river conditions change along its continuum (the entire route of the river, from the spring to the sea) in a complex manner. This is due to a number of factors: for example the changes in river slope, altitude, bottom sediment composition and many other variables. Nowadays only few riverine ecosystem are well studied, for this reason it is quite difficult to find ecological data in literature which are suitable to construct an ecosystem model. The most important positive aspect bright side of choosing a river is that it is the most classic receptor of the discharge of the Wastewater Treatment Plants (WWTP), which represents the way through the two studied chemicals are emitted to the environment.

For these reasons the river scenario has been chosen, indeed the lack of the ecology data and ecosystem analysis is a limit but it also means that this study represents an interesting chance to analyze a riverine environment in an integrated and novel manner and shed light on the processes taking place in the ecosystem.

The second step of this study was to choose the best way to model the river system. There were two possibilities: to create an " ideal" general river similarly to the classical approach in risk assessment (European Chemical Bureau, 2003) or to develop a model based on one of the few case studies present in the literature.

A key argument in this choice concerns the effects of the xenobiotics pollution that the study aim to measure. One of the aims of the study is indeed to show the interactions of pollutants with the flora and fauna of an aquatic ecosystem and the changes that occur in the ecosystem structure. For this purpose a food web was needed.

After some literature research it was clear that a creation of a theoretical riverine ecosystem and its food web could bring to unrealistic results, because not enough about river ecology is known to generalize river ecosystems to the point of creating an ideal river model. Data from an existing ecosystem had to be found. One of the requisites that was identified for such data was that they have to portray a food web that was described more in terms of functional roles of organisms in the ecosystem than on the single species present in the river. This choice was meant to guarantee the construction of a very representative and simple river ecosystem, potentially comparable with the ecosystem of others rivers having the same structure even if the presence of different species.

Xenobiotic pollution has an important role in large rivers, where they tend to concentrate given the large watershed and the intense use man makes of this ecosystems. Thus a large river was an ideal candidate for this work

The study that best fitted the requisites was the one of Mathews (1993). It is a study carried out at Reading by the Zoology department of Reading University. The river ecosystem was modeled using the ECOPATH approach and the food web compartments were subdivided based on their roles in the ecosystem. Average data of annual biomass (expressed on energy value) of the organisms were available. A simplified trophic web and several biological parameters such as consumption rate (Q/B), production rate (P/B) were shown in this study.

2.1. AQUATOX model

The software chosen to model the ecosystem is AQUATOX. It is a “general ecological risk assessment model that represents the combined environmental fate and effects of conventional pollutants, such as nutrients and sediments, and toxic chemicals. (Park & Clough, 2012). It is a model released by the Environmental Protection Agency of the United States (EPA) and it is probably nowadays one of the most used and advanced model to estimate environmental fate and ecological effects in aquatic ecosystems.

AQUATOX represents the aquatic ecosystem by simulating the changing concentrations (in mg/l or g/m^2) of organisms, nutrients, chemicals and sediments for a determined volume of water (Park & Clough, 2012).

It is an ecosystem model, that means it does not focus on the changes in the number of individuals in a population (population model) but it considers processes such as the interdependence of aquatic organisms in the ecosystem, recycling of nutrients and detritus and the combined effects of toxic chemicals.

Any ecosystem model consists of multiple components requiring input data: abiotic and biotic state variables, driving variables (Temperature, light, nutrients etc.), parameters and coefficients that allows the user to specify key process characteristics. Figure 2.1 shows the most important state variables in an AQUATOX model.

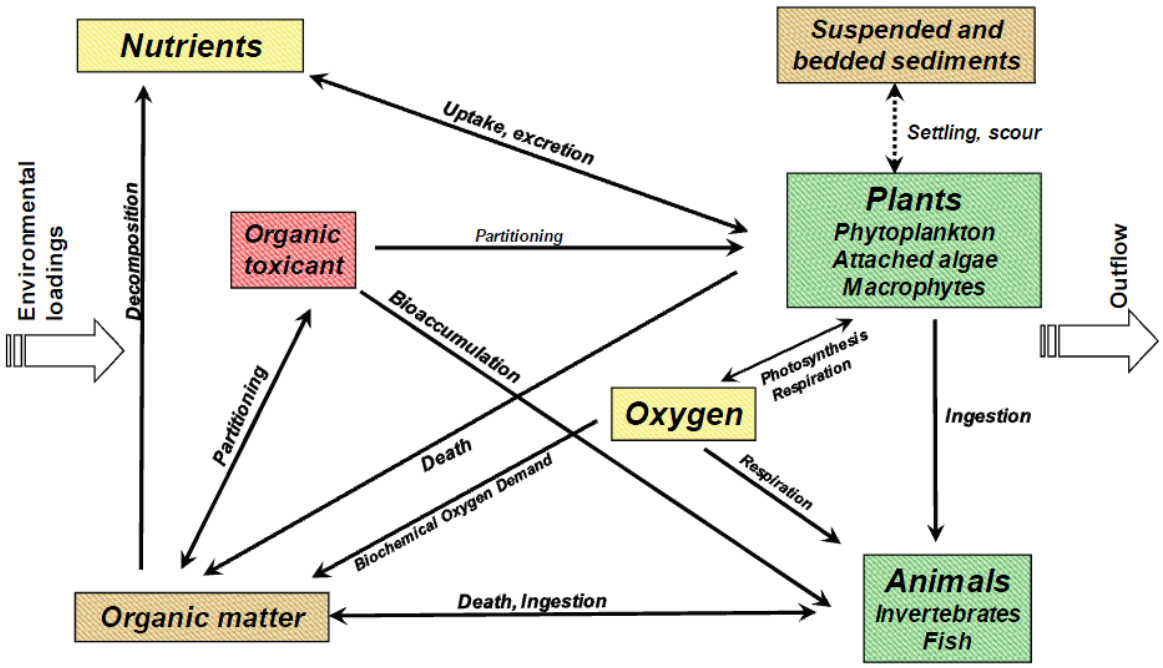

Figure 2.1 *Conceptual model of an aquatic ecosystem, represented by AQUATOX* (Park & Clough, 2012). *The double arrow describes a two way process while the single arrow an unidirectional process*

More detailed information are shown in the AQUATOX technical guide (Park & Clough, 2012).

The main inputs that AQUATOX requires to parameterize the River Thames ecosystem are shown in Tab 2.1. The only available dynamic data over a year were temperature and flow found in a paper by Berrie (Berrie, 1972). River Thames at Reading is highly studied but yet there is a lack of data in the literature or they are not published. For this reason, the other data

were inserted as average values and some of them were referred to different years or sites found upstream the volume of water considered (for example nutrients, DO and CO_2 concentrations)

Table 2.1 *The most important state variables present in AQUATOX for the stretch of River Thames analyzed in this study . The main references are reported. (more detailed information are given in the relative paragraph for each variable)*

Variable	**Main Reference**
Temperature	(Berrie, 1972)
Flow	(Berrie, 1972)
Site description	(Mann, 1964)/(Mann et al, 1972) /(Mathews, 1993)
Wind	http://www.decc.gov.uk/cgi-bin/nre/noabl1.pl
Light	(Mann et al, 1972)
Nutrients	(Neal & Robinson, 2000)
DO	(Neal & Robinson, 2000)
CO2	(Neal & Robinson, 2000)
Suspended detritus	(Mann et al, 1972)
Dissolved detritus	(Mann et al, 1972) (Park & Clough, 2012)
Labile and refractory factors for detritus	Estimation from (Mann K H, 1988) / (Mathews, 1993)
Animals and plants	(Mann, 1964) / (Mann K. H., 1965) / (Mathews, 1993)
Food web	(Mann K. H., 1965) / (Mathews, 1993)
Xenobiotics (LAS,Triclosan)	ECHA **[VI]** / (HERA, 2009)

Due to the low quality of data and the absence of dynamic data the method planned to parameterize the model was:

1) insertion of site input data and use of AQUATOX default values if not other data are available;
2) insertion of an initial raw food web;
3) choice of default organisms considered to be the best organisms representative of actual living beings in the real river;
4) stabilization of the model for a period simulation of one year. AQUATOX calculates the value of each variable for every day of the simulation considering its mass balance (Park & Clough, 2012). The period of simulation can vary from some days to more than one year. In the simulation having a period of one year the trend of each organism should have the initial value (1st of Jenuary) equal the last day of simulation (31th of December) and there would not been any organism biomass explosion or extinction. This process started from the organisms belonging to the low levels of the

trophic web to the ones that represent the higher levels in a continuous iterative manner;

5) calibration of the model for a simulation period of one year. The average value of organism annual biomasses should be as closest as possible to the values of the Mathew's study;
6) stabilization of the model for a simulation period of six years. In this step it was verified that the organisms would had the same biomass trend shape for the six years. They had to present the same maximum and minimum at the same period of time. The biomass value of the last day of simulation had to be as similar as possible to the first one;
7) calibration of the model for a simulation period of six years. The average biomass calculated on the new period of simulation (6 years) had to remain as close as possible to the average annual biomass measure by Mathews (Mathews, 1993);
8) insertion of chemicals in the system and evaluation of the effects on the ecosystem.

In AQUATOX there is the possibility to run the model in a Control and Perturbed method and the software is able also to represent the difference between the two methods of run.
In this study the control run is set to not consider the presence of the toxicant ("Control Setup" option in the "Setup" of the study) while in the perturbed simulation the input of the toxicant is taken into account.
As described in the AQUATOX guide (Park & Clough, 2012), when choosing this way of simulation (Control/Perturbed comparison) the best "size step" option for numerical integration is to "Use a fixed step size". In AQUATOX the fixed step size can be chosen between 0,1 [d] and 0,01 [d]. Lower is the step size higher is the accuracy of the results but an higher time of simulation is needed.
The lowest value of 0,01 d was chosen as the size step of the simulation of this study. It was verified that with higher step size values the results could be unrealistic.

2.2. Site location and abiotic variables

The stretch of the River Thames considered is the one at Reading UK (Lat: 51,3 °) **[II]** between Caversham Lock and Sonning Lock (Mathews, 1993). A vast literature is already

present in this part of River Thames. Some data of this research are taken from studies of the 60'. The major articles of the literature of this thesis are based on studies carried out on this stretch of the river (Mann, 1964) (Mann K. H., 1965) (Mann et al, 1972) (Berrie, 1972).
The length of the stretch is about 4 km. The width of the river in this part of the River Thames is between 50 m and 80 m. In this study a mean width of 65 was considered (Mann, 1964). The mean depth of the river is about 4m and the maximum depth 4,5 m (Mathews, 1993). The elevation of the site is 61 m on sea level **[II].**

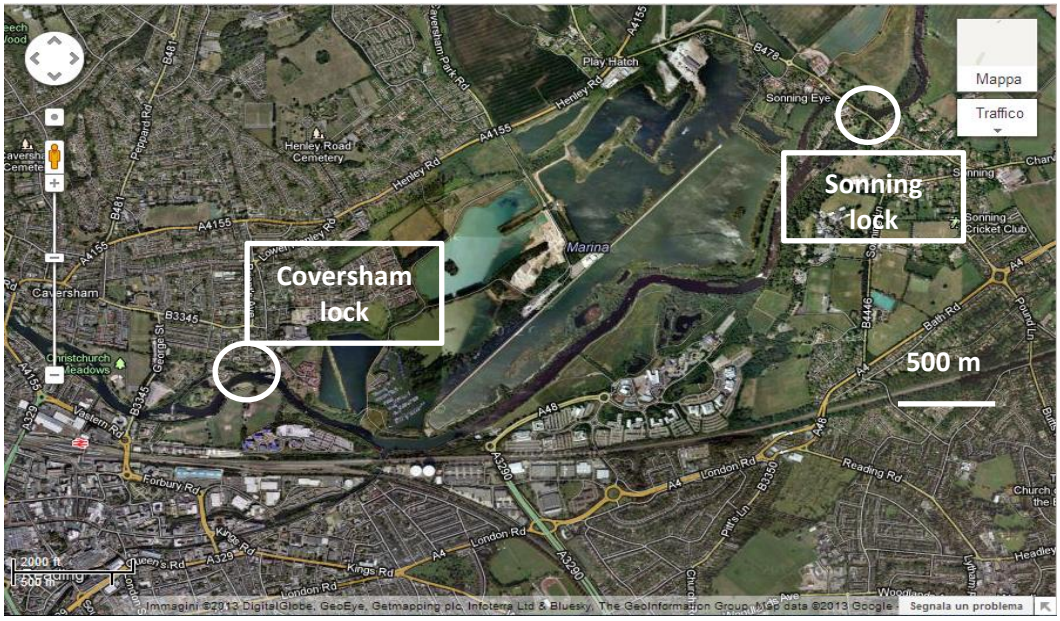

Figure 2.2 *A picture of the section of River Thames used in this study as volume of the river ecosystem. The two locks that determine the beginning and the finish of the volume are enclosed by the white rings. In white there is the scale of the map* **[III]**

The littoral zone of the River Thames in this part of the river is small because its bottom reaches rapidly the 4 m of depth. For this reason bathymetric equations were not used to model the shape of the bottom of the river but on the contrary the site is considered to have a constant section for the entire volume.

2.2.1. System volume characteristics

The volume of the system is set constant. Its value is 1040000 m^3, that is the multiplication of the average depth (4 m), the average width (65 m) and the length considered (4 km). The choice to set the volume constant derives from the presence of the two locks. They regulate

the water inflow and the water washout from the system volume. Furthermore the average depth and the maximum depth have similar values (there is a difference of only 0,5 cm), which means the volume does not change too much over the year.

The flow data set used (Figure 2.3) is the one published in Berrie's paper (Berrie, 1972) (The values are reported in Appendix A.1). The constant volume hypothesis defines the inflow rate equal to the discharge rate at the same instant of time.

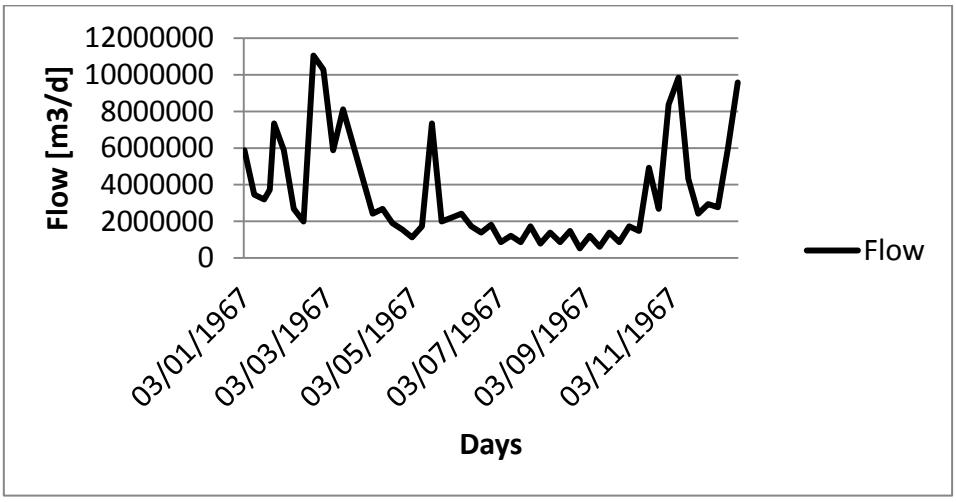

Figure 2.3 *Flow rate of River Thames at Reading in 1967 recovered from Berrie study*

In the reality River Thames in the four kilometers considered in this study is reached by one of its tributary, the Kennet river. Kennet river average flow at the mouth (Theale UK) is equal to about 9 m^3/s. This values represents one fourth of the River Thames flow at Reading. To simplify the model the Kennet river insertion is not considered. This assumption was taken because in the most important papers that compose the literature of this thesis the effects of Kennet interaction in this stretch of the River Thames has been already considered (Mann et al, 1972) (Mathews, 1993) (Berrie, 1972). Furthermore, the thesis is characterized by a wide scarcity of data and they derive from some measurements taken below Kennet mouth and others in a site above Kennet mouth. Indeed this assumption creates some uncertainties.

Water velocity are calculated by AQUATOX as the ratio between flow values and the river section.

The evaporation rate is equal to 482,6 mm/year (19,1inch/year AQUATOX input) (Evaporation rate found in (Penman, 1954)**)**.

2.2.2. Physical characteristics of the site

Temperature

The temperature varies from a minimum of 2,5 °C at the 11th of January to a maximum value of 19 °C in the end of July (Berrie, 1972) (Appendix A.2). The average temperature value is about 11,4 °C.

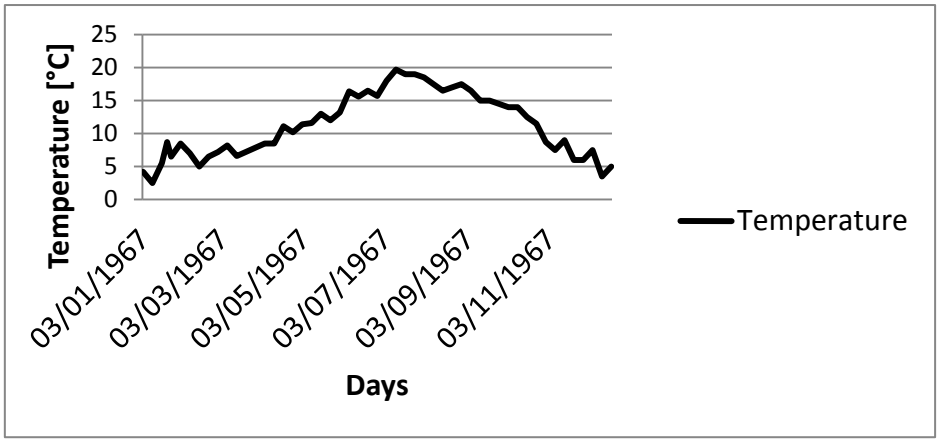

Figure 2.4 *Temperature of River Thames at Reading in the year 1967 (Berrie, 1972)*

Light

AQUATOX recreates the photoperiod using the average light and the annual light range. This values have been arranged in a way that AQUATOX calculates the minimum and the maximum values of light the most similar as possible to the ones present in the paper published by Mann (Mann et al, 1972). An average light of 370 Ly/d is supposed with an annual light range of 623,4 Ly/d (Ly/d = Langleys per day, 1Ly/d = 10 kcal/(m^2/d) = 41,87 kJ/(m^2 d).

AQUATOX considers also the extinction of light due to site characteristics (Dissolved organic matter concentration (DOM), Particulate organic matter (POM) concentration, water and inorganic sediment) and plant presence (Phytoplankton, Periphyton and Macrophyte) using some coefficients. The ones regarding site characteristics are shown in Table 2.2 while the extinction coefficient values for each plant are shown in the paragraph 2.3.1. These values are important to estimate the real amount of light usable by plants for their biological processes (Equation 38 of (Park & Clough, 2012) .

The default extinction light coefficients of AQUATOX are used in the ecosystem model both for the site characteristics and for plants. The first ones are taken from the Table 7 of the AQUATOX Technical Report (version 3.1) (Park & Clough, 2012), while the second values are taken from the default organisms chosen to represent the River Thames plants in the AQUATOX model.

Table 2.2 *Extinction coefficients for water, detritus and inorganic sediment (Park & Clough, 2012)*

Extinction light coefficient	**Value**	**Unit**
Extinct coeff water	0,02	1/m
Extinct coeff sediment	0,17	1/(m g/m^3)
Extinct coeff DOM	0,03	1/(m g/m^3)
Extinct coeff POM	0,12	1/(m g/m^3)

Another important parameter for the light characterization is the fraction of canopy of the system.
The value expresses the fraction of river surface covered by tree and plants. A rough value has been estimated from Fig 2 in Mann (Mann, 1964). The input value in AQUATOX is 0,08.

Wind

Wind is a physical factor that plays an important role in the ecosystem physical dynamics. Only partial data have been found**[IV]** (Data of 2010) for the wind of UK. For this reason the option of AQUATOX to describe variable wind speeds through a Furier series was chosen (Park & Clough, 2012).

2.2.3. Chemical state of the river

This section of the study is characterized by high scarcity of data and most of the data available are dated in a period of time far away from the AQUATOX simulated period. The reference study for this section is the one of Colin Neal of the year 2000 (Neal & Robinson, 2000). It has been considered the best choice because the water quality data were taken at a site approximately mid-way between Oxford and Reading (Neal & Robinson, 2000).
The pH hypothesized for the river is 8,14 (Tab 2 (Neal & Robinson, 2000)). This value remains constant over the year due to a lack of dynamic data.

Only constant data about O_2 concentration in water have been found (Neal & Robinson, 2000). Dissolved oxygen concentration in River Thames in Neal's paper is given as a ratio between actual oxygen dissolved and oxygen at saturation (Figure 7 (Neal & Robinson, 2000)). This ratio is almost 1, for this reason it is a good approximation to considered the dissolved oxygen value equal to the concentration of oxygen in water at saturation.

Using the average temperature is possible to calculate the dissolved oxygen concentration at saturation that is equal to the DO in the case of River Themes (equation 198 in the AQUATOX technical report (Park & Clough, 2012)).

The dissolved CO_2 concentration was found as $EpCO_2$ (Neal & Robinson, 2000). This value represents the number of times the water is oversaturated with carbon dioxide relative to the equilibrium concentration of water with the air. It is expressed as the ratio between actual partial pressure of CO_2 and partial pressure of CO_2 at equilibrium. The average value of $EpCO_2$ is equal to 6. The ratio is supposed to remain constant for the whole year even if actually the $EpCO_2$ varies from 2,5 to 15 (Neal & Robinson, 2000). The partial pressure of CO_2 at equilibrium is considered equal to the partial pressure of CO_2 at saturation.

The value of CO_2 concentration in water is calculated multiplying the values of Henry law constant (calculated for the average annual temperature of the site) for the atmospheric partial pressure of CO_2 (0,00035 atm (Park & Clough, 2012)).

Considering this data and the $EpCO_2$ ratio the actual partial pressure of CO_2 can be found.

Nutrients data refers to the Neal study of 2000 (Neal & Robinson, 2000). AQUATOX requires a value of Total soluble Phosphorus (TSP), NO_3-N and NH_4-N.

Nutrients, DO, CO_2 are considered constant loadings from upstream. AQUATOX takes into account also of the remineralization that occurs within the river. The default remineralization model offered by AQUATOX is used. The main chemical upstream loads are shown in Table 2.3.

Table 2.3 *Input loadings from upstream of the most important abiotic variables*

Variable	**Loading from upstream**
Dissolved Oxygen	11 g/m^3
Dissolved CO_2	4,6 g/m^3
TSP (Total soluble Phosphorous)	0,9 g/m^3
NH_4-N	0,04 g/m^3
NO_3-N	8,38 g/m^3
pH	8,14 g/m^3

2.2.4. Detritus

The definition of detritus in AQUATOX is: "all non-living organic material and associated decomposers" (Park & Clough, 2012). The detritus is subdivided in Dissolved, Suspended, Sediment and Buried fractions (Figure 2.5).

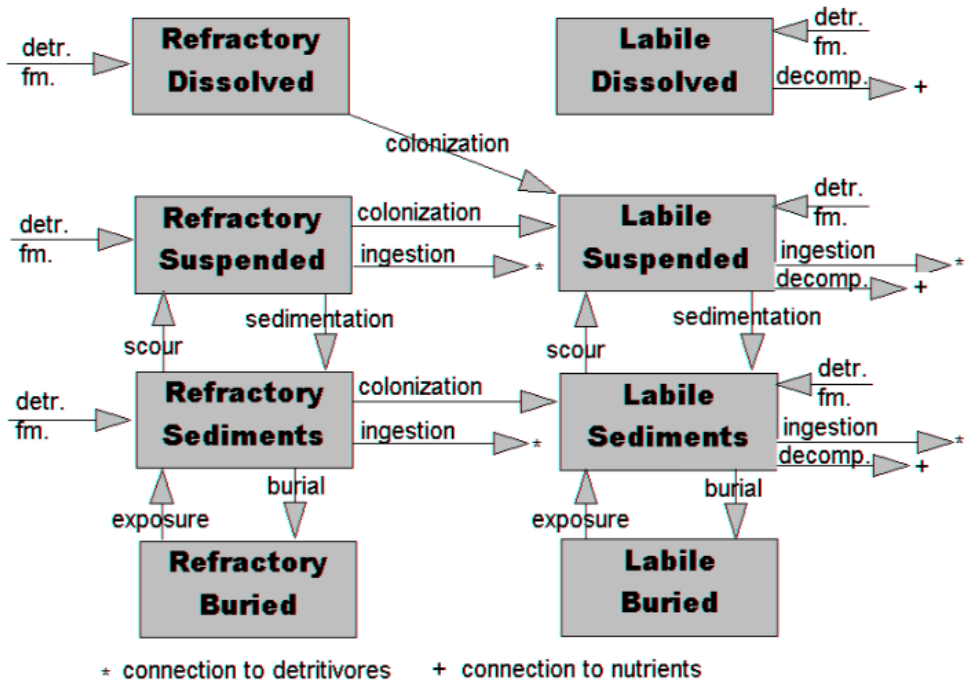

Figure 2.5 *Detritus fractions in AQUATOX* (Park & Clough, 2012)

The only value that can be recovered from the studies on the River Thames at Reading is the concentration of suspended detritus. An annual average value of about 5 g/ m^3 is assumed (Mann et al, 1972).

The dissolved organic material is generally ten times the suspended particulate matter (Park & Clough, 2012). Dissolved detritus has been assumed ten times the suspended one. The result of this assumption is that the fraction of dissolved and suspended detritus are respectively equal to 0,91 for the first one and 0,09 for the second one.

AQUATOX needs a percentage to divide detritus in the refractory fraction (detritus that is considered not to decompose directly, but rather to be converted to labile detritus through microbial colonization) and labile fraction (rapidly decomposable).

The labile fraction of suspended particulate detritus was recovered from the fish detritus assimilation that is about 7% (Mathews, 1993). It has been assumed that the detritus

assimilated by fishes can be considered the labile fraction of particulate detritus while the fraction egested (93%) is supposed the refractory particulate detritus. In the Fig 4 of the article of Mann is shown the correlation between size of particles in water and percentage of refractory detritus (Mann K H, 1988). The last part of the chart is characterized by particles diameters lower than 150 μm. The relation between particle diameter and refractory percentage of particles seems that can be described as a straight line in this part of the graph. The equation that describes this line was found through least-square fit in Excel. A diameter of the suspended particle of 0,22 μm (that is one of the basic size to divide particles between dissolved and suspended matter) was inserted in this equation to calculate the refractory percentage for dissolved particles. This value it is about 58,6 %.

A global refractory percentage for the detritus can be found (about 62 %) using the refractory percentage of dissolved and suspended particulate detritus, respectively 58,6 % and 93 %. These refractory fractions are considered constant for the whole year. The global refractory percentage for dissolved and suspended detritus is similar to others found in AQUATOX library default studies (Rum River).

Data on sediment detritus and burial detritus dynamics were not found in literature, for this reason sediment detritus input load is set to zero. A consequence of this assumption is that the bottom sediment depends only on the system dynamics. This fact can be justified in the realty by the presence of the two locks upstream and downstream.

Burial detritus is not modelled because the detritus fraction found in literature (Mathews, 1993) takes in consideration only that part of detritus directly accessible by the ecosystem organisms. That means all the sediment detritus in the River Thames study in AQUATOX is available for the living organisms.

Suspended detritus, dissolved detritus and TSS are considered constant loadings from upstream. A constant loading form upstream of 16 g/m^3 was calculated for TSS. To estimate TTS concentration in water the same ratio TSS/(algae conc. + POM) of Berrie (Berrie, 1972) was used, considering 1 g/m^3 the phytoplankton concentration (Mathews, 1993) and 5 g/m^3 the particulate organic detritus concentration (Mann et al, 1972). In Table 2.4 the loading from upstream for detritus and TSS are shown.

Table 2.4 *Detritus (Suspended and Dissolved) and TSS loading from upstream*

Variable	Loading from upstream
Particulate detritus (Susp. and Diss.)	55,6 g/m^3
TSS	16 g/m^3

2.3. Living organisms

Most of animals and plants belonging to the River Thames ecosystem are not present as default organisms in AQUATOX. Some AQUATOX default organisms have been chosen as "base organisms" to define the starting parameters of the River Thames living beings (Table 2.5) and then properly modified. The "base" organism chosen is the one having the most similar characteristics to the one of River Thames.

The organisms have been chosen considering the *Genera* and *Family* of the species. Another requisite was that the default organism should have similar weight, diet composition (for the animals) and living habitat.

This method is the best way to decrease uncertainties thank to a possible use of some parameters of the default organism just in case literature data of the real groups present in the ecosystem cannot be found.

Some living beings are collected in groups considering only their role in the ecosystem in Mathews study (Mathews, 1993). For plants and aquatic invertebrates this characteristics is maintained, instead for fish a mayor larger variety of species than in Mathews study has been chosen. The organism chosen to represent a class of living beings having the same ecosystem function is the one with the highest biomass in the river section considered.

Phytoplankton and Periphyton are represented by *Diatom* because in spring, summer and autumn it predominates.(80-90 % of total micro-algea cells (Mann et al, 1972).

The main zooplankton animals presented in the river Thames are *Cladocerans* and *Rotifers* (Berrie, 1972). *Rotifer* is the one used in AQUATOX because is the most present in River Thames (pag 19 of (Bass & May, 1996)).

Two species of macrophytes occur in the Thames at Reading: the *Acorus calamus* and the *Nuphar lutea* (Mathews, 1993). In this part of the River Thames the macrophytes grow on the river banks. They are both rooted macrophytes of the littoral zone. In AQUATOX there is not a default macrophyte that has similar characteristics to the two species present in the River Thames. Macrophytes are not so important in River Thames trophic web as energy source

even if they represents the river habitat where the density of the fauna is the highest (Mathews, 1993). For this reason they are however considered an important organism of the ecosystem model.

The invertebrates have been chosen considering the species present in the River Thames at Reading (Mann, 1964) (Mann et al, 1972). Browsers and Grazers category is represented by Gastropods. They are the ones with the highest biomass. For the Filter feeders the mussel *Unio spp.* (a bivalves) has been chosen. Leeches are the most common predators in this section of River Thames. The default animal chosen in AQUATOX to represent Invertebrate Predators category is the Oligochaete, because they belong to the same Genera.

Dace, Roach and Bream were created using the Dace fish already presented in AQUATOX. The three fishes belong to the same Genera. Perch derives from the AQUATOX animal "Logperch", because they have similar weight and they are *Perca*. Shiner was chosen as default animal for Bleak while Bullhead for Gudgeon.

Adult chironomids and External insects have been inserted in the ecosystem model because they represent an important source of food for the animals within the river even if they are aerial or terrestrial insects. They are considered as fictitious animals, for this reason the main biological parameters (mortality rate, consumption rate, respiration rate etc.) are set to zero to guarantee the lowest interaction with river ecosystem dynamics in AQUATOX model.

Table 2.5 *The default organisms of AQUATOX (first column) chosen to represent the ones of River Thames (second column)*

AQUATOX	**River Thames**
Phyto Diatom	Phytoplankton
Periphyton Diatom	Periphyton
Myriophyllum	Macrophytes
Chironomid	Adult chironomids
Mayfly	External Insects
Chironomid	Young chironomids
Gastropod	Browsers and Grazers
Rotifer (*Keratella*)	Zooplankton
Sensitive Mussel (*Unio*)	Filter feeders
Oligochaeta	Invertebrate predators
Dace	Dace (Leuciscus Leuciscus)
Shiner	Bleak (Alburnus Alburnus)
Logperch	Perch (Perca Fluviatilis)
Bullhead	Gudgeon (Gobio Gobio)
Dace	Roach (Rutilus Rutilus)
Dace	Bream (Abramis Brama)

AQUATOX requires the mass of organisms in [g/m^2 dry] as initial condition or input load. In the study of Mathews the values are expressed using energy unit [kcal/m^2] and only few caloric contents are shown. Organisms caloric content on dry weight basis used in the AQUATOX River Thames model are shown in Table 2.6.

Table 2.6 *The Caloric content of River Thames organisms and their relative reference*

Class of organisms	Caloric content	Caloric content	Reference
	kcal/g dry	kJ/g dry	
Phytoplankton	5	20,93	Mathews, 1993
Periphyton	5	20,93	Mathews ,1993
Macrophites	4,63	19,38	Estimation from Mathews, 1972
Adult chironomids	4,64	19,42	Set equal to Chironomidae
External insects	4,64	19,42	Set equal to Chironomidae
Chironomidae	4,64	19,42	Estimation from Mann,1964
Browsers and Grazers	3,26	13,65	Estimation from Mann,1964
Zooplankton	5	20,93	L.A Jorgensen,1971
Filter feeders	4,96	16,58	Estimation from Mann,1964
Inv.predators	5,44	22,77	Estimation from Mann, 1964
Dace	4,29	17,96	Estimation from Mathews, 1993 /FISHBASE
Bleak	4,29	17,96	Estimation from Mathews, 1993 /FISHBASE
Perch	4,29	17,96	Estimation from Mathews, 1993 /FISHBASE
Gudgeon	4,67	19,55	Estimation from Mathews, 1993 /FISHBASE
Roach	4,32	18,09	Estimation from Mathews, 1993 /FISHBASE
Bream	4,85	20,31	Estimation from Mathews, 1993 /FISHBASE

For the phytoplankton and the periphyton a value of 5 kcal/g has been considered (Mathews, 1993). Zooplankton is supposed to have a caloric content of 5 kcal/g (Jφrgensen, 1979).

For aquatic invertebrates, some data have been recovered by Mann (Tab 1 (Mann, 1964)**)**. In this table, the biomass of the bottom fauna on wet basis and the respective energy contents are shown. In AQUATOX some organisms with the same function in the ecosystem have been put together in the same way used by Mann and Mathews (Mann & et al, 1972) a (Mathews, 1993). The organisms groups are shown in detail in Appendix B. A weighted mean of the caloric contents of the organisms belonging to the same invertebrate category have been done

(Mann, 1964). Similar values for the invertebrates can be found in Salonen paper (Salonen et al, 1976).

The Macophytes caloric content has been estimated equal to 4,64 kcal/g (Mathews & Kowalczewsky, 1969)**.** It is similar to reference values (Jφrgensen, 1979). A caloric content for fish equal to 1,154kcal/g calculated on a living mass basis is expressed in Mathews paper. This value is considered on wet weight basis. Some ratios wM/dM (wet mass / dry mass) for fishes are needed to convert the caloric content based on wet weight in the dry weight one **[V]**.

2.3.1. Loading and washout assumption for the organisms

The River Thames is modelled in AQUATOX as a close system for large animals (fishes and invertebrates except Zooplankton). This choice is taken because of the presence of the two locks upstream and downstream that avoid the exchange of almost the totality of fauna biomass through the borders. The groups of the ecosystem that are described also by dynamics of inflow and washout are the Phytoplankton (and Periphiton because they are linked), the Zooplankton and Macrophytes. Phytoplankton and Zooplankton (rotifers) are micro-organisms that move mainly thank to the water flow. Furthermore they have an individual wet weight lower than 1E-6 g. The input biomass from the upstream is set to a value close to zero (1E-6 mg/l dry). This choice guarantees that the biomass changes that occur within the volume are only consequences of the processes that take place in the system analyzed and they are not influenced by the input loading. An high input could create distorted results. Enhanced phytoplankton-zooplankton retention /washout option is selected in AQUATOX. When this option is operative AQUATOX takes into account that the phytoplankton and zooplankton can quickly washout from a short reach, but they may be able to grow over an extensive reach of the river, included its tributaries (Park & Clough, 2012).

In this manner Phytoplankton and Zooplankton washout is different from water retention time in a way proportionate to the ratio between the length of the reach of the study and the total length of the river (Park & Clough, 2012).

Macrophytes in River Thames study are considered rooted in the littoral zone. The input from inflow is set equal to 1E-6, a low value that is used only to balance the low breakage effect (death of rooted macrophytes due to high flow velocities (Park & Clough, 2012)).

This assumptions were taken to try to have an ecosystem more independent as possible from flow dynamics since the inputs of the organisms through the inflow are not simulated dynamically, as stated above (this is a model limitation). Furthermore, they guarantee that the biological dynamics occurring in the system are chiefly related only to system characteristics and the relationships that occurs within the organisms.
This option is the one considered as the best way also to estimate effects of pollutants on the ecosystem.

2.3.2. Plants

In this paragraph are shown the main biological parameters used to model plants dynamics.

Phytoplankton

Diatom is the organism chosen to represent the river Thames phytoplankton at Reading. High rates of sedimentation are used coherently with the Mathews study (Mathews, 1993).
Phytoplankton biological parameters are shown in Table 2.7.

Table 2.7 *Biological parameters used to parameterize Phytoplankton in AQUATOX*

Parameters	**Values**	**Notes**
Saturating light (Ly/d)	22,5	Hill, 1996 64 (22.5) ~Cyclotella
P-half saturation (mg/l)	0,055	C&W 0.055;Horne & Goldman, 1996, C m .008
N-Half saturation (mg/l)	0,117	Collins & Wlosinski '83, p. 36, C. men.
T optimal (°C)	20	Collins & Wlosinski '83, p. 43 = 20
T min (°C)	2	
T max (°C)	35	
Max photosynthetic rate (1/d)	3,4	mean, Collins & Wlosinski '83 = 3.4 max
Photorespiration coefficient (1/d)	0,026	Collins & Wlosinski '83
Respiration rate at 20°C (g/(g d))	0,08	Riley and von Aux, 1949, cited in C.& W.1983
Mortality coefficient (g/(g d))	0,001	AQUATOX default organism value
Exponential mortality coefficient (g/(g d))	0,05	Same order of AQUATOX default organism value (0,01)
Light extinction (1/m-g/m^3)	0,14	Collins & Wlosinski '83, p. 17
Sedimentation rate (m/d)	0,02	Same order of Collins & Wlosinski '83, p. 30; Wetzel
Exponential sedimentation coefficient	0,45	Same order of Wetzel, 2001
Lipid fraction	0,015	Lyndall 2010

Periphyton

The organism considered to represent the periphyton category is diatom. Phytoplankton and Periphyton are linked using a tool of AQUATOX to avoid an underestimation of chlorophyll production. This option takes into account that phytoplankton sedimentation could increase the periphyton concentration and on the contrary periphyton resuspension could increase the phytoplankton one. There is continuously an exchange of matter. The inflow from upstream is set constant to 1E-6 g/m^2 (dry).
Biological parameters inserted in AQUATOX to model periphyton are shown in Table 2.8.

Table 2.8 *Biological parameters used to parameterize Periphyton in AQUATOX*

Parameters	**Values**	**Notes**
Saturating light (Ly/d)	22,5	Hill, 1996 64 (22.5) ~Cyclotella
P-half saturation (mg/l)	0,055	C&W 0.055;Horne & Goldman, 1996, C m .008
N-Half saturation (mg/l)	0,117	Collins & Wlosinski '83, p. 36, C. men.
T optimal (°C)	20	Collins & Wlosinski '83, p. 43 = 20
T min (°C)	2	
Tmax (°C)	35	
Max photosynthetic rate (1/d)	2,06	Collins & Wlosinski '83; EcoTox 1-96 = 2,06
Photorespiration coefficient (1/d)	0,026	Collins & Wlosinski '83
Respiration rate at 20°C (g/(g d))	0,08	Riley and von Aux, 1949, cited in C.& W.1983
Mortality coefficient (g/(g d))	0,001	AQUATOX default animal
Exponential mortality coefficient (g/(g d))	0,026	Same order of AQUATOX default value (0,01)
Light extinction (1/m-g/m^3)	0,14	Collins & Wlosinski '83, p. 17
Critical force (newtons)	0,001	Default for stream (AQUATOX)
Percent lost in slough event	0,6	Value of default organism of AQUATOX
Lipid fraction	0,015	Lyndall 2010

Macrophytes

An important parameter of macrophytes is the maximum velocity (max velocity) of the water that the plant can sustain before to have breakage and consequently a reduction of their biomass in the system. A maximum velocity of 400 cm/s has been chosen that is the AQUATOX default value. The load from upstream is set equal to 1E-6 g/m^2 (dry). Biological parameters needed by AQUATOX to model macrophites behavior are shown in Table 2.9.

Table 2.9 *Biological parameters used to parameterize Macrophites in AQUATOX*

Parameters	**Values**	**Notes**
Saturating light (Ly/d)	166	
T optimal (°C)	18	http://underwaterworld.altervista.org/Piante/acorus_calamus.html
T min (°C)	2	http://underwaterworld.altervista.org/Piante/acorus_calamus.html
Tmax (°C)	26	http://underwaterworld.altervista.org/Piante/acorus_calamus.html
Max photosynthetic rate (1/d)	0,15	Estimation from Mathews 1993
Photorespiration coefficient (1/d)	0,25	Collins et al. 1985 (daylight only) 0.25
Respiration rate at 20°C (g/(g d))	0,024	LeCren and Lowe-McConnell, 1980, p. 195
Mortality coefficient (g/(g d))	0,0006	Same order of AQUATOX default organism 0,001
Exponential mortality coefficient (g/(g d))	0,0059	Same order of AQUATOX default organism 0,01
Light extinction (1/m-g/m^3)	0,05	Fig. 5.2, LeCren & Lowe-McConnell '80
Vel max (cm/s)	400	Default AQUATOX
Lipid fraction	0,005	Lyndall 2010

2.3.3. Animals

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The average individual wet weights of the animal, lipid fractions and maximum consumption rates are ones of the most important animal parameters to study the effect of the chemicals in the biota. The latter parameter is important to evaluate animal ingestion while the first two parameters are key factors to estimate animals elimination constant for a given chemical. Consequently they are directly related to animal eco-toxicological parameters. Lipid fractions for each animals are shown in detail in the paragraphs written for each animal and in the ecotoxicology paragraph (§Paragraph 2.5)

The average individual wet weights of the invertebrates were calculated as a weight mean of the individual wet weights of the animals belonging to the same animal category (e.g. Different type of bivalves for the Filter feeder hypothetical animal of AQUATOX).

The individual wet weights of animals were calculated through the ratio between the total mass of the species in an area of the river divided for the number of animals of the same species in that area (Mann, 1964). The weight mean method is used to give an highest importance to the largest aquatic invertebrates.

$$W_c = \frac{\sum_{i=1} \left(\frac{gWi}{N_i * 1000} * gW_i \right)}{\sum_{i=1} gW_i} \quad (1)$$

where:

- W_c is the weighted mean of the individual wet weight of a class of invertebrates;
- gW_i is the global mass of specie "i" [mg] in a determined area (Mann, 1964);
- N_i is the number of animal of specie "i" in a determined area (Mann, 1964);
- 1000 is a conversion factor from mg to g.

Fish individual wet weights were calculated taken some data from Table 5 of Mann (Mann K. H., 1965). Using the data of the number of fishes per 100 m^2 for each fish age class and their average individual wet weight a weighted mean is calculated. This value is the average individual wet weight of the fish in this stretch of the river.

$$W_f = \frac{\sum_{i=1} W_i * N_i}{\sum_{i=1}^{k} N_i} \quad \textbf{(2)}$$

where:

- "i" is the class age of the fish;
- N_i is the number of fish of age "i" per square meter;
- W_i is the average individual wet weight of the fish of age "i" [g];
- k is the maximum age of the species of fish catch.

Bream and Perch represent an exception. Perch and Bream individual wet weights were calculated using the equation that describes the relationship between length and weight of a fish (Equation 3) **[V]**.

$$W = aL^b \quad \textbf{(3)}$$

where:

- W is the weight of the fish [g];
- L is the length of the fish [cm];
- a [g/cm] and b are coefficients that depend mainly from the site considered and the species of fish.

An average weighted mean of the length of the different fish age classes for Perch have been found (Table 7 (Williams, 1967)). This result is inserted in the length-weight equation to find the individual wet weight.
In the studies on the River Thames analyzed for the creation of the model there are no data about Bream length. The Roach average length (Table 6 (Williams, 1967)) is used to estimate Bream weight. This can be acceptable because they are fishes with similar behavior (i.e. they have similar diet and they are both bottom feeders) and because they have the same common length **[V]**. The "a" and "b" coefficients used are the one of Bream in the most similar literature site of River Thames (River Regalica. Poland **[V]**).
In Mathews study the average consumption of every organism is shown in Table 5 (Mathews, 1993). In AQUATOX it has been decided to try to maintain as much as possible the same ratio between animal consumptions expressed in Mathews study. This assumption tends to guarantee similar behaviors of animals in the two models. Zooplankton maximum consumption rate has been chosen as the "base" value used to estimate the maximum consumption rates of the other animals.

2.3.3.1. Aquatic Invertebrates

In this section the assumption taken to model invertebrates and their main biological parameters needed by AQUATOX are shown.

Zooplankton

Zooplankton biological parameters (Table 2.10) have been recovered from a rotifer default animal of Aquatox and some data from Mathews (Mathews, 1993), as well as from other sources.
Zooplankton category is described by rotifers, the most present zooplankton organism of this section of the river. It feeds mainly on phytoplankton and detritus. It is the smallest animal present in this stretch of river Thames.

Table 2.10 *Biological parameters used to parameterize Zooplankton in AQUATOX*

Parameters	**Values**	**Notes**
Half saturation feeding (mg/l)	0,12	Same order of AQUATOX default organism (0,2)
Maximum consumption (1/d)	3,4	Collins & Wlosinski 9183, p. 45 (B.r.)
Minimum prey for feeding (g/m^2)	0,06	Walz, 1995, p. 441
T optimum °C	25	Walz, 1995, p. 443
T min adapt °C	2	cold-adapted (see Walz, 1995)
T max °C	35	prof. opinion
Mean wet weight	2E-8	Walz, 1995, p. 441
Endogenous respiration	0,15	Mathews 1993
Mortality coefficient	0,04	Walz, 1995, p. 443 (0,067)
Lipid content	0,012	Lyndall 2010

Filter feeders

Filter feeders are represented by mussel *Unio spp.*, a freshwater bivalve. They feed on detritus and phytoplankton. Biological parameters have been recovered mainly from Mann and Mathews studies and from the AQUATOX default animal (Table 2.11)

Table 2.11 *Biological parameters used to parameterize Filter feeders in AQUATOX*

Parameters	**Values**	**Notes**
Half saturation feeding (mg/l)	0,63	Aquatox default value = 1
Maximum consumption (1/d)	0,1	Estimation from Mathews 1993 and Zooplankton maximum consumption value
Minimum prey for feeding (g/m^2)	0	filter feeding mollusc
T optimum °C	22	from Fig. 17.4 in Pusch et al., 2001
T min adapt °C	3	cold-adapted
T max °C	30	default
Mean wet weight	6,15	Estimation from Mann 1964
Endogenous respiration	0,001	From Mussel Unio AQUATOX
Mortality coefficient	5E-5	<10% over 5 yr Jansen et al., 2001
Lipid content	0,015	Lyndall 2010

Browsers and Grazers

Browsers and grazers are represented by the freshwater snail, a gastropod. They feed mainly on periphyton and detritus.

Biological parameters inserted in AQUATOX to model browsers and grazers are shown in Table 2.12.

Table 2.12 *Biological parameters used to parameterize Browsers and Grazers in AQUATOX*

Parameters	Values	Notes
Half saturation feeding (mg/l)	0,97	
Maximum consumption (1/d)	0,14	Estimation from Mathews 1993 and Zooplankton maximum consumption value
Minimum prey for feeding (g/m^2)	0	filter feeding mollusc
T optimum °C	18	http://www.aquaexperience.it/index.php?option=com_content&view=article&id=126
T min adapt °C	3	http://www.aquaexperience.it/index.php?option=com_content&view=article&id=126
T max °C	25	http://www.aquaexperience.it/index.php?option=com_content&view=article&id=126
Mean wet weight	1,47	Estimation from Mann 1964
Endogenous respiration	0,017	Mathews 1993
Mortality coefficient	0,00445	Estimation from Mathews 1993 (P/B)
Lipid content	0,0075	Lyndall 2010

Chironomids

The term "chironomids" in this study mean the larval state of chironomid because they are organisms living in the freshwater before to become aerial insect in their adult state (Adult chironomids). They feed on detritus. Biological parameters inserted in AQUATOX to model chironomids are shown in Table 2.13.

Table 2.13 *Biological parameters used to parameterize Chironomid in AQUATOX*

Parameters	Values	Notes
Half saturation feeding (mg/l)	1,085	Similar to one of chiornomid default animal in AQUATOX (= 1)
Maximum consumption (1/d)	0,53	Estimation from Mathews 1993 and Zooplankton maximum consumption value
Minimum prey for feeding (g/m^2)	0,2	
T optimum °C	25	default values (see Daphnia)
T min adapt °C	5	default values (see Daphnia)
T max °C	37	default values (see Daphnia)
Mean wet weight	0,006	Estimation from Mann 1964
Endogenous respiration	0,032	Mathews 1993
Mortality coefficient	0,09	Same order of L & P 80' (0,01 AQUATOX)
Lipid content	0,015	Lyndall 2010

Invertebrate Predators

Invertebrate predators are represented by leech, a segmented aquatic worm. They feed on aquatic invertebrates. Invertebrate predators biological parameters are shown in Table 2.14.

Table 2.14 *Biological parameters used to parameterize Invertebrate Predators in AQUATOX*

Parameters	**Values**	**Notes**
Half saturation feeding (mg/l)	0,31	
Maximum consumption (1/d)	0,15	Estimation from Mathews 1993 and Zooplankton maximum consumption value
Minimum prey for feeding (g/m^2)	0,1	
T optimum °C	20	Southern; default for zoobenthos = 15
T min adapt °C	5	AQUATOX default organism
T max °C	28,7	'www.soc.staffs.ac.uk/research/groups/cies2/
Mean wet weight	0,014	Estimation from Mann 1964
Endogenous respiration	0,01	Leidy & Ploskey, 1980, 20 degrees, p. D7
Mortality coefficient	0,0092	Estimated using P/B Mathews 1993
Lipid content	0,0075	Lyndall 2010

2.3.3.2. Fishes

The main difference between the Mathews study (Mathews, 1993) and the AQUATOX ecosystem is the way in which fish are considered.
In the former study the Fish are lumped in two categories:

Fish 1+, that includes all the fishes with more than one year of age
Fish 0, that represents the juveniles younger than one year

In AQUATOX the six major species of River Thames at Reading are considered separately, to increase the level of detail of the model. There is not juvenile-old fish separation anymore.
Due to a scarcity of data some parameters that describe fish biological dynamics had to be estimated taking some assumptions. Fishes consumption and respiration dynamics in AQUATOX contain some parameters that can be modelled using allometric functions or user input data (Park & Clough, 2012). The second following hypothesis is chosen because not enough information about fish allometric coefficients have been found.
In fish the respiration activity depends from different parameters: standard respiration, active respiration and specific dynamic action (Park & Clough, 2012).

Standard respiration is the most important and it is the basal respiratory loss modified by temperature. This aspect of respiration depends from endogenous respiration and density-dependent respiration. The last one is related to carrying capacity of the fish population (Park & Clough, 2012).

The endogenous respiration parameters for the fishes were found in Mann (Table 10 (Mann K. H., 1965)). For Bream, the Roach endogenous respiration was used because they are similar fishes.

In the literature found on River Thames at Reading there is not any data about carrying capacity of each species.

Carrying capacity is the maximum biomass of fish population that an ecosystem can support. The number of Bleak actually present in this River segment is 1,88 fish/m^2 and for Roach 1 fish/m^2 (Mann, 1964).

The hypothesis taken to estimate carrying capacity is that fish densities expressed by Mann represent the half of the fishes carrying capacity. It is a best guest choice indeed generated some uncertainties. The carrying capacity input value in AQUATOX has to be expressed in g/m^2. Therefore, these values have to be multiplied for the individual wet weight of the fish.

Roach and bleak carrying capacities are calculated using Equation 4.

$$K = 2D_f * W_f \quad \textbf{(4)}$$

where:

- K is carrying capacity [g/m^2];
- 2 is the value assumed to multiply fish actual density in River Thames and find a carrying capacity expressed as [individual / m^2];
- D_f is the fish density in the river segment [individual / m^2] (Mann, 1964);
- W_f is the individual mean wet weight of the fish population.

There was the need to find the carrying capacities of the other four species. A proportion between carrying capacity and P/B (production/biomass [1/d]) ratio has been estimated, as explained in the following paragraph.

Biological data for each species derive from Mathews (Mathews, 1993) and Mann (Mann K. H., 1965).

Ecological processes as respiration (R), production (P) and consumption (Q) are related to animal mass through power laws (Peters, 1983).

$$R \approx P \approx Q \approx m^{3/4} \quad \textbf{(5)}$$

The biological rates (R/B, P/B, Q/B) have an inverse proportionality with the animal biomass (Peters, 1983).

$$R/B \approx P/B \approx Q/B \approx m^{-1/4} \quad \textbf{(6)}$$

The carrying capacity is inversely proportionate to standard respiration (Park & Clough, 2012),

$$K \approx \frac{1}{R_{std}} \quad \textbf{(7)}$$

where:

- K is the carrying capacity [g/m^2];
- R_{stdl} is the standard respiration [g/m3 d].

$$K \approx \frac{1}{R_{std}} \approx \frac{1}{m^{3/4}} \approx m^{-\frac{3}{4}} \quad \textbf{(8)}$$
$$P/B \approx m^{-1/4}$$

This means that it is correct the assumption taken to correlate carrying capacity and P/B ratio. They are both inversely proportionate to mass.
The other four fishes (Gudgeon, Dace, Bream, Perch) carrying capacities are calculated using Equation 9.

$$K_i = K_{roach} * \frac{(P/B)_i}{(P/B)_{roach}} * W_{fi} \quad \textbf{(9)}$$

where:

- K_i is the carrying capacity of the fish species "i" [g/m^2];
- K_{roach} is the carrying capacity of Roach expressed as [fish/m^2] (equal to 2 [fish/m^2] from Equation 4;
- $(P/B)_i$ is production/biomass ratio of the fish species "i" [1/d] (Table 2.33 § Paragraph 2.4.3);
- $(P/B)_{roach}$ is production/biomass ratio of Roach [1/d] (Table 2.33 § Paragraph 2.4.3);
- W_{fi} is the mean individual wet weight of the fish species "i" [g].

Carrying capacities of fish are reported in tables that show the biological parameter needed by AQUATOX for each fish.

The optimal temperature of fishes could not be found in literature neither on FISHBASE. They were estimated multiplying living temperature of each fish (range of temperature between max T and min adaptation T (Park & Clough, 2012)) for a value included in a range between 0,8 and 0,9. Similar values of optimum temperature are present in AQUATOX default animals.

Bleak (Alburnus Alburnus)

Bleak is the most abundant fish in the River Thames at Reading (Williams, 1967). It is a small coarse fish of the *Cyprinid* family. Mathews defines Bleak as a surface feeder (Mathews, 1993). It feeds mainly on detritus and aerial insects.

The Bleak biological parameters are shown in Table 2.15

Table 2.15 *Biological parameters used to parameterize Bleak in AQUATOX*

Parameters	**Values**	**Notes**
Half saturation feeding (mg/l)	0,21	
Maximum consumption (1/d)	0,11	Estimation from Mathews 1993 and Zooplankton maximum consumption value
Minimum prey for feeding (g/m^2)	0,05	
T optimum °C	18	FISHBASE
T min adapt °C	10	FISHBASE
T max °C	20	FISHBASE
Mean wet weight	3,2	Estimation from Mann 1965
Endogenous respiration	0,025	Tab 10 Mann 1965
Mortality coefficient	0,006	from (P/B) (Palomares & Pauly, 1998)
Carrying capacity	12	Estimation from Mann 1964
Lipid content	0,02	AQUATOX default organism

Roach (Rutilus Rutilus)

Roach is a fish that belong to *Cyprinid* family. It is the bottom fish with the highest biomass in the River Thames at Reading (Mathews, 1993). It feeds mainly on detritus and it can be considered as a detritus browser (Mathews, 1993). The main biological parameters are shown in Table 2.16.

Table 2.16 *Biological parameters used to parameterize Roach in AQUATOX*

Parameters	**Values**	**Notes**
Half saturation feeding (mg/l)	0,083	
Maximum consumption (1/d)	0,1	Estimation from Mathews 1993 and Zooplankton maximum consumption value
Minimum prey for feeding (g/m^2)	0,05	
T optimum °C	18	FISHBASE
T min adapt °C	10	FISHBASE
T max °C	20	FISHBASE
Mean wet weight	16,6	Estimation from Mann 1965
Endogenous respiration	0,015	Tab 10 Mann 1965
Mortality coefficient	0,003	from (P/B) (Palomares & Pauly, 1998)
Carrying capacity	33	Estimation from Mann 1964
Lipid content	0,02	AQUATOX default organism

Dace (Leuciscus Leuciscus)

Dace is a freshwater fish of the family of cyprinid. It is a surface feeder. Detritus and aerial insects are its main source of food. The main biological parameters are shown in Table 2.17.

Table 2.17 *Biological parameters used to parameterize Dace in AQUATOX*

Parameters	**Values**	**Notes**
Half saturation feeding (mg/l)	0,165	
Maximum consumption (1/d)	0,11	Estimation from Mathews 1993 and Zooplankton maximum consumption value
Minimum prey for feeding (g/m^2)	0,05	prof judgment
T optimum °C	18	FISHBASE
T min adapt °C	4	FISHBASE
T max °C	22	FISHBASE
Mean wet weight	12,9	Estimation from Mann 1965
Endogenous respiration	0,023	Tab 10 Mann 1965
Mortality coefficient	0,0051	from (P/B) (Palomares & Pauly, 1998)
Carrying capacity	42	Estimation from Mann 1964
Lipid content	0,02	AQUATOX default organism

Gudgeon (Gobio Gobio)

Gudgeon is a small freshwater fish of the family of Cyprinid. It is a bottom fish and it feeds mainly on aquatic invertebrates. Gudgeon main biological parameters are shown in Table 2.18.

Table 2.18 *Biological parameters used to parameterize Gudgeon in AQUATOX*

Parameters	**Values**	**Notes**
Half saturation feeding (mg/l)	0,073	
Maximum consumption (1/d)	0,11	Estimation from Mathews 1993 and Zooplankton maximum consumption value
Minimum prey for feeding (g/m^2)	0,2	prof judgment
T optimum °C	18	FISHBASE
T min adapt °C	2	FISHBASE
T max °C	20	FISHBASE
Mean wet weight	9,95	Estimation from Mann 1965
Endogenous respiration	0,023	Tab 10 Mann 1965
Mortality coefficient	0,0044	prof. judgment from (P/B)
Carrying capacity	27	Estimation from Mann 1964
Lipid content	0,02	AQUATOX default organism

Perch (Perca Fluviatilis)

Perch is a freshwater gamefish belonging to the family *Percidae*. Perch is a surface feeder. It feeds on zooplankton external insects and other fish. Perch main biological parameters are show in Table 2.19.

Table 2.19 *Biological parameters used to parameterize Perch in AQUATOX*

Parameters	**Values**	**Notes**
Half saturation feeding (mg/l)	0,276	
Maximum consumption (1/d)	0,06	Estimation from Mathews 1993 and Zooplankton maximum consumption value
Minimum prey for feeding (g/m^2)	0,2	prof judgment
T optimum °C	19	FISHBASE
T min adapt °C	10	FISHBASE
T max °C	22	FISHBASE
Mean wet weight	21,1	Estimation from Mann 1965
Endogenous respiration	0,021	Tab 10 Mann 1965
Mortality coefficient	0,0077	prof. judgment from (P/B)
Carrying capacity	42,2	Estimation from Mann 1964
Lipid content	0,03	AQUATOX default organism

Bream (Abramis Brama)

Bream is a freshwater fish of the family of *Cyprinid*. It is a bottom feeder having a similar diet of Roach.

Detritus is its main source of food. Bream main biological parameters are shown in Table 2.20.

Table 2.20 *Biological parameters used to parameterize Bream in AQUATOX*

Parameters	**Values**	**Notes**
Half saturation feeding (mg/l)	0,22	
Maximum consumption (1/d)	0,09	Estimation from Mathews 1993 and Zooplankton maximum consumption value
Minimum prey for feeding (g/m^2)	0,05	prof judgment
T optimum °C	21	FISHBASE
T min adapt °C	24	FISHBASE
T max °C	10	FISHBASE
Mean wet weight	18,5	Estimation from Mann 1965
Endogenous respiration	0,015	Tab 10 Mann 1965
Mortality coefficient	0,0025	prof. judgment from (P/B)
Carrying capacity	28,3	Estimation from Mann 1964
Lipid content	0,02	

2.3.3.3. Adult chironomids and external insects

Adult chironomids and external insects are modelled exclusively for the food source role they represent. Their biomass trends depend only from a constant upstream input concentration (Table 2.21): the major part of their biological parameters is set to zero to avoid interferences in the ecosystem dynamics.

The biomass trends of these animals thus have the same trajectory of inflow. The parameters are set to have a continuous flow from upstream and downstream to avoid an excessive accumulation of these animals that would increase enormously their biomass in the system.

The loadings from upstream of these two animals are chosen verifying that their annual average biomass would be equal to the biomass values recovered by the Mathews study (§ Paragraph 2.4).

Table 2.21 *Loading from upstream for Adult chironomids and External insects. It is the only way to simulate animals that do not belong to the aquatic ecosystem.*

	Loading from upstream (g/m^2 dry)
Adult chironomids	2,34
External insects	5,45

2.4. Trophic web

The ecosystem is composed by primary producers (Phytoplankton, Periphyton and Macrophites), aquatic invertebrates (chironomids, filter feeders, invertebrate predators, browsers and grazers, zooplankton), fishes(divided in bottom e suspended feeders) and invertebrates coming from outside the system (External insect and Adult chironomids) (Figure 2.6).

An interesting characteristic of this ecosystem is the important role that detritus plays in the trophic web (Mathews, 1993).

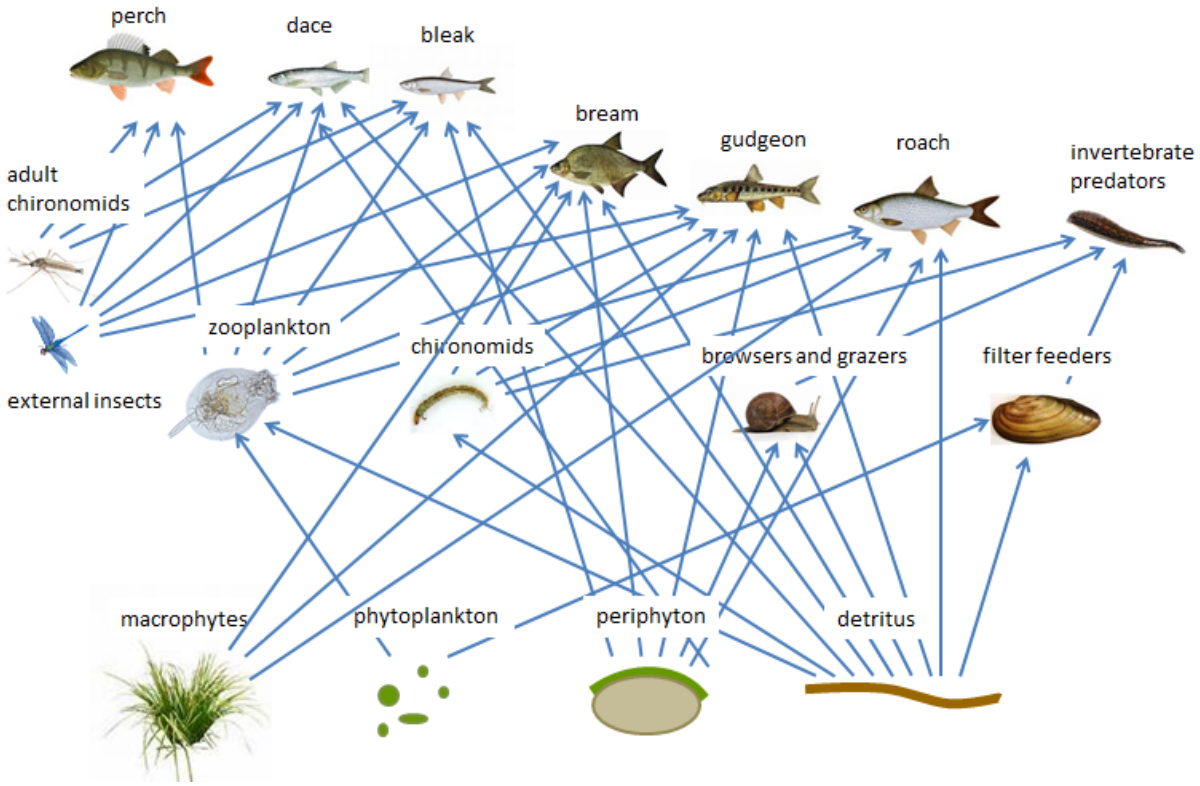


Figure 2.6 *Scheme of the food web used in the study*

2.4.1. Fish diet

The food web of this study is based on the one of Mathews (Mathews, 1993), but it has undergone some changes.

The lower part of the trophic web remained mainly the same, while the higher levels have been modified.

In Mathews trophic web the fishes are divided in two classes: the first one (Fish 0) describes the recruit and juvenile fishes behaviors while the second one (Fish 1+) describes a diet composition for the fishes of this stretch of the River Thames that have more than one year of age.

There was the need to separate the fish categories in the different fish species that composed the River Thames fish fauna to have a more detailed picture of river ecosystem and to understand the different ecological roles of the fishes within the river.

The fish species mainly presented in the River Thames are Bleak, Roach, Gudgeon, Dace, Perch, Bream.

The first two fishes represent the 80 % of the river fish fauna at Reading (Mann, 1964). For this reason, Mathews considers their diet composition separately from the other four species.

These six species of fishes represents approximately the 99 % of the fish fauna of the river (Williams, 1967).

In the Mathews study a diet percentage is covered by a category of food called “allocthonus”. With this category he describes the energy import in the food web coming from outside the system and from macrophytes.

Due to the fact that the major part of the food of this category is represented by some external insects, here it was decided to divide “River Thames allocthonus sources of food“ (described in the Figure 2.7- a) in two category: Macrophytes and External Insects (Figure 2.7- b).

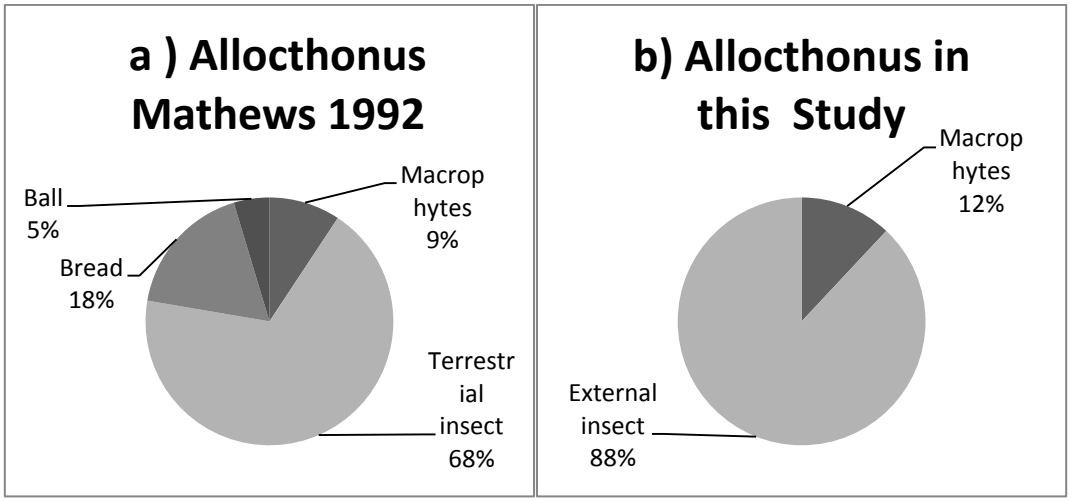


Figure 2.7 *Scheme of the allochtonus source of energy in Mathews study (a) and in the food web design for the AQUATOX model (b)*

2.4.1.1. Fish diets for the category of fish "Fish +1"

The estimation of the singular fish species diet composition for the category Fish 1+ was done using three main biological parameters for each specie:

- P production of new biomass [g/(m^2*y)];
- B biomass [g/m^2];
- Q food consumption [g/(m^2*y)].

P values were known from Mathews study (Table 2) (Mathews, 1993). In this table the species are divided in three category:

- Roach and Bleak;
- Other major species (Dace and Gudgeon);
- Minor species (Perch and Bream).

To separate the three values of Mathews study in the six values for each species, the data found in Table 1 of Mathews (Mathews, 1993) were used for Bleak, Roach, Gudgeon and Dace while the data from Mathews paper of 1971 (Table XX of (Mathews C. P., 1971)) were used for Perch and Bream.

The sum of the six production values has to be equal to the total production of Fish +1 group shown in Table 5 of Mathews (Mathews, 1993).

Mathews describes the trophic network using the energy flow between the organisms of the ecosystem. AQUATOX requires the biomass of animals as a measure of mass; for this reason, a conversion factor of 1 g live weight = 1,154 kcal (Mathews, 1993) was applied for fish.

The productions of the six species are shown in Table 2.21 :

Table 2.21 *Fish production in the River Thames at Reading. The second column describes the production as an energy value and the third is the relative conversion in a mass value*

Fish	**P**	**P**
	kcal /(m^2 y)	**g/(m y)**
Roach 1+	11,137	9,651
Bleak 1+	31,863	27,611
Dace 1+	1,790	1,551
Gudgeon 1+	9,910	8,587
Perch 1+	2,286	1,981
Bream 1+	3,714	3,218
tot	60,7	52,5997

The P/B values were used to find the biomass for each species of fish. P/B ratios of the major species were taken from the data of Table 1 of Mathews (Mathews, 1993). A mean P/B value was calculated using the weighted mean method.

$$\left(P/B_j\right) = \frac{\sum_{i=1}^{Age} \left(P/B\right)_{ij} * B_{ij}}{\sum_{i=1}^{Age} B_{ij}} \qquad \textbf{(10)}$$

where:

- $(P/B)_j$ is the weighted mean of the fish “j”;
- B_{ij} is the biomass of the fish “j” having the age “i”;
- $(P/B)_{ij}$ is the production-biomass ratio of the fish “j” at the age “i”;
- “Age” is the age of the fish from 1 year till the maximum value recorded by Mathews.

The values of P/B for the minor species (Perch and Bream) have been calculated iteratively, looking that the sum of the six values of fish biomass B_j (Equation 12) would be equal to the global value of B (Equation 13) of Table 5 of Mathews (Mathews, 1993). The weighed mean

of P/B ratio for the six species has to be equal to the value used by Mathews for the category Fish +1 (Mathews, 1993).

$$P/B = \frac{\sum_{j=1}^{6} (P/B)_j * B_j}{\sum_{j=1}^{6} B_j} \quad \textbf{(11)}$$

$$B_j = \sum_{i=1}^{Age} B_{ij} \quad \textbf{(12)}$$

$$B = \sum_{j=1}^{6} B_j \quad \textbf{(13)}$$

where:

- P/B is the global production-biomass ratio, i.e. the weighted mean of the P/B ratio of fishes (P/B_j). It must be equal to the value found in Table 5 of Mathews (Mathews, 1993);
- B_j is the total biomass of fish species "j";
- B is the global mass of fish, i.e. the sum of the biomasses of the fish. It must be equal to the value of Table 5 in Mathews study. (Mathews, 1993).

Perch and Bream production-biomass ratios have been assumed considering that P/B is higher for smaller species and also taking in account the size that could reach each singular species **[V]**. These two values have been found in an iterative way. The process stopped when the mean of P/B values for the all fishes (weighted on B) had been equal to the global value of P/B for Fish +1 category in Mathews study (Table 5 (Mathews, 1993)).
P/B and B values are shown in Table 2.22.

Table 2.22 *Fish biomasses and their P/B ratios in the River Thames at Reading. The global value for P/B is the weighted mean of the P/B ratios of fishes while the global biomass is the sum of the fish biomasses*

Fish	**P/B**	**B**
	1/y	**g/m^2**
Roach 1+	0,429	22,487
Bleak 1+	0,840	32,878
Dace 1+	0,508	3,055
Gudgeon 1+	0,593	14,480
Perch 1+	0,414	4,785
Bream 1+	0,308	10,449
Global	**0,597**	**88,134**

Consumption parameters (Q) are the last parameters needed to estimate the diet composition for each species of fish. A study carried out by Mann in the 1965 shows how the energy ingested by a fish species as food is absorbed and used by the organisms and at the same time the part of energy that is egested or excreted (Mann K. H., 1965) by the animal. He analyzed the behavior of five of the six fishes that are considered in this study.

Using this study the Q/B parameters for Bleak, Roach, Dace, Gudgeon and Perch have been found. An aspect that needs to be underlined is that using these values the respective P/Q values for each species are lower of the ones usually observed in aquatic ecosystems. The values found are slightly less than 0,1 and normally the production-consumption ratio should be in a range of 0,1 and 0,4 (Christensen et al, 2005).

To test if such values were justified the P/Q ratio was calculated from Mathews study (Mathews, 1993). The ratio gives a result similar to the ones found in the Mann's study (Mann K. H., 1965).

Also the Q/B parameters calculated using the Pauly and Palomares empirical equations (Palomares & Pauly, 1998) gave similar results.

For this reason, it was decided to use Mann (Mann K. H., 1965) values, because they are the ones found on fishes that are actually living in the Thames at Reading.

Bream Q/B value was not found in literature. An estimation of the consumption for this fish was done using Pauly and Palomares empirical equations (Equation 14 (Palomares & Pauly, 1998)).

$$\log Q/B = 5{,}847 + 0{,}280 \log Z - 0{,}152 \log W_{\infty} - 1{,}360 T' + 0{,}062 A + 0{,}510 h + 0{,}390 d \qquad \textbf{(14)}$$

"Z", that is the instantaneous rate of total mortality, has been considered equal to P/B (Palomares & Pauly, 1998) and the asymptotic weight was estimated from the length-weight relationship found on Fishbase (Palomares & Pauly, 1998) **[V]**.

$$W_{\infty} = aL_{\infty}^{\ b} \qquad \textbf{(15)}$$

Asymptotic weight is the mean weight the fish would reach if it could grow up indefinitely.
The asymptotic length assumed for the calculation of the asymptotic weight is equal to 50 cm that is a value equal to the double of Bream common length **[V]**. It is a value lower than the maximum length found on FISHBASE but it takes in account that all the species of fishes in the River Thames at Reading have an average length shorter (Williams, 1967) than their common length found in literature **[V]** .
" T' ", the data of temperature, is the average value of the dataset found in Berrie's study (Berrie, 1972). The coefficients "d = detrivore" and "h = herbivore" can assume the value 0 or 1, it depends on the major source of food for the fish. The Bream is considered a bottom and detrivorous feeder so the "d" parameter has been considered equal to 1 while the "h" parameter equal to 0.
"A" is the aspect ratio; the ratio between the depth of the caudal fin and its surface. It was found on FISHBASE website **[V]**.
A value of Q/B for each fishes now is available (Table 2.23). As shown before for the calculation of B, the sum of Q for each species has to be equal to the value calculated using the results of Table 5 in Mathews study (Mathews, 1993). And the global Q/B for the Fish 1+ category has to be equal to the one found in Table 5 of Mathews (Mathews, 1993)

$$Q/B = \frac{\sum_{j=1}^{6} (Q/B)_j * B_j}{\sum_{j=1}^{6} B_j} \qquad \textbf{(16)}$$

$$Q = \sum_{j=1}^{6} Q_j \qquad \textbf{(17)}$$

- Q/B is the global consumption-biomass ratio i.e. the weighted mean of the Q/B ratios of fishes(Q/B_j). It must be equal to the value found in Table 5 of Mathews (Mathews, 1993);
- Q_j consumption of fish species "j";
- Q is the global consumption of fishes. It must be equal to the value of Table 5 in Mathews study. (Mathews, 1993).

Table 2.23 *Fish biomass and fish consumption in the River Thames at Reading recovered from Mann (1965). The second column describes the ratio between consumption and Biomass and the third the value of biomass per square meter of each fish*

Fish	**Q/B**	**B**	**Q**	**Reference**
	1/y	**g/m2**	**g/(m^2 y)**	
Roach 1+	7,613	22,487	171,200	Mann,1965
Bleak 1+	12,563	32,878	413,030	Mann,1965
Dace 1+	11,250	3,055	34,368	Mann,1965
Gudgeon 1+	11,000	14,480	159,280	Mann,1965
Perch 1+	10,065	4,785	48,157	Mann,1965
Bream 1+	7,390	10,449	77,218	Palomares, 1998
Global	**10,249**	**88,134**	**903,253**	

Using these values the global Q and global Q/B tend to be higher than the one found in Mathews 1993.The global parameters have to be the same as the ones shown by Mathews to recreate a similar food web (Mathews, 1993).

A new set of Q/B was calculated leaving the composition of global Q equal to the one found (Table 2.23) and also the ratio between the different values of Q remain unchanged. The Q values used to estimate the diet compositions of fishes are the ones shown in Table 2.24

Table 2.24 *Fish biomass and fish consumption values used. to estimate fish diets.*

	Q/B	**B**	**Q**
	1/y	**g/m^2**	**g/(y*m^2)**
Roach 1+	6,803	22,487	152,981
Bleak 1+	11,226	32,878	369,076
Dace 1+	10,053	3,055	30,711
Gudgeon 1+	9,829	14,480	142,330
Perch 1+	8,993	4,785	43,033
Bream 1+	6,603	10,449	69,000
Global	**9,158**	**88,134**	**807,129**

A resume of the biological parameter is shown in Table 2.25

Table 2.25 *Resume of the main Fish +1ecological parameters*

Fish	P/B	P/Q	Q/B	B	Q
	1/y		1/y	g/m^2	g/(m^2 y)
roach 1+	0,429	0,063	6,803	22,487	152,981
bleak 1+	0,840	0,075	11,226	32,878	369,076
dace 1+	0,508	0,051	10,053	3,055	30,711
gudgeon 1+	0,593	0,060	9,829	14,480	142,330
perch 1+	0,414	0,046	8,993	4,785	43,033
bream 1+	0,308	0,047	6,603	10,449	69,000
Global	**0,597**	**0,065**	**9,158**	**88,134**	**807,129**

The diet compositions of the six fish species have been calculated using diet composition data in Mathews (Table 3) (Mathews, 1993).

The global diet composition for the Fish 1+ of the River Thames should be equal to the one in Mathews (Table 4) (Mathews, 1993). The global diet is the diet composition formed putting together the diets of each fish considering the different consumption (Q) of each species.

In Table 2.26 the global diet composition of Fish 1+ is shown (Mathews, 1993).

Table 2.26 *The global diet composition of fishes at Thames*

Food item	Fish 1+
Fish 1+	0
Fish 0	0,005
Invertebrate predator	0,001
Invertebrate browsers	0,017
Filter feeders	0,013
Young chironomids	0,023
Adult chironomids	0,144
External insects	0,216
Macrophytes	0,029
Zooplankton	0,026
Periphyton	0,177
Detritus	0,350
tot	**1,000**

Qualitative and quantitative data from literature and FISHBASE **[5]** have been used for a "rough" primary estimation of fish diet compositions. To calculate the global diet and compare it with the one of Table 2.26 the weighted mean method was used.

$$F_i = \frac{\sum_{j=1} F_{ij} * Q_j}{\sum_{j=1} Q_j} \quad \textbf{(18)}$$

$$\sum_{i=1} F_i = 1 \quad \textbf{(19)}$$

$$\sum_{i=1} F_{ij} = 1 \quad \textbf{(20)}$$

- F_i is the percentage of the "i" category of food in the global diet. It has to be equal to the one of the Mathews study;
- F_{ij} is the percentage of the "i" category of food in the diet of the fish "j";
- Q_j is the consumption of the fish "j" [g/(m^2*a)].

The "supposed" singular fish diet composition was adjusted considering the fish qualitative food preferences to create a weighted global composition equal to the one of Mathews (Mathews, 1993).

Mathews divides qualitatively River Thames fish fauna as water surface feeders and river bottom feeders.

The first ones are Bleak, Dace, Perch while the second ones are Roach, Gudgeon, Bream. The changes applied on the singular diet composition of the fishes were done considering Mathews study observations on fishes and Berrie partial diet compositions (Table 3 of Berrie's study (Berrie, 1972)).

Perch and Bleak are the ones with the lowest detritus composition because they are mainly carnivorous, for this fact they are the main consumers of external insects and adult chironomids. Dace diet composition changes with the seasons: during the winter it prefers detritus probably due to the low number of insects and during the summer it eats mainly insects. Roach and Bream are the ones that feed mainly on detritus (Mathews, 1993) while Gudgeon feeds on detritus and benthic invertebrates.

The bottom feeders are the ones considered the main consumers of the benthic invertebrates.

The resulting compositions are shown in Table 2.27 and Table 2.28.

Table 2.27 *The diet composition of Roach 1+ and Bleak 1+*

Diet	Roach 1+	Bleak 1+	Global Diet of Roach and Bleak
Detritus	0,620	0,238	34,99%
Periphyton	0,107	0,205	17,67%
Zooplancton	0,044	0,019	2,62%
Macrophytes	0,076	0,010	2,94%
External insects	0,007	0,303	21,61%
Young chironomids	0,064	0,006	2,28%
Adult chironomids	0,008	0,200	14,36%
Filter feeders	0,027	0,007	1,25%
invertebrate browser	0,037	0,009	1,71%
Invertebrate predators	0,001	0,001	0,11%
Roach 0	0,004	0,000	0,11%
Bleak 0	0,007	0,002	0,34%
Tot	**1,0000**	**1,000**	**100,00 %**

Table 2.28 *The diet composition of Dace 1+, Gudgeon 1+, Perch 1+ and Bream 1+*

Diet	Dace 1+	Gudgeon 1+	Perch +1	Bream 1+	Global diet for Dace, Gudgeon, Perch and Bream
Detritus	0,348	0,371	0,010	0,519	34,99%
Periphyton	0,053	0,258	0,021	0,161	17,67%
Zooplancton	0,011	0,04	0,011	0,014	2,62%
Macrophytes	0,009	0,036	0,000	0,043	2,94%
External insects	0,269	0,159	0,425	0,18	21,61%
Young chironomids	0,005	0,034	0,000	0,022	2,28%
Adult chironomids	0,298	0,052	0,496	0,044	14,36%
Filter feeders	0,002	0,02	0,004	0,007	1,25%
invertebrate browser	0,003	0,029	0,001	0,009	1,71%
Invertebrate predators	0,002	0,001	0,001	0,001	0,11%
Bleak 0	0,000	0,000	0,020	0,000	0,30%
Dace 0	0,000	0,000	0,006	0,000	0,08%
Perch 0	0,000	0	0,006	0,0	0,08%
Total	**1,000**	**1,000**	**1,000**	**1,000**	**100,00%**

2.4.1.2. Fish diets for the category of fish "Fish 0"

The Fish 0 (recruits and juveniles) group has been considered in a different way. The same P/B and Q/B are considered for each fish species due to the scarcity of data on recruits and making the assumption that the alimentary behaviors of recruits are equal for every species. The P/B and Q/B data on recruits used are the ones of Mathews study are used (Mathews, 1993).

The P/Q value is 0,5. It is higher of the normal values (range 0,1-0,4) (Christensen et al, 2005). This value is supposed a possible value for recruits because their size and their production dynamics are more similar to the ones of zooplankton thank to the ones of bigger fishes. A resume of the main biological parameters of Fish 0 category is shown in Table 2.29

Table 2.29 *Resume of the main fish 0 ecological parameters*

Fish	**P/B**	**P/Q**	**Q/B**	**B**	**Q**	**P**
	1/y		1/y	g/m^2	$g/(m^2 y)$	$g/(m^2 y)$
Roach 0	7,210	0,505	14,269	2,858	40,785	20,608
Bleak 0	7,210	0,505	14,269	8,439	120,421	60,847
Dace 0	7,210	0,505	14,269	0,824	11,763	5,944
Gudgeon 0	7,210	0,505	14,269	2,625	37,456	18,926
Perch 0	7,210	0,505	14,269	0,623	8,886	4,490
Bream 0	7,210	0,505	14,269	1,012	14,437	7,295
Global	**7,210**	**0,505**	**14,269**	**16,382**	**233,748**	**118,111**

Using this data and the same method explained for Fish 1+ the diet composition for the recruits of each species was found (Table 2.30, Table 2.31)

Table 2.30 *The diet composition of Roach 0 and Bleak 0*

Diet	**Roach 0**	**Bleak 0**	**global**
Zooplankton	0,757	0,442	0,522
Periphyton	0,062	0,000	0,016
Young Chironomide	0,052	0,184	0,151
Adult Chironomids	0,041	0,174	0,140
Detritus	0,088	0,200	0,172
Tot	**1,000**	**1,000**	**1,000**

Data on diet composition of juveniles were found in Berrie study in Table 3 (Berrie, 1972). In this paper there is a "rough" diet composition for fish shorter of 5 cm and bigger of 5 cm.

Table 2.31 *The diet composition of the minor fishes Dace 0, Gudgeon 0, Perch 0 and Bream 0*

Diet	**Dace 0**	**Gudgeon 0**	**Perch 0**	**Bream 0**	**global**
Detritus	0,271	0,230	0,01	0,039	0,172
Periphyton	0,029	0,000	0,095	0,000	0,016
Zooplankton	0,29	0,509	0,703	0,631	0,522
Young chironomids	0,029	0,181	0,021	0,251	0,151
Adult chironomids	0,381	0,080	0,171	0,079	0,140
tot	**1,000**	**1,000**	**1,000**	**1,000**	**1,000**

2.4.1.3. Egestion rates

A further verification done to understand if the suppositions made could be appropriate is to calculate the global egestion rate for the two class of fishes (fish 1+ and fish 0) using the diet compositions found for each singular fish species and to compare the values found with the ones of Mathews. The egestion rate represents the food ingested that is not assimilated by the organism.

Mathews considers the food assimilation equal to 0,8 for each category of food except the detritus one.

Detritus fraction has a low assimilation for fish, the average value chosen by Mathews is 0,07 (Mathews, 1993) (range 0,0285 – 0,145) (Mann et al, 1972).

The result of this two assumptions is that the egestion rate for each food except detritus is considered 0,2. The egestion rate for the detritus is equal to 0,93.

The error between the resulting global egestion rates for the two category of fishes (fish 0 and fish 1+) calculated and the ones published in the study of Mathews (Table 5 (Mathews, 1993) can be considered acceptable (in a range of 0 % and 4 %).

2.4.2. Aquatic invertebrates diet

The invertebrates diets data are shown in Table 2.32 (Mathews, 1993). They feed manly on detritus, phytoplankton and periphyton

Table 2.32 *Invertebrates diet composition from Mathews study*

Prey\Predator	Zooplankton	Young chironomids	Filter feeders	Browsers and grazers	Invertebrate predators
Detritus	0,5	1	0,5	0,67	
Phytoplankton	0,5		0,5		
Periphyton				0,33	
Zooplankton					
Young chironomids					0,34
Filter feeders					0,33
Browsers and grazers					0,33
Invertebrate predators					

2.4.3. AQUATOX trophic web requirements

2.4.3.1. AQUATOX trophic web requirements for fish

An initial simplification of the system was done putting together for each species the Fish 0 category and the Fish 1+ category recovered from the data present in Mathews study (Mathews, 1993). In Table 2.33 the parameters used for fish to create AQUATOX trophic web are shown.

Table 2.33 *Fish biological parameters used to estimate trophic web inserted in AQUATOX.*

Fishes	P/B	P/Q	Q/B	B	Q
	1/y		1/y	g/m^2	$g/(m^2\ y)$
Roach	1,19	0,16	7,64	25,35	193,77
Bleak	2,14	0,18	11,85	41,32	489,50
Dace	1,93	0,18	10,95	3,88	42,47
Gudgeon	1,61	0,15	10,51	17,10	179,79
Perch	1,20	0,12	9,60	5,41	51,92
Bream	0,92	0,13	7,28	11,46	83,44

P/Q values, putting together the two categories, belong to the range present in literature (0,1-0,4) (Christensen et al, 2005).

The diets of juveniles and adult fishes of each species have been grouped in a singular diet. This diet is formed calculating the weighted mean on consumption for each prey category of Fish 0+ and Fish 1+.

AQUATOX divides the detritus in various compartments (dissolved detritus, suspended particulate detritus, sediment detritus etc.). For this reason the detritus diet percentage of the organisms has to be divided in the different fraction of detritus modelled by the software.
This step has a key role in the ecosystem because the River Thames trophic web at Reading is highly dependent from detritus (Mathews, 1993).
In Mathews study (Mathews, 1993) there were not any data about detritus classification, refractory and labile coefficients and detritus subdivision in the trophic web.
Rational suppositions and estimations from the Mathews study (Mathews, 1993) have been done to divide the detritus in the different category presented in AQUATOX.
About 20% of the detritus of the Mathews study (Mathews, 1993) can be considered sediment detritus and the rest 80% as particulate detritus. Dissolved detritus is not a fraction that could be ingested as a food source by the organisms in AQUATOX model (Park & Clough, 2012).
The detritus dietary fraction recovered from Mathews study is divided in four fractions: labile particulate detritus, refractory particulate detritus, labile sediment detritus and refractory sediment detritus.

$$D_{ij} = D_i * a * b \quad \textbf{(21)}$$

- D_{ij} is the fraction "j" of detritus considered as food for the species of fish "i" ("j" can be: labile particulate detritus, refractory particulate detritus, labile sediment detritus, refractory sediment detritus);
- D_i is the total detritus percentage of fish diet estimated from Mathews (Mathews, 1993) Considering the fact that the juvenile and adult fish diets are put together;
- a coefficient to divide the total detritus in particulate (0,8) or sediment detritus (0,2) (Mathews, 1993);
- b coefficient to divide particulate or sediment detritus in labile fraction (0,07) or refractory fraction (0,93) (Mathews, 1993)

The surface feeder fishes are supposed to eat only suspended detritus, except for Dace. It has a different alimentary behavior that changes over the year. The main source of food for Dace are small invertebrates during the hot season on the contrary during the cold season it prefers

detritus probably due to the lower presence of invertebrate (Caffrey et al, 2007). The bottom feeders feed on suspended and sediment detritus.

For fishes It is supposed that the labile fraction of detritus is complete assimilated (egestion factor equal to 0) and the refractory one is egested completely (egestion fraction equal to 1)

2.4.3.2. AQUATOX trophic web requirements for invertebrates

Data of detritus consumption of invertebrates can be found in Mathews study (Mathews, 1993).

Zooplankton has been considered suspended detritus feeder. The same is for Filter feeders because the organism that represents the group is a bivalve. A gastropod represents the Browsers and grazers category for this reason the main detritus source is the sediment one. Chironomid consumes both sediment and suspended detritus.

The subdivision of detritus has to comply with two characteristics. The sum of the different values of detritus fractions has to be equal to the original one present in Mathews study (Mathews, 1993) and the sum of the values representing the detritus consumptions of a detritus category for each invertebrate has to be equal to the value found in Mathews study (Mathews, 1993).

$$D_k = D * a * b \quad \textbf{(22)}$$

- D_k is the fraction "k" of detritus consumed by all the invertebrates ("k" can be: labile particulate detritus, refractory particulate detritus, labile sediment detritus, refractory sediment detritus);
- D is the percentage of total detritus consumed by invertebrates from Mathews (Mathews, 1993);
- a coefficient to divide the total detritus in particulate (0,8) or sediment detritus (0,2) (Mathews, 1993);
- b coefficient to divide particulate or sediment detritus in labile fraction (0,07) or refractory fraction (0,93) (Mathews, 1993).

$$D_k = \sum_{i=1} D_{ki} \quad \textbf{(23)}$$

$$D_{ki} = D_i * f_{ik} \quad \textbf{(24)}$$

$$D_i = \sum_{k=1} D_{ki} \quad \textbf{(25)}$$

$$D = \sum_{i=1} D_i \quad \textbf{(26)}$$

- D_{ki} is the value of the detritus fraction "k" of the species "i";
- D_i is the amount of detritus consumed by the species "i" (Mathews, 1993) [kcal/m^2 year];
- f_{ik} is the fraction of D_k consumed by the species "i" (chosen using iterative method).

The repartition of detritus in the diets of aquatic invertebrates is shown in Table 2.34

Table 2.34 *Repartition of detritus in the aquatic invertebrates diets. B&G(Browsers and Grazers), F.F (filter feeders), Y. C. (Young Chironomids), Zo (Zooplankton)*

Detritus	**D_i kcal /(m^2 y)**	**f_{ik}**	**refract susp D_{ik} kcal /(m^2 y)**	**f_{ik}**	**labile susp. D_{ik} kcal /(m^2 y)**	**f_{ij}**	**refract sed D_{ik} kcal /(m^2 y)**	**f_{ij}**	**labile sed D_{ik} kcal /(m^2 y)**
B&G	131,4	0,00	0,00	0,00	0,00	0,24	119,31	0,32	11,97
F.F	387,6	0,19	377,83	0,07	9,73	0,00	0,00	0,00	0,00
Y.C	1718,4	0,61	1213,02	0,69	102,53	0,76	377,83	0,68	25,45
Zo	435,4	0,20	397,71	0,25	37,42	0,00	0,00	0,00	0,00
Tot	**2672,8**	**1,00**	**1988,56**	**1,00**	**149,68**	**1,00**	**497,14**	**1,00**	**37,42**

Using this values the consumption of each fraction of detritus by the invertebrate is found (Table 2.35)

Table 2.35 *Fraction of detritus eaten by the aquatic invertebrates*

Invertebrates	**Refractory part**	**Labile part**	**Refract sed**	**Labile sed**
Browsers and Grazers	0,00	0,00	0,91	0,09
Filter feeders	0,97	0,03	0	0
Young chironomids	0,71	0,06	0,22	0,01
Zooplankton	0,91	0,09	0	0

These values have to be multiplied for the percentage of diet that cover the detritus for each invertebrate to have the invertebrate diet required by AQUATOX (Table 2.36) .

Table 2.36 *Aquatic invertebrates food web*

Prey\Predator	Zooplankton	Young chironomids	Filter feeders	Browsers and grazers	Invertebrate predators
Refractory Part. Detr		0,71		0,61	
Labile Part. Detr		0,06		0,06	
Refractory Sed Detr	0,46	0,22	0,49		
Labile Sed. Detr	0,04	0,01	0,01		
Phytoplankton	0,5		0,5		
Periphyton				0,33	
Zooplankton					
Young chironomids					0,34
Filter feeders					0,33
Browsers and grazers					0,33
Invertebrate predators					

The egestion rate of detritus for the invertebrate is equal to 0 for the labile fractions while a value of 0,2 is supposed for the other sources different for detritus. The egestion factor for refractory detritus for each aquatic invertebrate was found using an iterative method.

First of all an egestion factor for the refractory detritus is supposed. In Table 2.37 (1st column) the amount of food consumed by each invertebrate is shown. The global consumption, expressed as the sum of the consumption of each source of food, is calculated.

Using the consumption of each source of food and the respective egestion factors the egestion of each source of food is calculated (3rd column). The global egestion for an invertebrate is equal to the sum of the egestion values.

The global egestion factor is the ratio between the global consumption and the global egestion. This value has to be equal to the egestion factor of the same invertebrate shown in the Table 5 of Mathews study (Mathews, 1993).

The refractory detritus egestion factor is the only unknown of the system together with the global egestion factor. The egestion factor of the refractory detritus for an invertebrate has to be changed iteratively until the invertebrate global egestion factor results equal to the one found in Table 5 of Mathews (Mathews, 1993).

Aquatic invertebrates egestion rates are shown in Table 2.37.

Table 2.37 *Estimation of Aquatic invertebrates egestion rates. The global egestion rate of each aquatic invertebrate has to be equal to the one of Mathews*

Browsers and Grazers	**Consumption kcal /(m^2 y)**	**Egestion rate**	**Egestion kcal /(m^2 y)**
Periphyton	64,70	0,2	12,94
Refractory sediment detritus	119,31	0,71	84,71
Labile sediment detritus	11,97	0	0
Global	**195,99**	**0,50**	**97,65**
Filter feeders	**kcal /(m^2 y)**		**kcal /(m^2 y)**
Phytoplancton	387,60	0,2	77,52
Refractory suspend	377,82	0,82	309,82
Labile suspend	9,73	0	0
Global	**775,16**	**0,50**	**387,34**
Young chironomids	**kcal /(m^2 y)**		**kcal /(m^2 y)**
Refractory suspended detritus	1213,02	0,54	655,03
Labile suspended detritus	102,53	0	0
Refractory sediment detritus	377,83	0,54	204,03
Labile sediment detritus	25,45	0	0
Global	**1718,82**	**0,50**	**859,06**
Zooplankton	**kcal /(m^2 y)**		**kcal /(m^2 y)**
Phytoplancton	435,40	0,2	87,08
Refractory suspended detritus	397,71	0,87	346,01
Labile suspended detritus	37,42	0	0
Global	**870,53**	**0,50**	**433,09**

2.4.3.3. Initial AQUATOX trophic web

The egestion factors of the detritus fractions for each animals were shown in the previous two paragraphs (§ Paragraph 2.4.3.1 , and Paragraph 2.4.3.2). The egestion rates of the categories of food diverse from detritus are set equal to 0,2 for every animal (Mathews, 1993).

Taking this assumptions the egestion factors of every prey for every predator are supposed (Table 2.38).

Using the animal diet calculated in paragraph 2.4.1 (for the fishes) and paragraph 2.4.2 (for the invertebrates) an initial food web is recovered to start the parameterization of the ecosystem in AQUATOX (Table 2.39)

Table 2.38 *Egestion rate for each food source. Phy= Phytoplanlkton, Peri = Periphyton, M=Macrophytes, E.I= External Insects, A.C.= Adult Chironomid, Zo= Zooplankton, Y.C= Young Chironomids, F.F = filter feeders, B&G= Browsers and Grazers, I. P= Invertebrates Predators, R= Roach, Bl= Bleak, D= Dace, G=Gudgeon, P=Perch, Br= Bream*

Egestion coefficient	Y.C	B.&G.	Zo	F.F	I.P	D	Bl	P	G	R	B
Det Sed ref	0,54	0,71				1,00			1,00	1,00	1,00
Det Sed lab	0,00	0,00				0,00			0,00	0,00	0,00
Det Part ref	0,54		0,87	0,82		1,00	1,00	1,00	1,00	1,00	1,00
Det Part lab	0,00		0,00	0,00		0,00	0,00	0,00	0,00	0,00	0,00
Phy			0,2	0,20							
Peri		0,2				0,20	0,20	0,20	0,20	0,20	0,20
M						0,20	0,20	0,20	0,20	0,20	0,20
A.C.						0,20	0,20	0,20	0,20	0,20	0,20
E.I.						0,20	0,20	0,20	0,20	0,20	0,20
Y.C					0,20	0,20	0,20	0,20	0,20	0,20	0,20
B.&G.					0,20	0,20	0,20	0,20	0,20	0,20	0,20
Zo						0,20	0,20	0,20	0,20	0,20	0,20
F.F					0,20	0,20	0,20	0,20	0,20	0,20	0,20
I.P						0,20	0,20	0,20	0,20	0,20	0,20
D								0,20			
Bl							0,20	0,20		0,20	
P								0,20			
G											
R										0,20	
Br											

Table 2.39 *River Thames primary food web. Phy= Phytoplanlkton, Peri = Periphyton, M=Macrophytes, E.I= External Insects, A.C.= Adult Chironomid, Zo= Zooplankton, Y.C= Young Chironomids, F.F = filter feeders, B&G= Browsers and Grazers, I. P= Invertebrates Predators, R= Roach, Bl= Bleak, D= Dace, G=Gudgeon, P=Perch, Br= Bream*

Diet composition	Y.C	B&G	Zo	F.F	I.P	D	Bl	P	G	R	Br
Det Sed ref	0,220	0,608				0,064			0,067	0,099	0,085
Det Sed lab	0,015	0,061				0,005			0,005	0,007	0,006
Det Part ref	0,706		0,457	0,487		0,240	0,213	0,009	0,251	0,373	0,320
Det Part lab	0,060		0,043	0,013		0,018	0,016	0,001	0,019	0,028	0,024
Phy			0,500	0,500							
Peri		0,330				0,046	0,155	0,034	0,204	0,098	0,133
M						0,007	0,008	0,000	0,028	0,060	0,036
A.C						0,321	0,194	0,440	0,058	0,015	0,050
E.I						0,194	0,228	0,352	0,126	0,005	0,149
Y.C					0,340	0,012	0,050	0,004	0,065	0,061	0,062
B&G					0,330	0,002	0,007	0,001	0,023	0,029	0,007
Zo						0,088	0,123	0,129	0,138	0,194	0,121
F.F					0,330	0,001	0,005	0,003	0,016	0,021	0,006
I.P						0,001	0,001	0,001	0,001	0,001	0,001
D								0,005			
Bl							0,002	0,017		0,005	
P								0,005			
G											
R										0,003	
Br											

2.5. Ecotoxicity

In this paragraph an overview on the parameters used for the estimation of the effect of the two xenobiotics (LAS and Triclosan) in the environment is given.

AQUATOX requires for the organisms ecotoxicological parameters as LC_{50}, $EC_{50growth}$, EC_{50repr}.

The median effective concentration (EC_{50}) is the statistical derived concentration of a substance in an environmental medium expected to produce a certain effect in 50% of test organism in a given population after a defined set of condition. In the specific case of LC_{50} the effect is the death of the targeted organisms.

For $EC_{50growth}$ the effect measured is the change in body growth of the organisms while for EC_{50repr} the effect tested is the changing in organisms reproduction due to the pollutant.

Ecotoxicological data are not present in literature for all the organisms of this study. It was necessary to choose ecotoxicological data for similar organisms and to estimate missing EC_{50} using the read-across method.

The associations were done by expert judgments (Marshal, 2013) based on taxonomic classification or on analogies of traits (e.g. physiological, habitat/food preferences).

The organisms associations for the ecotoxicological parameters are shown in Table 2.40. Normally the ecotoxicological association of species takes in account also allometric parameters for the singular species but in this case. It was not possible to use the latter method due to a scarcity of data and because the organisms presented in River Thames are not listed in the "Interspecies toxicity correlation model" of AQUATOX.

Ecotoxicity is estimated in literature using various coefficients that describes the kind of toxicity test carried out (EC_{50},$IC_{50,}$ LOEC, NOEC, etc.). As explained AQUATOX requires acute toxicity (EC_{50} ,LC_{50}) but in literature some ecotoxicity values found are expressed as chronic toxicity (LOEC,NOEC).

To fill this literature gap there is the need to convert chronic toxicity values in acute toxicity values. Three values are needed for this action:

- The median Acute/chronic ratio (ACR) for all species combined, that is expressed as the ratio between LC_{50} and chronic toxicity (LOEC and NOEC). This value is about 6

(Median of the values in the Table C1 of the ECETOC technical report 91) (ECETOC, 2003)

- The average ratio of lethal acute toxicity and effect acute toxicity ratio for animals or plants LC_{50}/EC_{50}. For plants this ratio value chosen is about 10 (AQUATOX default studies) for both the pollutants. It was used to estimate LC_{50} because only data of EC_{50} were found in literature for both the toxicants.

  Animal average LC_{50}/EC_{50} change from Linear alkilbenzene sulfonate (LAS) and Triclosan (TCS). For LAS is equal to 1.67 and for TCS is equal to 3.86.
- The ratio between acute effect toxicity (EC_{50}) and chronic toxicity (CT) (LOEC or NOEC) .

  This value is unknown. A single constant value equal to 2 has been chosen for both the pollutants to simplify the assumptions. This value was chosen by professional judgment (Marshal, 2013) to guarantee that the ACR founds for the two Chemicals were as close as possible to the median value of 6

The three ratio are correlated through the Equation 27

$$ACR = \frac{LC_{50}}{EC_{50}} * \frac{EC_{50}}{CT} \quad \textbf{(27)}$$

In AQUATOX it could be possible to recover BCF (bioconcentration factor), K1 (uptake rate) and K2 (elimination constant) from relationship with the K_{ow} parameter. This value is highly variable and in the reality the behavior of the pollutant in the environment can be influenced from other factors, for these reasons the data here presented are recovered as much as possible from literature studies and field or laboratory analysis.

Table 2.40 *This table shosw the test organisms used for the tox record in literature to estimate toxicity parameters that are used in AQUATOX for the organisms present in River Thames.*

AQUATOX STATE VARIABLE	Main species Thames	Classification	Tox record (LAS)	Tox record (TCS)
Phytoplankton	Diatom, Cyclotella	Algae	*Selenastrum capricornutum*	*Desmodesmus subspicatus*
Periphyton	Filamentous algae, Diatoms	Algae	*Microcystis aeruginosa*	*Anabaena flos aquae*
Macrophytes	Acorus Calamus, Nuphar Lutea	Acoraceae, nymphaeaceae	*Lemna minor*	*Lemna gibba*
Chironomids	Chironomidae		*Chironomus riparius*	*Chironomus tentans*
Browsers and Grazers	*Viviparus v.*	Gastropods, oligochaeta	*Limnodrilus hoffmeis*	*Hyalella azteca*
Zooplankton	*Rotifer Keratella*	planktonik rotifer	*Brachionus calyciflorus*	*Paramecium caudatum*
Filter Feeders	*Unio, anodonta anatina*	Mussels	*curbicula*	*Perna Perna*
Inv. predators	*Helobdella stagnalis*	leech, oligochaeta	*Limnodrilus hoffmeis*	*Chironomus tentans*
Dace Thames	*Leuciscus L*		*Pimephales promelas*	*Pimephales promelas*
Bleak	*Alburnus A*		*Pimephales promelas*	*Pimephales promelas*
Perch	*Perca fluviatilis*		*Lepomis macrochirus*	*Lepomis macrochirus*
Gudgeon	*Gobio gobio*		*Pimephales promelas*	*Pimephales promelas*
Roach	*Rutilus rutilus*		*Tilapia mossambica*	*Pimephales promelas*
Bream	*Abramis brama*		*Tilapia mossambica*	*Pimephales promelas*

2.5.1. LAS

Linear alkylbenzene sulphonate (LAS) (CAS number 68411-30-3) is the most used ingredients in household detergents worldwide (Figure 2.8). It is an anionic surfactant composed by a mixture of closely related isomers and homologues, each containing an aromatic ring sulphonated at the *para* position and attached to a linear alkyl chain (HERA, 2009).

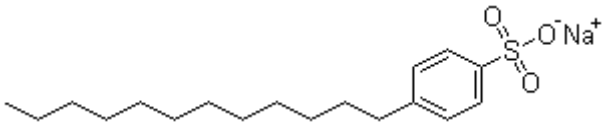


Figure 2.8 *LAS typical molecular structure*

Detergents application of LAS represents more than 80% of the total European consumption of this product **[18]**.

Physicochemical parameters are shown in Table 2.41 (HERA, 2009) **[VI]**

Table 2.41 *LAS physicochemical Parameters*

Physicochemical Parameters	**Unit**	**Value / Value range**		**Notes**
Vapor pressure	Pa	negligible		
Octanol-water partition coefficient (log Kow)		3,32		Calculated as C11.6
Water solubility	g/l	250		experimental
Organic carbon water partition coefficient (Koc)	l/kg	2500		Calculated as C11.6
Sorption coefficient between soil/sediments and water (Kd)	l/kg	3	300	experimental
Henry's constant	Pa * m3/mol	0,00635		calculated as C12
Molecular weight	g/mol	342,4		(C11.6H24.2)C6H4SO 3Na
Dissociation constant				Not present. It is a salt

Biodegradation rates and half-life time are shown in Table 2.42 (HERA, 2009) **[VI]**

Table 2.42 *LAS Biodegradation*

Biodegradation properties		**half life time**			**k**			**Notes**
		unit	**Value / Value range**		**unit**	**Value / Value range**		
Biodegradation rate in river water	Die-away	h	12		1/h	0,06		(prim. biod)
	Die-away	h	18		1/h	0,04		(ultim. biod.)
	River monitoring	h	1	3	1/h	0,69	0,23	(prim. biod)
Biodegradation rate in soil	Field study	d	1	7	1/d	0,69	0,10	(prim. biod)
	Lab. study	d	2	26	1/d	0,35	0,03	(ultim. biod.)
Biodegradation rate in oxic sediments		d	7		1/d	0,1		
Biodegradation rate in bulky sediments		d	70		1/d	0,01		

The term primary biodegradation means the alteration of the chemical structure of a substance resulting in loss of a specific property of that substance **[VI]**.
This degradation differs from ultimate biodegradation that is the complete breakdown of a compound to either fully oxidized or reduced simple molecules **[VI]**.
Only the primary biodegradation is considered in this study because metabolites toxicity is not taken into account.
The rate of anaerobic degradation in the environment can be considered equal to zero (HERA, 2009) because LAS biodegrades mainly under aerobic condition (rate 0,06 1/h).
Reactions of hydrolysis and photolysis of LAS are described in literature in conditions not relevant to the environment (HERA, 2009)**.**
It seems LAS does not display bioaccumulation characteristics (HERA, 2009).

2.5.1.1. Toxicological data

Animals

Minnow (*Phimphales Promelas*) toxicity records have been used for Bleak (*Alburnus Alburnus*), Dace (*Leuciscus Leuciscus*), Gudgeon (*Gobio Gobio*) because they have similar size and alimentary behavior. For the same reason Roach (Rutilus Rutilus) and Bream (*Abramis Brama*) have toxicity records of Tilapia (*Oreochromis Mossambicus*).
Studies on Bluegill (*Lepomis Macrochirus*) has been used for Perch because it is the only fish in River Thames at Reading that shows mainly pescivours/insectivorus alimentary behaviors. Browsers and grazers and invertebrate predators are linked to an aquatic worm (*Limnodrilus Hoffmeisteri*). They belong to the same genera *Oligochaeta*.
Some animal toxicological parameters are not expressed as LC_{50} or EC_{50} but AQUATOX requires this values as ecotoxicological input parameters.
Roach and Bream EC_{50} for growth and reproduction are set equal to 2xLOEC. The chronic test (LOEC) is carried out on Tilapia (*Oreochromis Mossambicus*).
The EC_{50} of Bluegill (*Lepomis Macrochirus*) is assume 2xNOEC.
Only four LC_{50} were present in literature (*Chironomus riparius*, *Lepomis Macrochirus*, *Phimepales Promelas*, *Limnodrilus Hoffmeisteri*). To estimate the remaining LC_{50} an average ratio LC_{50}/EC_{50} for animals is used. This ratio is calculated as the mean of LC_{50}/EC_{50} ratio of

different animal having different role and trophic level in the ecosystem. LC_{50} values for animals are shown in Table 2.43, $EC_{50growth}$ and EC_{50repr} respectively in Table 2.44 and 2.45.

Table 2.43 *LC_{50} literature values for LAS chosen for the animals of River Thames*

Animal name	LC50 (ug/L)	LC50 exp. time (h)	LC50 references
Bleak	3200	48	From test on *Phimepales Promelas* (ECHA)
Perch	1670	96	From test on *Lepomis Macrochirus* (ECHA)
Dace	3200	48	From test on *Phimepales Promelas* (ECHA)
Gudgeon	3200	48	From test on *Phimepales Promelas* (ECHA)
Roach	1695[a]	48	From test on *Oreochromis mossambicus* (ECHA)
Bream	1695[a]	48	From test on *Oreochromis mossambicus* (ECHA)
Zooplankton	3357[b]	48	From test on *Brachionus Calyciflorus* (ECHA)
Filter feeders	1024[c]	48	From test on *Curbicula* (ECHA)
Browsers and Grazers	2400	48	From test on *Limnodrilus hoffmeisteri* (ECHA)
Chironomid	8600	48	From test on *Chironomus Riparius*(ECHA)
Inv. Predator	2400	48	From test on *Limnodrilus hoffmeisteri* (ECHA)

[a] Estimated using avg. letal/sub letal ratio for LAS and EC_{50} of *Oreochromis mossambicus*

[b] Estimated using avg. letal/sub letal ratio for LAS and EC_{50} of *Brachionus Calcyflorus*

[c] Estimated using avg. letal/sub letal ratio for LAS and EC_{50} of *Curbicula*

Table 2.44 *$EC_{50growth}$ literature values for LAS chosen for the animals of River Thames*

Animal name	EC50 growth (ug/L)	Growth exp. (h)	EC50 references
Bleak	2400	4704	From test on *Phimepales Promelas* (ECHA)
Perch	2000[d]	672	From test on *Lepomis Macrochirus* (ECHA)
Dace	2400	4704	From test on *Phimepales Promelas* (ECHA)
Gudgeon	2400	4704	From test on *Phimepales Promelas* (ECHA)
Roach	1010[c]	504	From test on *Oreochromis mossambicus* (ECHA)
Bream	1010[c]	504	From test on *Oreochromis mossambicus* (ECHA)
Zooplankton	2000	48	From test on *Brachionus Calyciflorus* (ECHA)
Filter feeders	610	768	From test on *Curbicula* (ECHA)
Browsers and Grazers	1430[a]	48	From test on *Limnodrilus hoffmeisteri* (ECHA)
Chironomid	8000[b]	672	From test on *Chironomus Riparius*(ECHA)
Inv.Predator	1430[a]	48	From test on *Limnodrilus hoffmeisteri* (ECHA)

[a] Estimated using avg. letal/sub letal ratio for LAS and LC_{50} of *Limnodrilus hoffmeisteri*

[b] Set equal to EC_{50rep}

[c] LOECx2

[d] NOECx2

The EC_{50} of Perch calculated as LOECx2 results higher than its LC_{50}. Theoretically that situation could seem unrealistic but it has to take into account that they are based on different studies and so probably on diverse conditions and fish body masses. This choice do not create any error in the estimation of the effects of the chemicals on the animal in AQUATOX (Park & Clough, 2012).

Table 2.45 *EC_{50repr} literature values for LAS chosen for the animals of River Thames*

Animal name	EC50 repro (ug/L)	Repro. exp. time(h)	EC50 references
Bleak	2400	4704	From test on *Phimepales Promelas* (ECHA)
Perch	2000[a]	672	From test on *Lepomis Macrochirus* (ECHA)
Dace	2400	4704	From test on *Phimepales Promelas* (ECHA)
Gudgeon	2400	4704	From test on *Phimepales Promelas* (ECHA)
Roach	1010[b]	504	From test on *Oreochromis mossambicus* (ECHA)
Bream	1010[b]	504	From test on *Oreochromis mossambicus* (ECHA)
Zooplankton	2000[c]	48	From test on *Brachionus Calyciflorus* (ECHA)
Filter feeders	610[d]	768	From test on *Curbicula* (ECHA)
Browsers and Grazers	1430	48	From test on *Limnodrilus hoffmeiseri* (ECHA)
Chironomid	8000	672	From test on *Chironomus Riparius*(ECHA)
Inv.Predator	1430	48	From test on *Limnodrilus hoffmeiseri* (ECHA)

[a] Set equal to $EC_{50growth}$ *Lepomis Macrochirus*

[b] Set equal to $EC_{50growth}$ *Oreochromis mossambicus*

[c] Set equal to $EC_{50growth}$ *Brachionus Calyciflorus*

[d] Set equal to $EC_{50growth}$ *Curbicula*

[e] Set equal to $EC_{50growth}$ *Limnodrilus hoffmeiseri*

The organism response to a chemical pollution is described by ecotoxicological parameters and at least three other biological parameters: the uptake constant (K1) the elimination constant (K2) and the bio-concentration factor (BCF). K2 is a measure of the rate of elimination of the toxicant from the organism. It depends mainly on K_{OW}, individual wet weight of the organism and lipid fraction. AQUATOX can calculate it in two way: the first one with a relationship that considers the allometric exponent of respiration (RB) and the second one from Barber equation (Park & Clough, 2012).

The second one is chosen because in this model the respiration has been set using constant values as a user input. Allometric parameters are not used in this study.

An exception is made for Rotifers because Barber equation depends on individual wet weight. The Rotifer individual wet weight is smaller than the one of the other invertebrates (there is a difference of 10^4). It seems that the smallest organism where the equation is graphically verified is for Daphnia (Park & Clough, 2012) that has a body mass higher than the one of rotifers (an order of 10^3). Using barber the K2 of zooplankton was too high and could cause an overestimation of the toxicant effect. The choice taken has been to set the zooplankton K2 equal to the highest one calculated using Barber equation for the ecosystem organisms (It is equal to 77,8, the same of Chironomid).

In AQUATOX the relation between BCF, K1 and K2 (Park & Clough, 2012) is described by the Equation 28.

$$BCF = \frac{K1}{K2} \quad \textbf{(28)}$$

The program gives the possibility to estimate one of these parameters knowing the others. The animal parameters for LAS were estimated using the option "Enter K2 and BCF". K2 is calculated by AQUATOX and BCF values are found in literature. Elimination constant for animals subjected to LAS are shown in Table 2.46

Table 2.46 *Elimination constant (K2) for the animals of the ecosystem*

Animal name	K2 Elim. rate const (1/d)	Ave. wet wt. (g)	Lipid Frac
Bleak	16,94	3,2	0,02
Perch	3,89	21,1	0,03
Dace	6,43	12,9	0,02
Gudgeon	6,77	9,95	0,02
Roach	6,12	16,6	0,02
Bream	5,99	18,5	0,02
Zooplankton	77,80	2E-08	0,012
Filter feeders	9,93	6,15	0,015
Browsers and Grazers	52,65	1,47	0,0075
Chironomid	77,80	0,006	0,015
Inv.Predator	19,753	0,014	0,0075

The BCF values for the animals can highly change (from 2 to 1000 [L/kg]) depending on the LAS alkyl chain length **[VI]**. The LAS mixture composition is supposed to have the alkyl

chain equal to $C_{11.6}$. Here it has been tried to use literature ecotoxicological parameters related to a LAS mixture similar as much as possible to this composition.

AQUATOX could estimate also BCF using equation recovered from empirical studies that link BCF value with K_{ow}. This choice could bring to high uncertainties because it takes into account only of chemical equilibrium and it assumes no metabolic transformation.

The option chosen is to find and insert BCF data from literature. AQUATOX requires BCF and K1 parameters expressed in dry weight basis. Most of the data found in literature are on wet basis so they were converted to dry basis using the Wet/Dry ratio for each organism. It represent the ratio between the individual wet weight and the individual dry weight. If the weight basis is not specified the BCF is considered related to the wet weight.

$$BCF_{dry} = BCF_{wet} * WettoDry \quad \textbf{(29)}$$

BCF_{wet} of fish is equal to 80 [L/kg] that is an average value of a study carried out on minnow (*Phimepales Promelas*) (Versteeg & Rowlings, 2003) .

The BCF_{dry} of fishes are found multiplying the BCF_{wet} from literature for the Wet/dry ratio characteristic of each fish species.

Some data of BCF_{wet} for invertebrates have been found in literature (Versteeg & Rowlings, 2003). The invertebrates analyzed are *Curbicula*, *Hyallella* and *Elimia* (Table 2.47).

The data of *Curbicula* are used for the filter feeders category while the ones on *Elimia* for invertebrate predators and browsers and grazers categories. Zooplankton and Chironomid BCF_{wet} are expressed as the average value of the BCF found in this study.

Table 2.47 *Bioconcentration factor (BCF) for LAS of some aquatic invertebrates found in literature* (Versteeg & Rowlings, 2003)

Invertebrates	**BCF_{wet} [L/kg]**
Curbicula	21,25
Hyalella	73,7
Elimia	27
Average value	37,6

The wet/dry values for fishes were recovered from FISHBASE while the invertebrates ones from Lyndall paper (Lyndall et al, 2010)**,** except for Zooplankton (found in the Rotifer Brachionus default animal of AQUATOX). Wet/dry ratios for animals are shown in Table 2.48 and BCF_{dry} values in Table 2.49.

Table 2.48 *Wet to dry ratio for the animals of the model*

Animals	**Wet/dry**
Zooplankton	6,75
Filter feeders	4,7
Browsers and grazers	4,8
Chironomid	4,7
Invertebrate predators	4,8
Bleak	3,7
Roach	3,75
Perch	3,7
Dace	3,7
Gudgeon	4,05
Bream	4,2

Table 2.49 *BCF_{dry} of animals for LAS*

Animal name	**BCF_{dry} (L/kg)**	**Ave. wet wt. (g)**	**Lipid Frac**
Bleak	296	3,2	0,02
Perch	296	21,1	0,03
Dace	296	12,9	0,02
Gudgeon	324	9,95	0,02
Roach	300	16,6	0,02
Bream	336	18,5	0,02
Zooplankton	254	2,00E-08	0,012
Filter feeders	100	6,15	0,015
Browsers and Grazers	130	1,47	0,0075
Chironomid	177	0,006	0,015
Inv.Predator	130	0,014	0,0075

K1 is calculated using AQUATOX (Park & Clough, 2012) relationship shown in Equation 30. Uptake constant values are shown in Table 2.50.

$$K1 = K2 \cdot BCF \quad \textbf{(30)}$$

Table 2.50 *K1 of animals for LAS*

Animal name	$K1_{dry}$ Uptake const (L/(kg d))	Ave. wet wt. (g)	Lipid Frac
Bleak	5013,5	3,2	0,02
Perch	1152,5	21,1	0,03
Dace	1904,7	12,9	0,02
Gudgeon	2194,3	9,95	0,02
Roach	1836,9	16,6	0,02
Bream	2013,9	18,5	0,02
Zooplankton	19761,2	2,00E-08	0,012
Filter feeders	992,8	6,15	0,015
Browsers and Grazers	6844	1,47	0,0075
Chironomid	13771	0,006	0,015
Inv.Predator	2567,8	0,014	0,0075

Plants

In literature only data on EC_{50} were found for plants (Table 2.51). Macrophytes ecotoxicological parameters were recovered by a study on biomass growth on *Lemna Minor.*
The effect on cell density of *Selenastrum Capricornutum* has been used to estimate EC_{50} on phytoplankton.
A cyanobacteria (*Microcystis Aeruginus*) describes the ecotoxicological behavior of Periphyton

Table 2.51 *Plant EC_{50} for LAS*

Plant name	EC50 (ug/L)	EC50 exp. time (h)	EC50 References
Macrophyte	3600	504	From test on *Lemna Minor* (ECHA)
Periphyton	910	96	From test on *Microcystis Aeruginus* (ECHA)
Phytoplankton	29000	96	From test on *Selenastrum Capricornutum* (ECHA)

The LC_{50} parameters have been estimated as ten times the EC_{50} (Table 2.52). This assumption can be found in other AQUATOX default studies (Ohio stream in the U.S. and Skensved stream in Denmark) (Park & Clough, 2012).

Table 2.52 *Plant LC_{50} for LAS*

Plant name	LC50 (ug/L)	LC50 exp. time (h)	LC50 References
Macrophyte	36000	504	From test on *Lemna Minor* (ECHA)
Periphyton	9100	96	From test on *Microcystis Aeruginus* (ECHA)
Phytoplankton	290000	96	From test on *Selenatrsum Capricornutum* (ECHA)

AQUATOX offers a computational method to estimate elimination rates for primary producers. The parameters that play an important role in this phenomena are K_{OW}, lipid fraction and "wet to dry" (Park & Clough, 2012). This option is used for macrophytes.
BCF_{dry} and K2 for algae have been found in literature (Renaud et al, 2011) (Table 2.53).

Table 2.53 *Elimination constant (K2) of plants for LAS . The ones of phytoplankton and periphyton are data from literature. The K2 of macophytes is calculated using AQUATOX internal equation*

Plant name	K2 Elim. rate const (1/d)	Lipid Frac
Macrophyte	0,62	0,004
Periphyton	9,6	0,015
Phytoplankton	9,6	0,015

No any data about macrophyte BCF has been found in literature. Only a literature study shows a chart that describes the variation of BCF during the period of the experiment of an aquatic plant subjected to LAS. As described by the author of the article, the primary biodegradation occurs in the first two days (first peak in the Figure 9 of the paper of Yongyan (Yongyan et al, 1991)). Based on the plot a value of BCF_{wet} for macrophytes has been calculated (12,5 [L/kg]). This value is converted to BCF_{dry} using the wet/dry ratio for macrophytes (Lyndall et al, 2010) (Table 2.54) .
BCF_{dry} for algae represents the average of the two value found in the study of Florent Renaud for diatom (Renaud et al, 2011).

Table 2.54 *Wet to dry ratio for plants*

Plant	Wet/dry
Phytoplankton	14,3
Periphyton	14,3
Macrophyte	9,5

The uptake constant is calculated using the Equation 30. BCF and Uptake constant are shown in Table 2.55.

Table 2.55 *The BCF and K1 of plants for LAS. BCF are values from literature*

Plant name	$K1_{dry}$ Uptake Const (L/(kg d))	BCF_{dry} (L/kg)	Lipid Frac
Macrophyte	73,9	119	0,004
Periphyton	52320	5450	0,015
Phytoplankton	52320	5450	0,015

2.5.2. Triclosan

Triclosan (TCS) (5-chloro-2-(2,4-dichlorophenoxy)-phenol / CAS number 3380-34-5) is a broad-spectrum antimicrobial used principally in medical and personal hygiene products (Lyndall et al, 2010). Molecular structure of LAS is shown in Figure 2.8

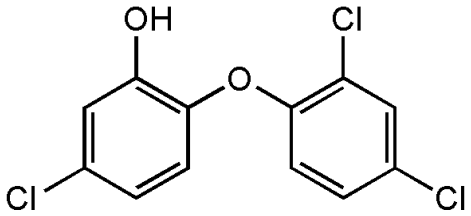


Figure 2.9 *TCS typical molecular structure*

Physicochemical parameter are shown in Table 2.56 (Lyndall et al, 2010)**[VI]**.

Table 2.56 *TCS physicochemical parameters*

Physicochemical parameters	**Unit**	**Value**
Vapour pressure	Pa	18000
Octanol-water partition coefficient (log Kow)	l/kg	4,76
Water solubility	g/l	0,01
Organic carbn water partition coefficient (Koc)	l/kg	4,28
Henry's constant	Pa * m3/mol	0,0023
Molecular weight	g/mol	289,54
pka		8,14

Because it contains a phenolic group Triclosan is ionizable. Biodegradation rates are shown in Table 2.57 (Lyndall et al, 2010).

Table 2.57 *TCS Biodegradation*

Property	**k**	
	unit	**Value**
Biodegradation rate in river water	1/d	0,012
Biodegradation rate in soil	1/d	0,006
Biodegradation rate in sediments	1/d	0,001

Triclosan is susceptible to biodegradation particularly under aerobic conditions and the ionized form is subject to photodegradation.

Under aerobic condition the degradation rate is set equal to the one in the river water. It is a value similar to literature studies (about 0,01 1/d) **[VI]**. In water no concrete evidence for the biodegradation of Triclosan under anaerobic condition were observed **[VI]**.

2.5.2.1. Toxicological data

Animals

Minnow toxicity is used for Dace (*Leuciscus Leuciscus*), Bleak (*Alburnus Alburnus*), Gudgeon (*Gobio Gobio*), Roach (*Rutilus Rutilus*) and Bream (*Abramis Brama*) for the same reasons exposed for LAS. Perch toxicity is recovered by tests on Bluegill. The toxicity behavior of Filter feeders is described using effect concentrations on *Perna Perna* (Sanzi Cortez et al, 2012). Chironomid and invertebrate predator toxicity parameters are based on *Chironomus Tentants*. *Hyalella Atzteca* has been chosen for Browsers and Grazers category and *Paramecium Caudatum* for zooplankton (Miyoshi et al, 2003).
LC_{50} values for animals subjected to TCS are shown in Table 2.58 while $EC_{50growth}$ and EC_{50repr} in Table 2.59 and 2.60

Table 2.58 *LC_{50} literature values for TCS chosen for the animals of River Thames*

Animal name	**LC50 (ug/L)**	**LC50 exp. time (h)**	**LC50 references**
Bleak	260	96	From test on *Phimepales Promelas(CEPA)*
Perch	370	96	From test on *Lepomis Macrochirus (CEPA)*
Dace	260	96	From test on *Phimepales Promelas (CEPA)*
Gudgeon	260	96	From test on *Phimepales Promelas (CEPA)*
Roach	260	96	From test on *Phimepales Promelas (CEPA)*
Bream	260	96	From test on *Phimepales Promelas (CEPA)*
Filer feeder	1260[b]	48	From test on *Perna Perna* (Sanzi Cortez et al, 2012)
Chironomid	400	240	From test on *Chironomus Tentants (CEPA)*
Browsers and grazers	200	240	From test on *Hyalella Atzteca (CEPA)*
Inv.predator	400	240	From test on *Chironomus Tentants (CEPA)*
Zooplankton	1544[a]	48	From test on *ParameciumCaudatum* (Miyoshi et al, 2003)

[a] Estimated using avg. letal/sub letal ratio for Triclosan and EC_{50} of *ParameciumCaudatum*

[b] Estimated using avg. letal/sub letal ratio for Triclosan and the average between $EC_{50growth}$ and EC_{50repr} of *Perna Perna.*

Table 2.59 *$EC_{50growth}$ literature values for TCS chosen for the animals of River Thames*

Animal name	EC50 growth (ug/L)	Growth exp. (h)	$EC50_{growth}$ references
Bleak	67[a]	96	From test on *Phimepales Promelas (CEPA)*
Perch	96[b]	96	From test on *Lepomis Macrochirus (CEPA)*
Dace	67[a]	96	From test on *Phimepales Promelas (CEPA)*
Gudgeon	67[a]	96	From test on *Phimepales Promelas (CEPA)*
Roach	67[a]	96	From test on *Phimepales Promelas (CEPA)*
Bream	67[a]	96	From test on *Phimepales Promelas (CEPA)*
Filer feeder	135	48	From test on *Perna Perna* (Sanzi Cortez et al, 2012)
Chironomid	280	240	From test on *Chironomus Tentants(CEPA)*
Browsers and Grazers	250	240	From test on *Hyalella Atzteca (CEPA)*
Inv.predator	280	240	From test on *Chironomus Tentants (CEPA)*
Zooplankton	400[c]	120	From test on *Paramecium Caudatuma* (Miyoshi et al, 2003)

[a] Estimated using avg. letal/sub letal ratio for Triclosan and LC_{50} of *Phimepales Promelas*

[b] Estimated using avg. letal/sub letal ratio for Triclosan and LC_{50} of *Lepomis Macrochirus*

[c] Estimated from IC_{50}

Table 2.60 *EC_{50repr} literature values for TCS chosen for the animals of River Thames*

Animal name	EC50 repro (ug/L)	Repro. exp. time (h)	$EC50_{reprod}$ references
Bleak	67[a]	96	From test on *Phimepales Promelas (CEPA)*
Perch	96[b]	96	From test on *Lepomis Macrochirus (CEPA)*
Dace	67[a]	96	From test on *Phimepales Promelas (CEPA)*
Gudgeon	67[a]	96	From test on *Phimepales Promelas (CEPA)*
Roach	67[a]	96	From test on *Phimepales Promelas (CEPA)*
Bream	67[a]	96	From test on *Phimepales Promelas (CEPA)*
Filer feeder	490	1	From test on *Perna Perna* (Sanzi Cortez et al, 2012)
Chironomid	280[c]	240	From test on *Chironomus Tentants (CEPA)*
Browsers and Grazers	250	240	From test on *Hyalella Atzteca(CEPA)*
Inv.predator	280[c]	240	From test on *Chironomus Tentants (CEPA)*
Zooplankton	400[d]	120	From test on *Paramecium Caudatum* (Miyoshi et al, 2003)

[a] Set equal to $EC_{50growth}$ *Phimepales Promelas*

[b] Set equal to $EC_{50growth}$ *Lepomis Macrochirus*

[c] Set equal to $EC_{50growth}$ *Chironomus Tentants*

[d] Set equal to $EC_{50growth}$ *Paramecium Caudatum*

An average LC_{50}/EC_{50} for Triclosan was estimated for animal using the literature data available. This ratio is used to estimate toxicological parameters that have not been found in literature.

EC_{50repr} and EC_{50prod} for a species are set with the same value if there is a lack of data in literature (Table 2.59 and Table 2.60).

Elimination rate constant (K2) (Table 2.61) is calculated using Barber (2003) (Park & Clough, 2012).

Table 2.61 *Elimination constant (K2) of the animals of River Thames for TCS*

Animal name	K2 Elim. rate const (1/d)	Ave. wet wt. (g)	Lipid Frac
Bleak	0,62	3,2	0,02
Perch	0,14	21,1	0,03
Dace	0,23	12,9	0,02
Gudgeon	0,25	9,95	0,02
Roach	0,22	16,6	0,02
Bream	0,22	18,5	0,02
Filer feeder	0,36	6,15	0,015
Chironomid	2,82	0,006	0,015
B.G.	1,91	1,47	0,0075
Inv.predator	4,78	0,014	0,0075
Zooplankton	42,36	2,00E-08	0,012

Fish BCF_{lipid} for Triclosan could be up to 165000 [L/kg] (Rudel et al, 2013). Using this value, the lipid fraction and wet/dry ratios (Table 2.48) the BCF_{dry} for fish are calculated. The lipid fraction of the organimsm required by AQUATOX and express in this thesis are on wet weight basis.

$$BCF_{dry} = BCF_{lipid} \cdot f \cdot WettoDry \quad \textbf{(31)}$$

- BCF_{dry} is the BCF on dry basis [L/kg_{dry}];
- BCF_{lipid} is the BCF on lipid basis [L/kg_{lipid}];
- F is the lipid fraction [kg_{lipid}/kg_{wet}];
- Wettodry is the wet/dry ratio [kg_{wet}/kg_{dry}].

BCF_{dry} for a mussel were found in literature equal to 1700 [L/kg] (Gatidou et al, 2010) . This value is supposed as BCF for all the invertebrates.

BCF_{dry} values are shown in Table 2.62

Table 2.62 *Bioconcentration factor (BCF) of the animals of River Thames for TCS*

Animal name	BCF_{dry} (L/kg)	Ave. wet wt. (g)	Lipid Frac
Bleak	12210	3,2	0,02
Perch	18315	21,1	0,03
Dace	12210	12,9	0,02
Gudgeon	13365	9,95	0,02
Roach	12375	16,6	0,02
Bream	13860	18,5	0,02
Filer feeder	1700	6,15	0,015
Chironomid	1700	0,006	0,015
B.&G.	1700	1,47	0,0075
Inv.predator	1700	0,014	0,0075
Zooplankton	1700	2,00E-08	0,012

K1 is calculated using its relationship with K2 and BCF (Equation 30). The values of animals uptake constant for TCS are shown in Table 2.63

Table 2.63 *uptake constant K1 of the animals of River Thames for TCS*

Animal name	$K1_{dry}$ Uptake const (L/(kg d))	Ave. wet wt. (g)	Lipid Frac
Bleak	7508,6	3,2	0,02
Perch	2589,2	21,1	0,03
Dace	2852,7	12,9	0,02
Gudgeon	3286,5	9,95	0,02
Roach	2751,2	16,6	0,02
Bream	3016,2	18,5	0,02
Filer feeder	612,8	6,15	0,015
Chironomid	4802,3	0,006	0,015
B.&G.	3249,5	1,47	0,0075
Inv.predator	8128,1	0,014	0,0075
Zooplankton	72003,7	2,00E-08	0,012

Plants

Macrophite toxicity is described by tests on *Lemna Gibba*. A cyanobacteria (*Anabaena flow-aquae*) toxicity parameters are used to represent Periphyton.
Desmodeus Subspica is chosen to estimate Phytoplankton response behavior to Triclosan pollution. Plant EC_{50} values for TCS are shown in Table 2.64.

Table 2.64 *Plant EC_{50} for TCS*

Plant name	EC50 photo (ug/L)	EC50 exp. time (h)	EC50 references
Macrophyte	62,5	240	From test on *Lemna Gibba (ECHA)*
Periphyton	1,6	96	From test on *Anabaena flow-aquae (ECHA)*
Phytoplankton	1,61	72	From test on *Desmodeus Subspica (ECHA)*

LC_{50} of plants are equal to ten times the EC_{50} for the same reasons described for LAS (Table 2.65).

Table 2.65 *Plant LC_{50} for TCS*

Plant name	LC50 (ug/L)	LC50 exp. time (h)	LC50 references
Macrophyte	625	240	From test on *Lemna Gibba (ECHA)*
Periphyton	16	96	From test on *Anabaena flow-aquae(ECHA)*
Phytoplankton	161	72	From test on *Desmodeus Subspica (ECHA)*

Elimination rate of macrophytes has been estimated using AQUATOX option. K2 and $K1_{dry}$ for phytoplankton and periphyton have been found in literature (Vogs et al, 2013) .
BCF for macrophites is recovered from CEPA site **[VII]**. The BCF_{wet} of *Sesbania Herbacea* and *Bidens Frondosa* belong to a range of 0,4 – 101 [L/kg]. Using an average value of 50 [L/kg] and the wet/dry ratio of macrophyte (Table 2.54) its BCF_{dry} is calculated. The BCF_{dry} of phytoplankton and periphyton is calculated using the AQUATOX option (Equation 28).
The macrophyte K1 is calculated using K2 (calculated by AQUATOX) and BCF from literature. A resume of the parameters that describe the dynamics of pollutants in plants (BCFdry, K1dry, and K2) are shown in Table 2.66.

Table 2.66 *Elimination constant (K2), uptake constant (K1) and BCF_{dry} for plants*

Plant name	K2 Elim. rate const (1/d)	$K1_{dry}$ Uptake Const (L/(kg d))	BCF_{dry} (L/kg)	Lipid Frac
Macrophyte	0,42	199,9	476	0,004
Periphyton	15,504	563289	36332	0,015
Phytoplankton	15,504	563289	36332	0,015

2.6. Initial conditions, Input loading, and pollutant scenarios

In the Table 2.67 the input loads and the initial values of the main variables of the ecosystem are shown.

Table 2.67 *Main system variables initial values*

Variables	Initial values	Input load
Total ammonia as N (mg/L)	0,04	0,04
Nitrate as N (mg/L)	8,32	8,32
Total soluble P (mg/L)	0,9	0,9
Carbon dioxide (mg/L)	4,6	4,6
Oxygen (mg/L)	11	11
Total susp solid (mg/L)	16	16
Refract sed detritus (mg/L)	52	0
Labile sed detritus (mg/L)	35	0
Phytoplankton (mg/L)	0,0031	1E-6
Periphyton (g/m^2)	0,1	1E-6
Macrophyte (g/m^2)	2,25	1E-6
Adult chironomid (g/m^2)	15,6	2,34
External insects (g/m^2)	36	5,35
Chironomid (g/m^2)	5,75	0
Browsers and Grazers (g/m^2)	3,04	0
Zooplankton (g/m^2)	0,05	1E-6
Filter feeders (g/m^2)	19,62	0
Inv. Predators (g/m^2)	0,065	0
Dace (g/m^2)	1,08	0
Bleak (g/m^2)	12,2	0
Perch (g/m^2)	1,43	0
Gudgeon (g/m^2)	5,43	0
Roach (g/m^2)	8,36	0
Bream (g/m^2)	3,1	0

The model is run for both the toxicants in three different scenarios for three different period of time (1 year, 3 years and 6 years). The ecosystem at control simulation is stable for at least 6 years.

The xenobiotics in the perturbed scenario are inserted in the ecosystem as a constant load from upstream.

The first scenario simulation has a pollutant input load from upstream equal to the actual toxicant concentration in water present in the inland water of England nowadays. The simulations of the second and third scenarios are based on concentrations higher than the one of the first scenario. The toxicant input concentration of the second scenario is set equal to the lowest EC_{50} of the organisms of the River Thames ecosystem while the third scenario is set equal to the lowest LC_{50}. The perturbed scenarios for the two toxicants are shown in Table 2.68.

Table 2.68 *Simulation scenarios for LAS and TCS*

Variables	Scenario 1		Scenario 2		Scenario 3	
	Initial conditions	Load	Initial conditions	Load	Initial conditions	Load
LAS (μg/l)	40[a]	40	610[c]	610	1024[e]	1024
TCS (μg/l)	0,05[b]	0,05	1,6[d]	1,6	16[f]	16

[a] Similar to real values found in the England Rivers (Price et al, Data requirement of GREAT-ER: Modelling and Validation using LAS in four UK catchments , 2009)

[b] Similar to real values found in the England Rivers (Price et al, Predicting accurate and ecologically relevant regional scale concentrations of Triclosan in rivers for use in higher-tieraquatic risk assessment, 2010)

[c] Equal to the lowest EC_{50} of the ecosystem for LAS (Filter feeders)

[d] Equal to the lowest EC_{50} of the ecosystem for TCS (algae)

[e] Equal to the lowest LC_{50} of the ecosystem for LAS (Filter feeders)

[f] Equal to the lowest LC_{50} of the ecosystem for TCS (algae)

2.7. *Ecological risk assessment indicators*

Some environment indicators have been chosen to estimate the variations in the ecosystem due to the xenobiotic presence.
They can be grouped in three different categories:

1) Objective variation indicators
2) Biological variation indicators
3) “Ecosystem Services” and “ Good Ecological status “ indicators

The first category is related on the objective variation of the biomass of the system. To estimate the objective variation an indicator on the average perturbation in the system has been chosen

$$\bar{\varepsilon} = \sum_{i=1}^{N} \frac{\left| B_{iPERT} - B_{iCONT} \right|}{B_{iCONT}} * \frac{1}{N} \quad \textbf{(32)}$$

- $\bar{\varepsilon}$ is the average objective perturbation in the system;
- N is the number of biological species modelled in the system;
- B_{iPERT} is the average biomass of species "i"during the perturbed simulation [g dry/m2];
- B_{iCONT} is the average biomass of species "i" during the control simulation [g dry/m2].

According to ecological theory the maturity of the ecosystem can be measured as the ratio between the primary production and the respiration of the ecosystem community (Odum, 1983). AQUATOX calculates the GPP (Gross Primary Production) [$gO_2/(m^2\ d)$] and the "Community respiration " [$gO_2/(m^2\ d)$].
The ratio between the average annual value of this two parameter is the P/R indicator used to estimate ecosystem maturity

$$P/R = \frac{GPP}{R_{comm}} \quad \textbf{(33)}$$

- GPP is the gross primary production;
- R_{comm} is community respiration;

Another parameter used to estimate the ecological risk is an indicator to evaluate the biodiversity of the ecosystem and how it changes in response to the inputs of chemicals
The Shannon index is the indicator chosen (Legendre & Legendre, 1998). The more organisms have the same biomass the higher the Shannon index will be.

$$SD = -\sum_{i=1}^{N} p \ln p \quad \textbf{(34)}$$

$$p = \frac{\overline{B_i}}{\overline{B_{tot}}} \quad \textbf{(35)}$$

$$\overline{B_i} = \frac{\sum_{t=0}^{T} B_{it}}{T} \quad \textbf{(36)}$$

$$\overline{B_{tot}} = \sum_{i=1}^{N} \overline{B_i} \quad \textbf{(37)}$$

- SD is the Shannon index;
- p is the ratio between average B_i and average B_{tot};
- Average B_i is the average of the the values of biomass of organism "i" at the time "t" for the entire period of simulation;
- B_{tot} is the total biomass of the ecosystem expressed as the sum of the biomasses of all the organisms of the ecosytem.

For the third class of indicators, the ones that describes the values of the ecosystem from a human point of view, a qualitative approach is chosen to estimate the "Good Ecological Status" while two quantitative indicators describes the "Ecosystem Services".

The "Good Ecological Status" of the ecosystem is evaluated as described in the ANNEX V of the Water Framework Directive 2000. In that directive not data or values are published to estimate quantitatively the ecosystem variations. Furthermore the high ecological status is expressed as the absolute unperturbed status of the river but this is an utopic view because the humans live close to the main rivers of the earth since many centuries ago. Therefore a qualitative and quantitative estimation of the ecological perturbation of the river after the addition of the xenobiotics is done, thus assuming the control simulation as a sort of reference state (although this is not exactly what the WFD aims to). The variation of ecosystem actual status has been classified as expressed in Table 2.69. The organisms are grouped in the same way of the ANNEX V of the Water Framework Directive

Table 2.69 Qualitative estimation of the magnitude of ecosystem perturbation

No visible Perturbation	0-5%
Low Perturbation	5-15%
Moderate perturbation	15-25%
Moderate-High perturbation	25-50%
High perturbation	50%

For the Ecological services quantification two indicators have been chosen. The first representing the turbidity of the water as " The secchi depth". It is the depth at which a Secchi disk disappear from view (Park & Clough, 2012). An increase in water turbidity brings to a decrease in the recreational quality of the river

The second one is the variation in the fish catch quality of the system. A decrease in the Biomass of those species that could be fish is a decrease in the service of the ecosystem to human beings.

Chapter 3

3. Results

This chapter is divided in three main paragraphs. The first one explains the changes done to the assumptions taken in the pre-modeling phase to guarantee stability to the model. The second paragraph is dedicated to the methodologies used to stabilize and calibrate the model and verify that the stabilization was guaranteed for a period of time of 6 years. The third part of the chapter is focused on the effects of LAS and TCS in the different perturbed scenarios.

3.1. Control Ecosystem

Some changes have been done on the initial trophic web hypothesis to stabilize the ecosystem and to guarantee the survival to all the groups Some changes have. The trophic web structure is remained substantially the same even if some modifications have been done in:

- the repartition of the Mathews detritus in the different fractions required by the AQUATOX model for the aquatic invertebrates (labile and refractory particulate suspended detritus / labile and refractory sediment detritus);
- the egestion rates of the food fraction of some animals.

There were an excessive formation of sediment labile detritus in the initial supposed trophic web during the ecosystem stabilization that was not consumed by any organism. So the new diet have been chosen to guarantee a stabilization also of detritus over a period of simulation of 6 years.

The initial conditions of the sediment detritus have been chosen using the same method applied for the biota. The initial concentrations of labile and refractory sediment detritus should be close to their values at the last day of simulation. Invertebrate predators have not been subjected to variation because their diet do not depend on detritus consumption.

Table 3.1 *Diet compositions of aquatic invertebrates supposed in the pre-modelling step*

Initial diet composition for invertebrates	Zooplankton	Young chironomids	Filter feeders	Browser and grazers
Det Sed ref		21,99%		60,84%
Det Sed lab		1,48%		6,11%
Det Part ref	45,67%	70,59%	48,74%	
Det Part lab	4,30%	5,97%	1,26%	
Periphyton				33,00%
Phytoplankton	50,00%		50,00%	

Table 3.2 *Final diet compositions of Aquatic invertebrates*

Final diet composition for invertebrates	Zooplankton	Young chironomids	Filter feeders	Browser and grazers
Det Sed ref		10%		33,5%
Det Sed lab		23%		33,5%
Det Part ref	37%	52%	45%	
Det Part lab	13%	15%	5%	
Periphyton				33,0%
Phytoplankton	50,00%		50,00%	

The global amount of detritus consumption for each class of invertebrates remain the same published by Mathews (Mathews, 1993). The term global amount means the sum of the four fractions of detritus eaten by each animal of the modelled ecosystem (refractory and labile suspended particulate detritus / refractory and labile sediment detritus). The invertebrates egestion factors for the detritus fractions supposed at the beginning of the modeling phase have been changed. The assimilation of detritus for some invertebrates results higher of the normal one found in literature (5% – 35%) (Kumming & Klug, 1979)). This fact could be due to some assumptions taken:

- refractory and labile coefficients for the particulate detritus are based on detritus assimilation of the fish and this one could be a lower than the one of the invertebrates;
- in this system it is not considered that the invertebrates feed also on microorganisms. Invertebrates assimilation of microorganisms is higher than the detritus one (Kumming & Klug, 1979). Microorganisms in the River Thames AQUATOX model could be already considered in the detritus fraction eaten by the invertebrates;

- the default sedimentation model of AQUATOX is used because of scarcity of data. This assumption probably has brought to a different sediment detritus presence from the real one.

The phytoplankton egestion rate of Zooplankton is higher than 0,2 (value supposed at the beginning). Similar values of 0,35 con be found in Christensen paper (Christensen et al, 2005). The only variation occurred in the higher part of the trophic web is the assimilation of detritus for Roach. Its egestion rate is set to 0,9 for the refractory detritus. The global assimilation of detritus (that means the assimilation that derives from each kind of source of detritus) remains in the range measured by some experiment carried out by Mann (Mann et al, 1972). The final egestion rates and the final ecosystem food web matrix are shown respectively in the Table 3.3 and Table 3.4

Table 3.3 *Egestion rates for each food source. Phy= Phytoplanlkton, Peri = Periphyton, M=Macrophytes, E.I= External Insects, A.C.= Adult Chironomid, Zo= Zooplankton, Y.C= Young Chironomids, F.F = filter feeders, B&G= Browsers and Grazers, I. P= Invertebrates Predators, R= Roach, Bl= Bleak, D= Dace, G=Gudgeon, P=Perch, Br= Bream (The numbers in "BOLD" are the fractions changed)*

Egestion coefficient	**Y.C**	**B.&G.**	**Zo**	**F.F**	**I.P**	**D**	**Bl**	**P**	**G**	**R**	**Br**
Det Sed ref	**0,71**	**0,9**				1,00			1,00	**0,9**	1,00
Det Sed lab	0,00	0,00				0,00			0,00	0,00	0,00
Det Part ref	**0,71**		**0,6**	**0,8**		1,00	1,00	1,00	1,00	**0,9**	1,00
Det Part lab	0,00		0,00	0,00		0,00	0,00	0,00	0,00	0,00	0,00
Phy			**0,35**	0,20							
Peri		0,2				0,20	0,20	0,20	0,20	0,20	0,20
M						0,20	0,20	0,20	0,20	0,20	0,20
A.C.						0,20	0,20	0,20	0,20	0,20	0,20
E.I.						0,20	0,20	0,20	0,20	0,20	0,20
Y.C					0,20	0,20	0,20	0,20	0,20	0,20	0,20
B.&G.					0,20	0,20	0,20	0,20	0,20	0,20	0,20
Zo						0,20	0,20	0,20	0,20	0,20	0,20
F.F					0,20	0,20	0,20	0,20	0,20	0,20	0,20
I.P						0,20	0,20	0,20	0,20	0,20	0,20
D								0,20			
Bl							0,20	0,20		0,20	
P								0,20			
G											
R										0,20	
Br											

Table 3.4 *River Thames final food web. Peri = Periphyton, Phy= Phytoplanlkton, M=Macrophytes, E.I= External Insects, A.C.= Adult Chironomid, Zo= Zooplankton, Y.C= Young Chironomids, F.F = filter feeders, B&G= Browsers and Grazers, I. P= Invertebrates Predators, R= Roach, Bl= Bleak, D= Dace, G=Gudgeon, P=Perch, Br= Bream (The numbers in "BOLD" are the fractions changed)*

Diet composition	**Y.C**	**B&G**	**Zo**	**F.F**	**I.P**	**D**	**Bl**	**P**	**G**	**R**	**Br**
Det Sed ref	**0,100**	**0,335**				0,064			0,067	0,099	0,085
Det Sed lab	**0,230**	**0,335**				0,005			0,005	0,007	0,006
Det Part ref	**0,520**		**0,370**	**0,450**		0,240	0,212	0,009	0,250	0,374	0,320
Det Part lab	**0,150**		**0,130**	**0,050**		0,018	0,016	0,001	0,019	0,028	0,024
Phy			0,500	0,500							
Peri		0,330				0,046	0,155	0,034	0,204	0,098	0,133
M						0,007	0,008	0,000	0,028	0,060	0,036
A.C						0,322	0,194	0,440	0,058	0,015	0,050
E.I						0,194	0,227	0,352	0,126	0,005	0,149
Y.C					0,340	0,012	0,050	0,004	0,065	0,061	0,062
B&G					0,330	0,002	0,007	0,001	0,023	0,029	0,007
Zo						0,088	0,123	0,129	0,138	0,194	0,121
F.F					0,330	0,001	0,005	0,003	0,016	0,021	0,006
I.P						0,001	0,001	0,001	0,001	0,001	0,001
D								0,005			
Bl							0,002	0,017		0,005	
P								0,005			
G											
R										0,003	
Br											

3.1.1. The Ecosystem stabilized

The control ecosystem is stabilized and calibrated for a period of time at least of 6 years that is the maximum period chosen for the simulations.

To carry out the stabilization of the model the concept based on the fact that the ecosystem should be governed by cyclic dynamics that repeat every year is taken in consideration. It is a simplification of a riverine ecosystem because in the reality organisms biomass could change every year depending on biotic and abiotic factors (e.g. the flow of water changes over a year, the temperature etc.). However this is the best choice to evaluate changes occurring within the ecosystem due to toxicant effects. Calibration phase was considered completed when the annual average biomasses of the organisms of the AQUATOX model were equal to the ones found in literature.

In the Table 3.5 a comparison between the Mathews average annual biomasses of the organisms and the ones modelled by AQUATOX in the same period of time is done .

Table 3.5 *Difference between the average annual biomass in Mathews study and the average annual biomass of the model of AQUATOX*

Organisms	Biomass g dry / m^2 (Estimated from Mathews 1993)	Biomass g dry /m^2 (AQUATOX model)	Difference ε_i%
Phytoplankton	4,00	4,01	0,3%
Periphyton	1,04	1,04	0,1%
Macrophytes	2,16	2,17	0,2%
Zooplankton	0,94	0,94	0,4%
Young chironomids	11,11	11,13	0,2%
Invertebrate predators	0,07	0,07	1,6%
Filter feeders	18,34	18,34	0,0%
Browsers and grazers	3,77	3,79	0,5%
Adult chironomid	7,77	7,73	0,6%
External insects	17,94	17,93	0,0%
Bleak	11,11	11,11	0,1%
Roach	6,77	6,76	0,1%
Dace	1,04	1,03	1,2%
Gudgeon	4,22	4,20	0,5%
Perch	1,45	1,46	0,2%
Bream	2,73	2,73	0,2%

The difference between Mathews' value and the AQUATOX model value for a period of simulation of one year has been calculated using equation 38.

$$\varepsilon_i\,\% = \frac{B_{mi} - B_{Ai}}{B_{mi}} \cdot 100 \qquad \textbf{(38)}$$

- ε_i% is the variation of values between the Mathews and Aquatox model for the organism "i";
- B_{mi} is the average annual biomass of the organism "i" in the Mathews study;
- B_{Ai} is the average annual biomass of the organism "i" in the AQUATOX model run for one year;

The highest variation between Mathews values and AQUATOX values is equal to 1,6% (Invertebrate predators)(Table 3.5).
In the Table 3.6 is showed the stabilization of the model among a period longer than one year in AQUATOX.

Table 3.6 *Difference between the average biomass of one year simulation and the average biomass of six years of simulation in AQUATOX*

Organisms	**Biomass g dry /m^2 (AQUATOX model) 1 year**	**Biomass g dry /m^2 (AQUATOX model) 6 year**	**Difference $\varepsilon_{i(1\_6)}$%**
Phytoplankton	4,01	4,03	0,3%
Periphyton	1,04	1,04	0,1%
Macrophytes	2,17	2,17	0,3%
Zooplankton	0,94	0,94	0,2%
Young chironomids	11,13	11,18	0,4%
Invertebrate predators	0,07	0,074	2,3%
Filter feeders	18,34	18,27	0,4%
Browsers and grazers	3,79	3,85	1,6%
Adult chironomid	7,73	7,74	0,1%
External insects	17,93	17,95	0,1%
Bleak	11,11	11,16	0,5%
Roach	6,76	6,79	0,4%
Dace	1,03	1,04	1,2%
Gudgeon	4,20	4,23	0,6%
Perch	1,46	1,47	0,6%
Bream	2,73	2,75	0,8%

The difference between the average biomass of an organism during a period simulation of one year and the average biomass of an organism during a period simulation of six years has been calculated using equation 39

$$\varepsilon_{i(1\_6)}\% = \frac{B_{Ai(1)} - B_{Ai(6)}}{B_{Ai(1)}} \cdot 100 \quad \textbf{(39)}$$

- $\varepsilon_{i(1\_6)}\%$ is the variation of average biomass of the organism "i" in the period of simulation of 1 year and 6 years in AQUATOX
- $B_{Ai(1)}$ is the average biomass of the organism "i" in during the period simulation of 1 year
- $B_{Ai(6)}$ is the average biomass of the organism "i" in during the period simulation of 6 years

The highest variation from the first year to the sixth year is equal to 2,3 % (Invertebrate predators)(Table 3.6). This value is considered acceptable because the resulting error coming from the sum of measurement instrument errors and the various assumptions taken in this work is higher than this variation.

The TSS (Total suspended solids), Nutrients (P, N-NO_3, N-NH_4), CO_2 and Oxygen concentrations are plotted in the Figure 3.1 and Figure 3.2. There is a visible peak of oxygen concentration in the summer season due to the phytoplankton bloom.

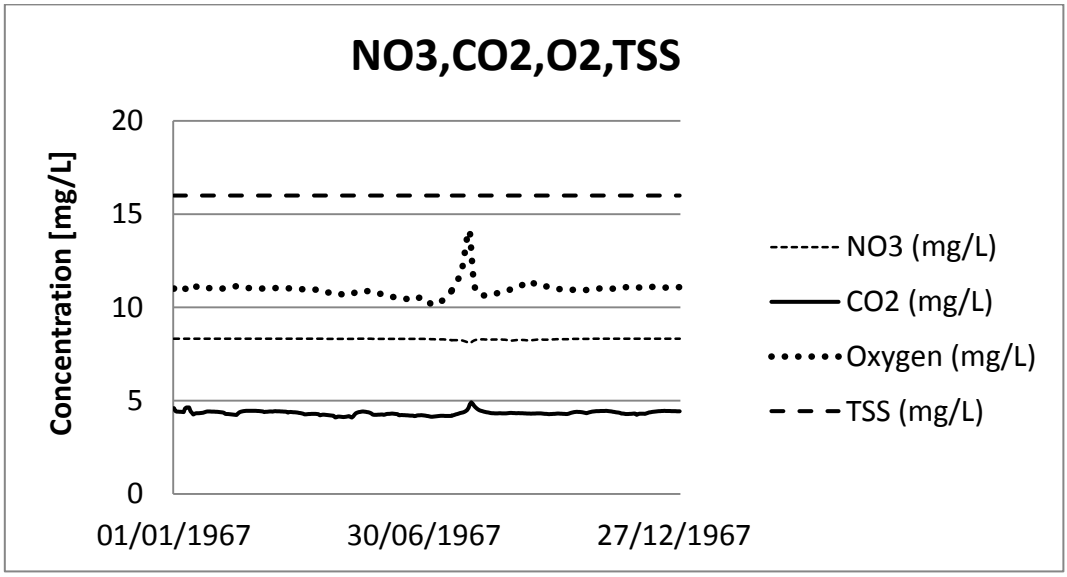


Figure 3.1 *NO_3, CO_2, O_2,TSS trends in the control simulation of one year*

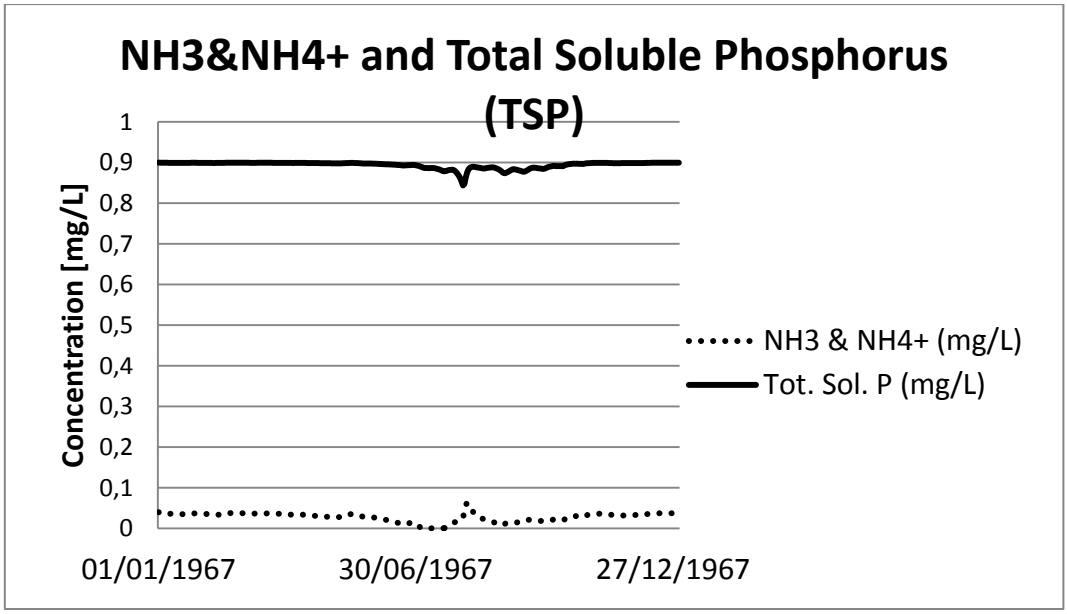


Figure 3.2 *NH_3 & NH_4, Total Soluble P (TSP) trends in the control simulation of one year*

The suspended particulate detritus and the dissolved detritus concentrations remain mainly constant among the year (Figure 3.3). The sediment detritus has a maximum in March and a minimum in September (Figure 3.4)

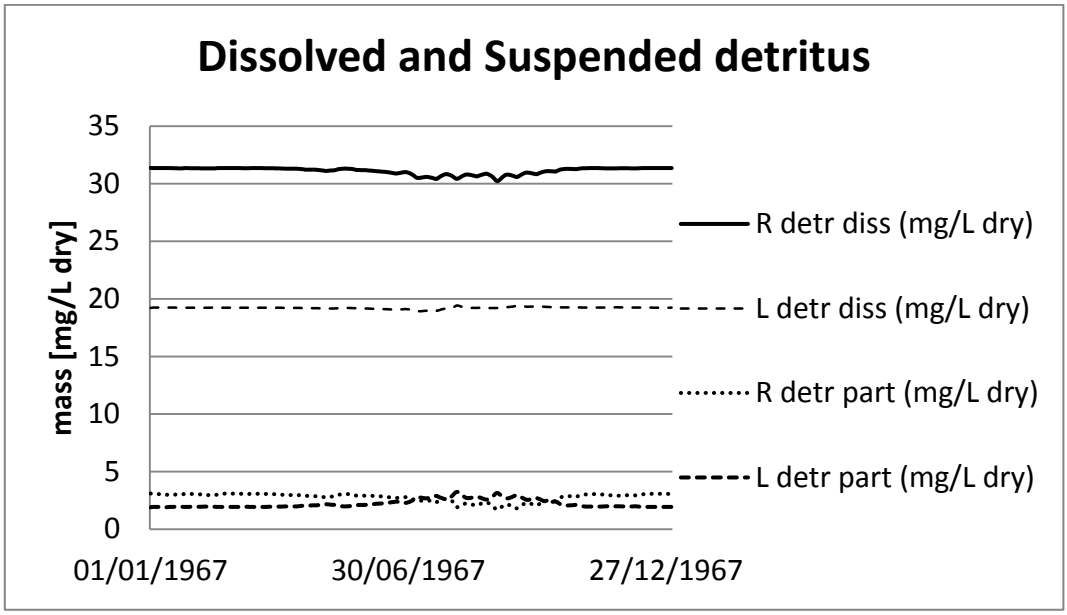


Figure 3.3 *Dissolved and suspended detritus trends in one year control simulation. "L" means labile and "R" refractory*

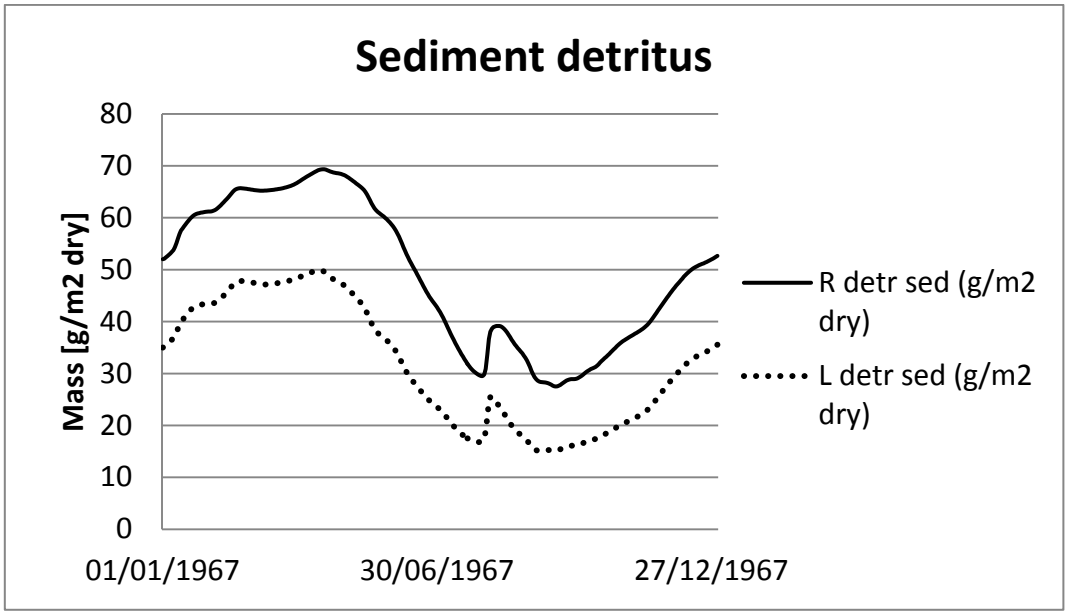


Figure 3.4 *Labile and refractory sediment detritus detritus trends in one year control simulation*

The main phytoplankton peak is in the center of summer between July and August (Figure 3.5). Peaks of Periphyton occur from June to October (Figure 3.6). Macrophyte biomass variation has a minimum at the end of winter and a maximum at the end of the summer (Figure 3.6).

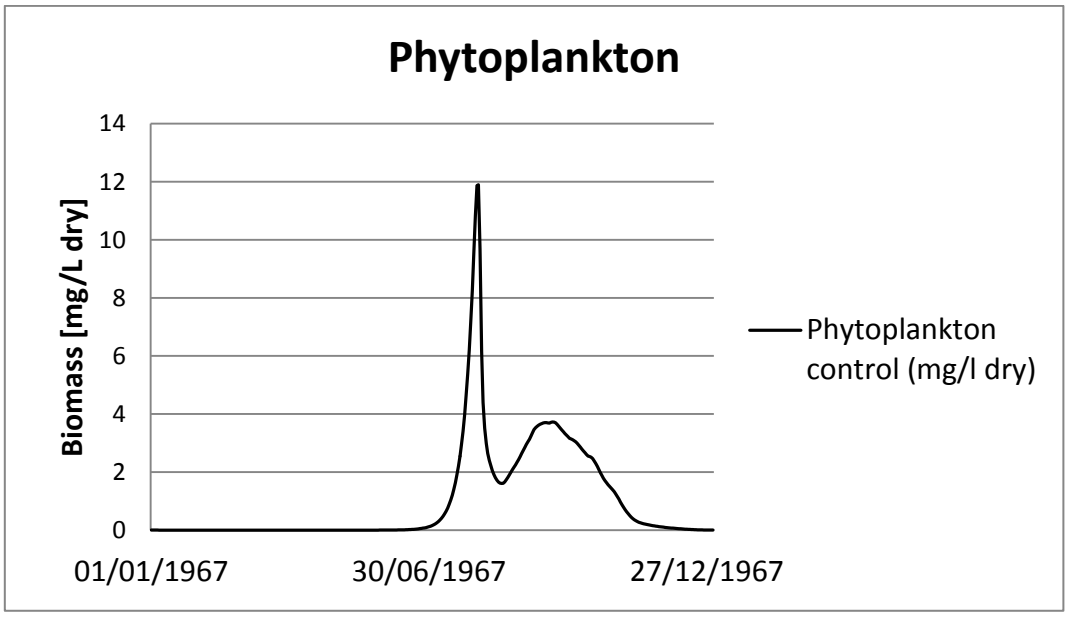


Figure 3.5 *Phytoplankton trend in one year control simulation*

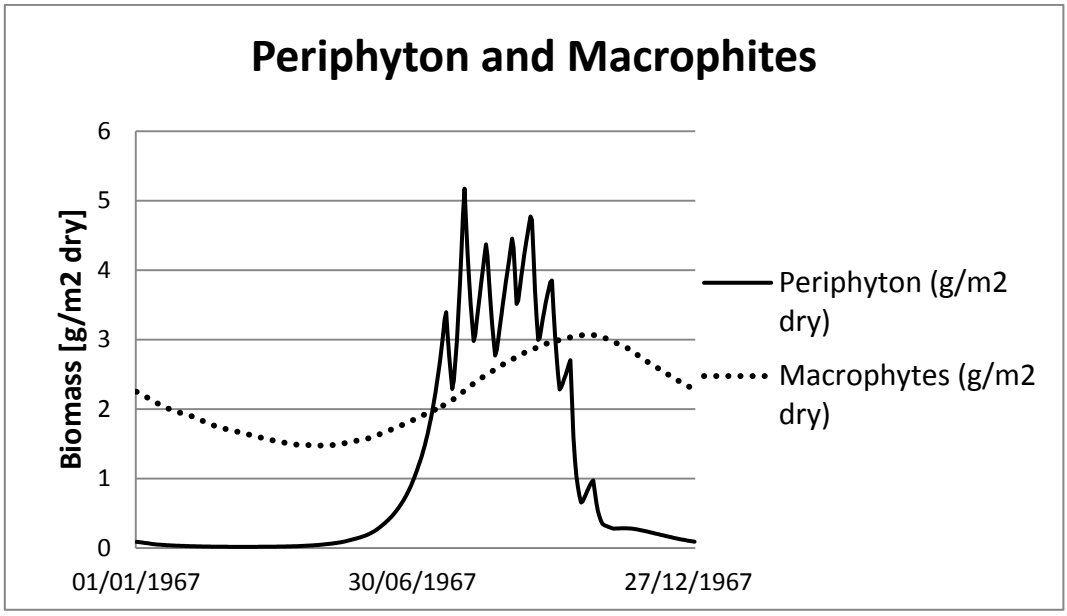


Figure 3.6 *Periphyton and macrophytes trends in one year control simulation*

In the Figure 3.7 the biomass trend of detrivore invertebrates are shown. Zooplankton has an high peak similar to the one of phytoplankton in July. Chironomids and Filter Feeders are two of the organisms groups with the highest biomass. They have the peaks of biomass in a similar period of the year, at the end of summer for chironomids and at the beginning of autumn for Filter feeders.The biomass of browsers and grazers remains mainly the same among the entire year.

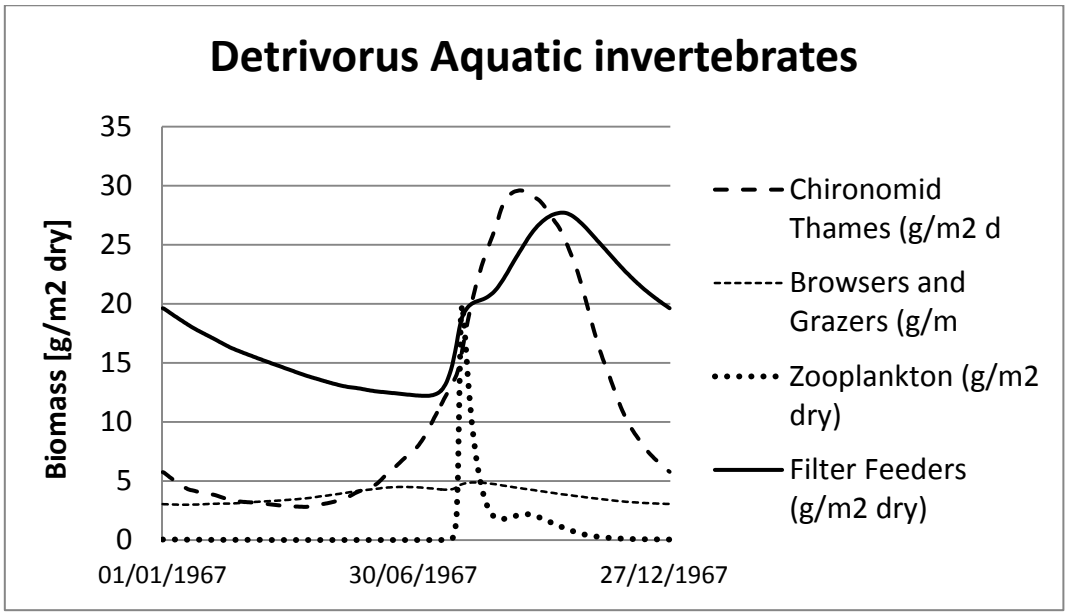


Figure 3.7 *Detrivorus aquatic invertebrates trends in one year control simulation*

The invertebrate predators category is the one with the lower biomass within the ecosystem and their biomass has one of the highest fluctuation over a year. Its major peak is in autumn (Figure 3.8).

Bleak and Roach cover 80 % of the entire fish biomass in this segment of the River Thames. They both have the minimum value of biomass in August. Roach reaches its biomass peak in autumn instead Bleak in spring (Figure 3.9).

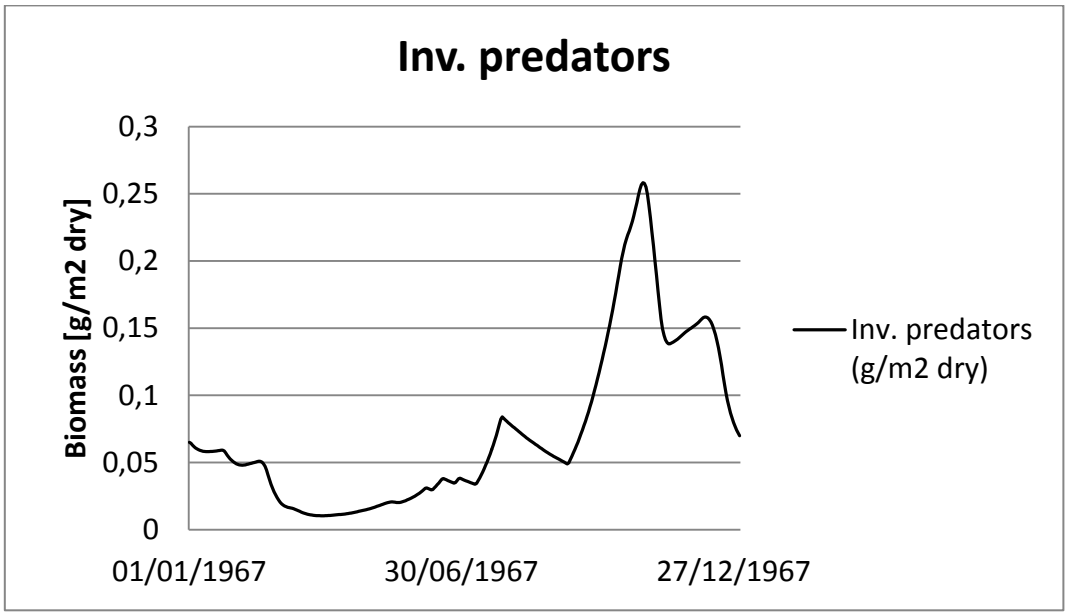


Figure 3.8 *invertebrate predators trend in one year control simulation*

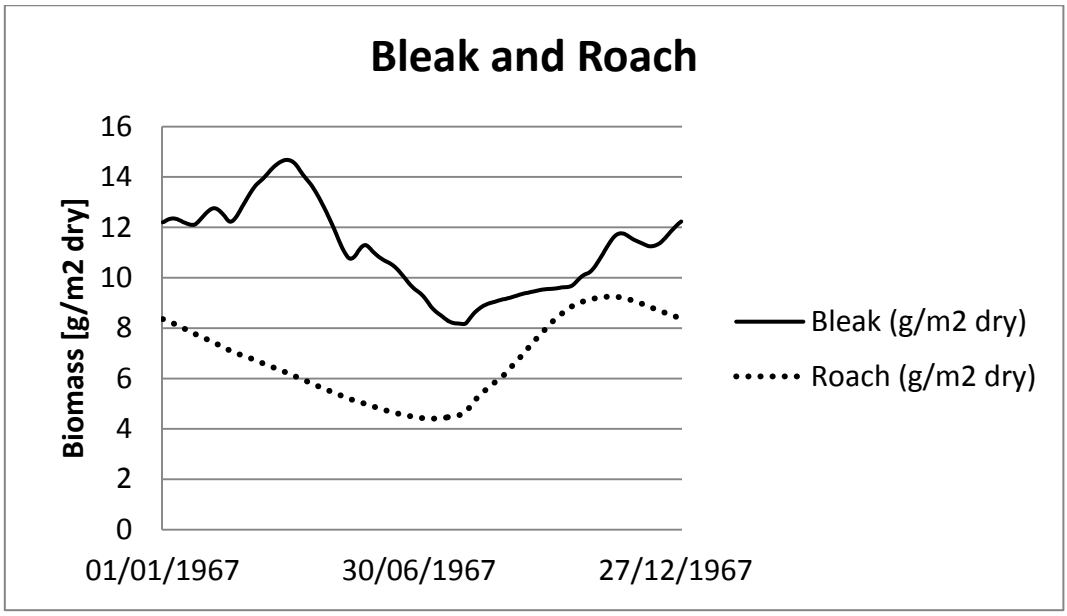


Figure 3.9 *Bleak and Roach trends in one year control simulation*

Surface feeders (Perch and Dace) have similar trend to Bleak instead Bottom feeders (Gudgeon and Bream) have similar trend of Roach (Figure 3.10)

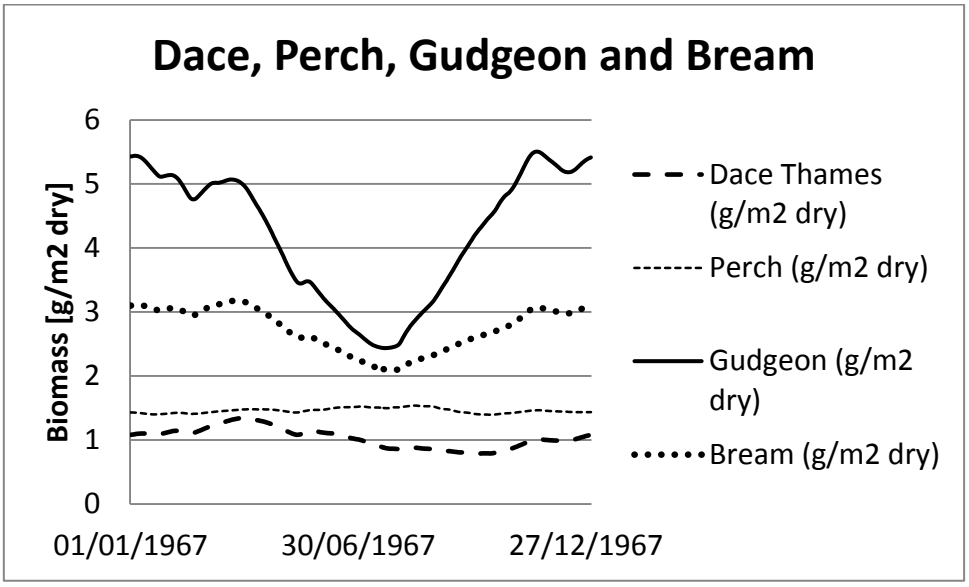


Figure 3.10 *Dace, Perch, Gudgeon and Bream trends in one year control simulation*

The biomass annual trends of Adult chironomid and Esternal insects are shown in Figure 3.11. They are similar to the water flow trend because their presence in the ecosystem depends only on the input from upstream (Figure 2.3).

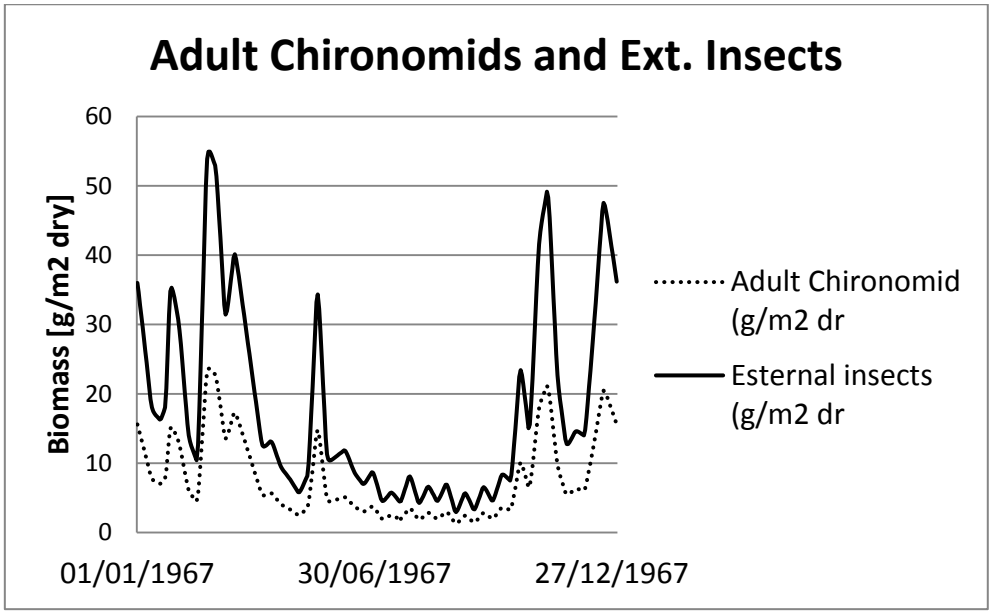


Figure 3.11 *Adult chironomids and External insects trends in one year control simulation*

The model was stabilized for a period of six years. Organism trends of control ecosystem for a period of simulation of six years are shown in Figure 3.34, Figure 3.35, Figure 3.36 and Figure 3.37 . They are used to compare the long term effects of pollutants on the ecosystem.

3.2. Perturbed Ecosystem

This paragraph is divided in two main scenarios. The first one represents the effects of the two toxicants at a relative short-term simulation of 1 year and the second one shows the effects of pollution on the ecosystem at longer term simulations (3 years and 6 years). The ecological indicators are evaluated only for the short-term simulations. Clear rational explanations have not found for some results occurring in long-term simulations (e.g. the biomass explosion of macrophytes at high concentrations of pollutants in water). In an ecosystem model a change in an organism biomass can create a "cascade" of variations in the ecosystem dynamics. For that reason the results of the long-term simulations (included also the ecological indicators) have not been taken in consideration.

As touched on, at long-term simulations having high concentration of pollutants in water (more than ten times the actual concentration present in the river for both of the toxicant) there is a continuously explosion of the macrophytes biomass. The reason of this effect could have various origins.

It could be:

1) the result of the interaction between the organisms of the ecosystem, i.e. a change in macrophyte biomass due to a reduction of predation;
2) an effect due to the way in which macrophytes biomass dynamic is modelled in AQUATOX. The exponential behavior of macrophytes could be due to some of the equations chosen to model the biological processes of macrophytes in the ecosystem (mortality, respiration, photorespiration etc.);
3) a consequence of some choices taken to model macrophytes in this study (The bathymetry equations have not been used and this could generate incongruences for the calculation of the littoral area that is the place where rooted macrophytes live).

It has not been possible to identify the main process that create these results. An eventual excessive increase of macrophytes biomass could generate erroneous results in the estimation of the toxicant effects in the ecosystem. Yet, it should be remarked that macrophytes are partially uncoupled from the rest of the ecosystem (e.g., see diet matrices), thus their potentially problematic simulation should not strongly affect the other modeled organism s

3.2.1. The perturbed ecosystem in 1 year of simulation

In this paragraph the results of the perturbation of the ecosystem due to the input of the toxicants are described. Two distinct simulations are carried out for LAS and TCS, thus neglecting the possible synergy of the effect of the two pollutants and to be able to estimate the main effects of each pollutant.

3.2.1.1. LAS perturbation

Three scenarios of the perturbation have been created to estimate the effect of the pollutant in the environment. In the first one the LAS concentration in water is equal to its concentration actually presents in the river of UK nowadays. The second scenario has an input load from upstream and initial conditions equal to the EC_{50} for the most sensitive organism (i.e. Filter feeders) while for the third one the concentration is equal to the LC_{50} of the most sensitive organism (Filter feeders) (§ Paragraph 2.6).

In the Figure 3.12 the control trend is not visible because it is completely hidden behind the line of the scenario having LAS concentration in water equal to 40 μg/L.

Plants have different reactions to LAS pollution. Phytoplankton shows a small increase in biomass (Figure 3.12 – a) while periphyton biomass decreases at the end of June with the increase of the concentration of the pollutant (Figure 3.12 – b).

Macrophytes in the perturbed scenarios increase their biomass. In Autumn during the perturbed scenario of LAS = 1024 μg/L the biomass of Macrophytes has a peak double of the control simulation (Figure 3.12 – c).

Animals seems to be more sensitive to the LAS pollution than plants. Filter feeders, Browsers and Grazers and Inv. Predators are categories where the change of biomass is clearly visible (3.12 – d,e,g). Zooplankton biomass does not show a visible change in biomass but probably

this is due to the close dependence with Phytoplankton, which is scarcely affected by the chemical presence (3.12 – f).

Perch, Roach and Bream are the fish that demonstrate the highest sensitivity to LAS pollution (3.12 – k, m, n) .

Bleak and Dace response is similar, probably because they are strongly dependent on Adult cironomids and External insect that are not subjected to pollution because they are aerial insects (Figure 3.12 – i,j).

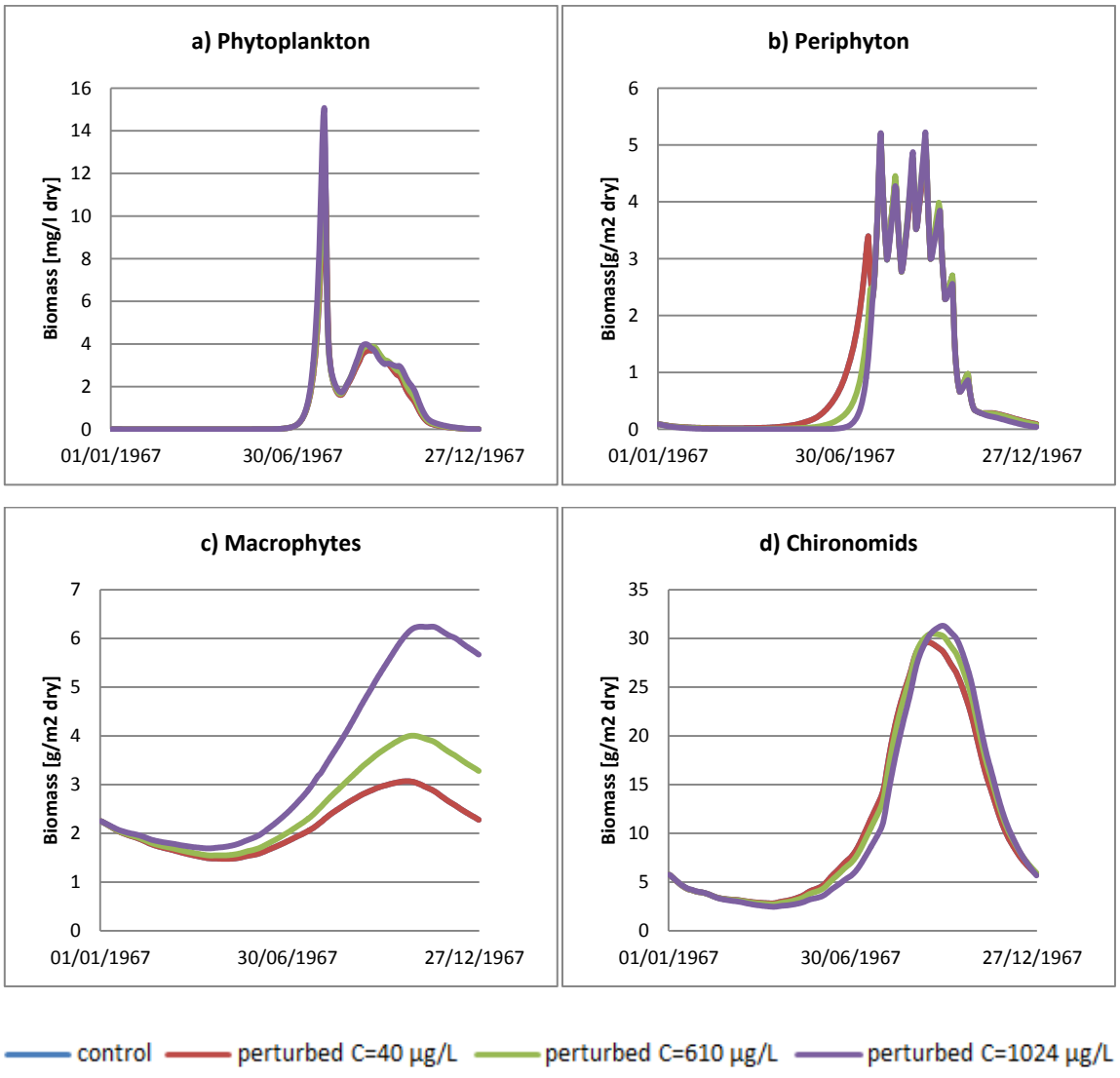


Figure 3.12- part 1 *Biomass trends of the ecosystem organisms subjected to different LAS concentrations in water. a) Phytoplankton, b) Periphyton, c) Macrophytes, d) Chironomids*

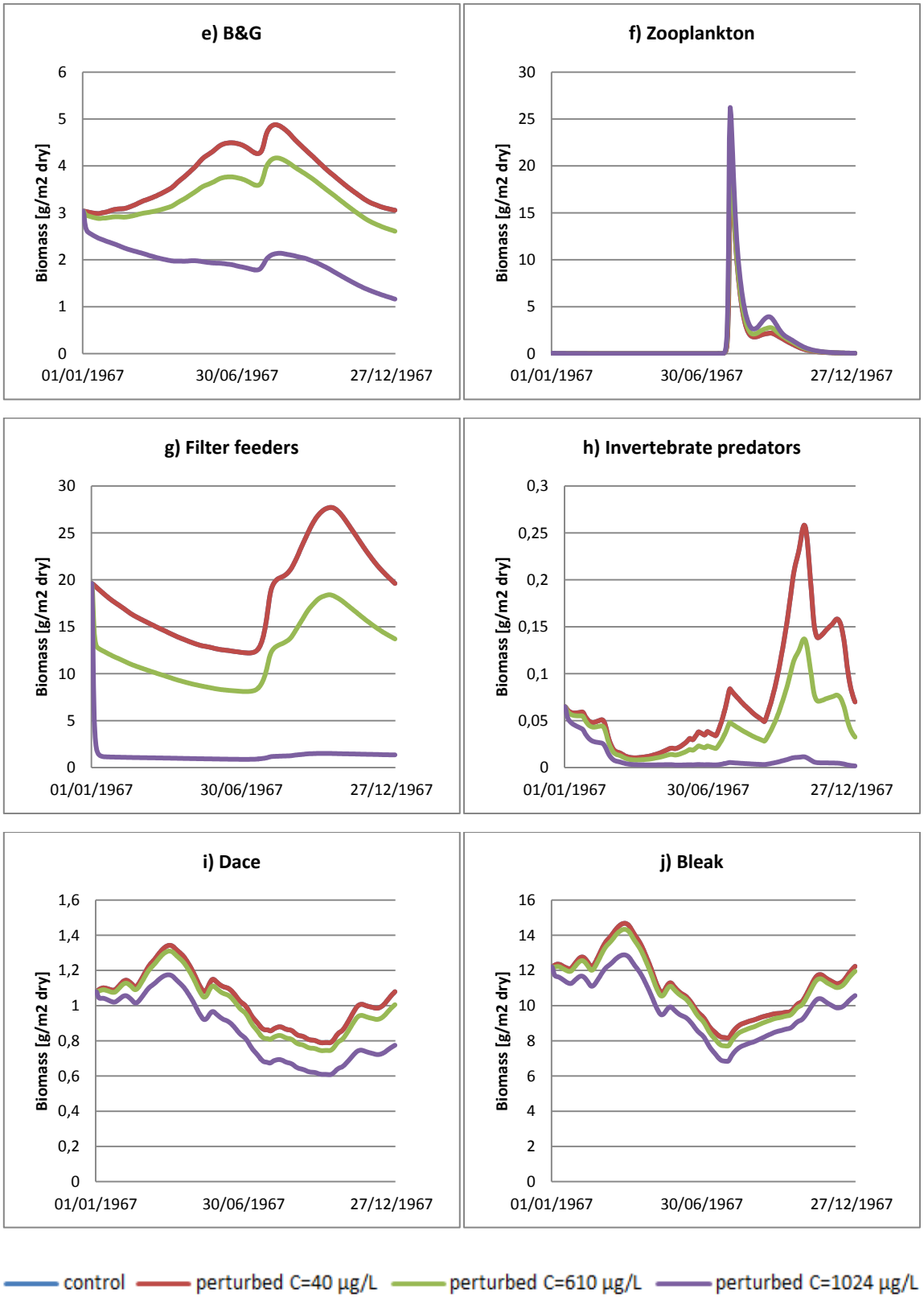


Figure 3.12- part 2 *Biomass trends of the ecosystem organisms subjected to different LAS concentrations in water. e) Browsers and Grazers, f) Zooplankton g) Filter feeders, h) Inv. Predators, i) Dace, j) Bleak*

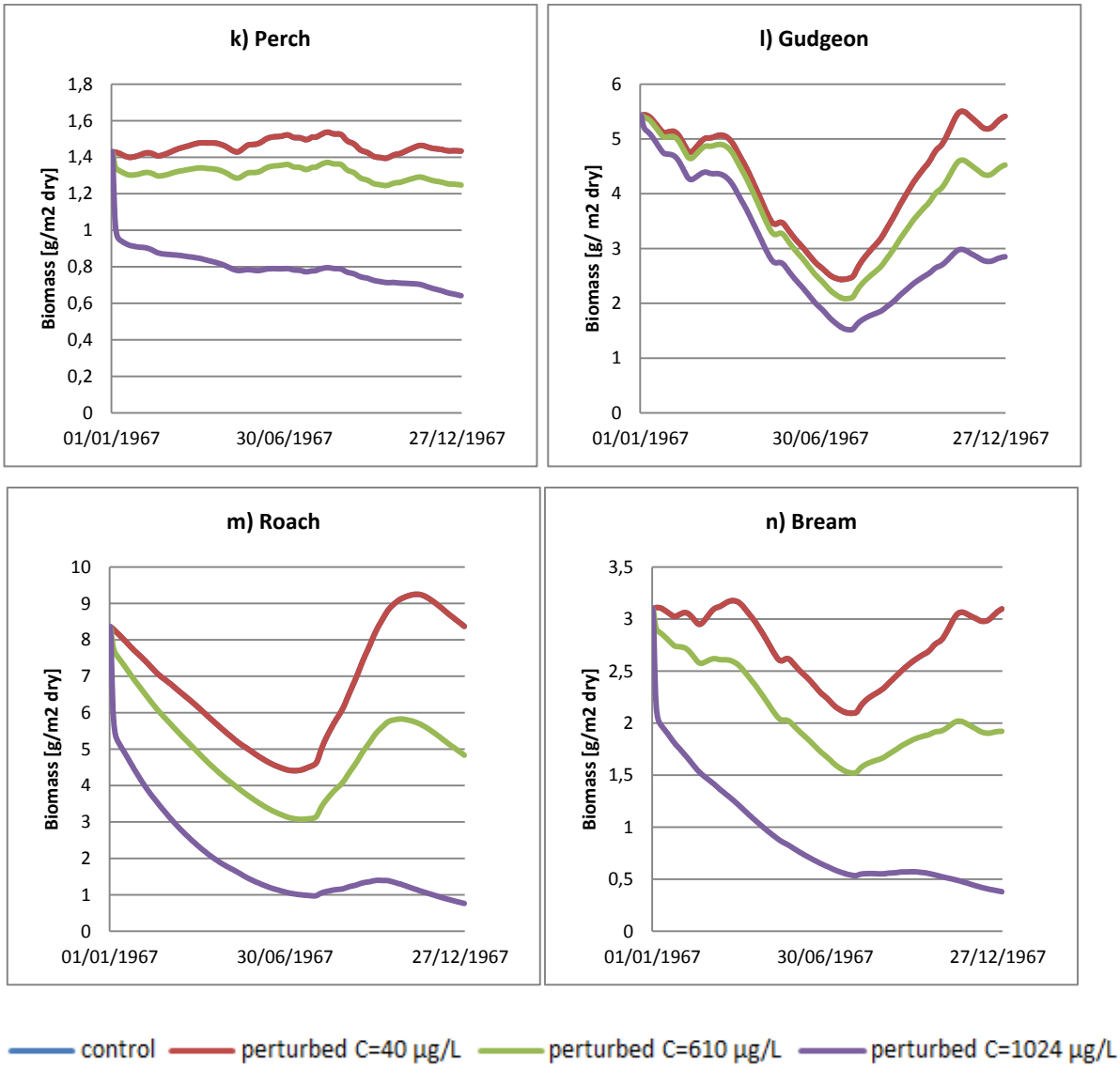


Figure 3.12- part 3 *The Biomass trend of the ecosystem organisms subjected to different LAS concentrations in water. k) Perch, l) Gudgeon, m) Roach, n) Bream*

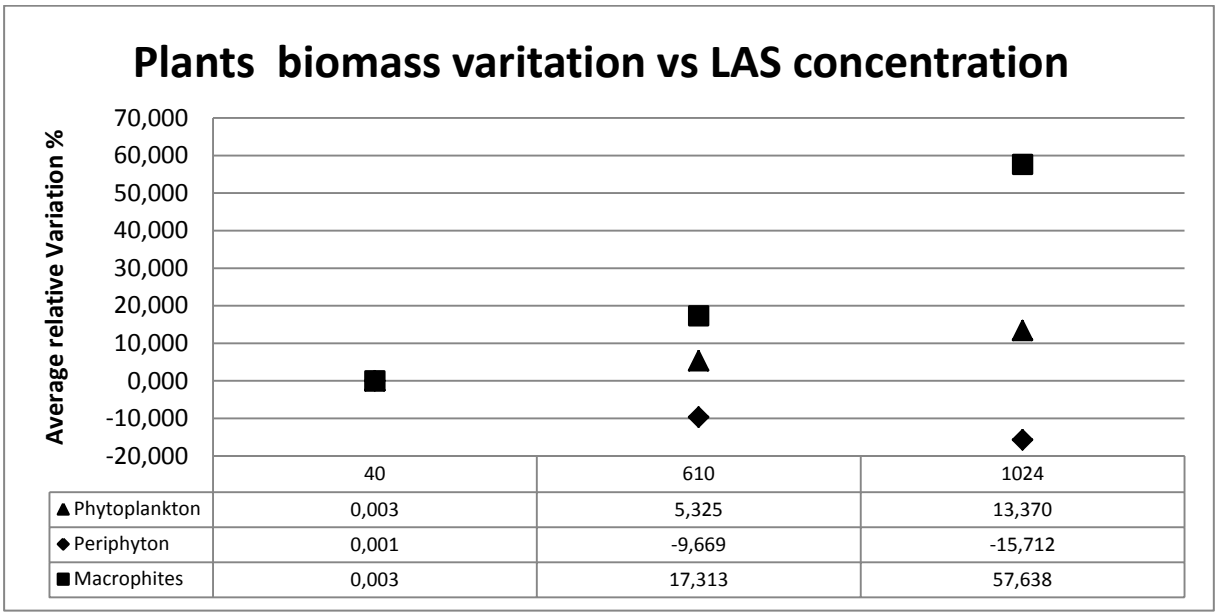
The previous figures describe the variation of organism biomass in [g/m2 dry] but they do not show what organism is the one subjected to the highest relative variation (equation 40).

$$\bar{v}_{ij} = \frac{\overline{B\,pert_{ij}} - \overline{Bcont_i}}{\overline{Bcont_i}} * 100 \qquad \textbf{(40)}$$

- "Average v_{ij}" is the average relative variation of the organism "i" during the pert. scenario "j"
- "Average $Bpert_{ij}$" is the average biomass of the organism "i" during the pert. scenario "j"

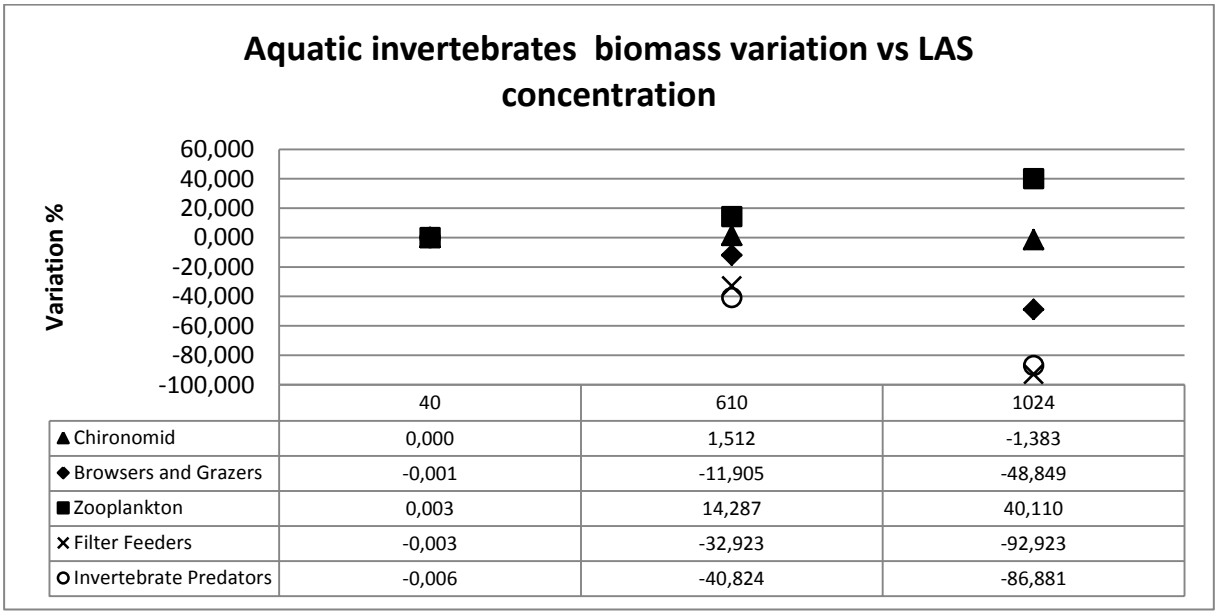
- "Average $Bcont_i$" is the average biomass of the organism " i" during the contr. scenario

The plants with the highest average relative variation is macrophites, having an average biomass increase of about 60 % during the perturbed scenario of C = 1024 μg/L. The macrophytes variation is positively related to the increase of pollutant concentration (Figure 3.13).



	40	610	1024
▲ Phytoplankton	0,003	5,325	13,370
◆ Periphyton	0,001	-9,669	-15,712
■ Macrophites	0,003	17,313	57,638

Figure 3.13 *Average relative variation for plants subjected to LAS*



	40	610	1024
▲ Chironomid	0,000	1,512	-1,383
◆ Browsers and Grazers	-0,001	-11,905	-48,849
■ Zooplankton	0,003	14,287	40,110
✕ Filter Feeders	-0,003	-32,923	-92,923
○ Invertebrate Predators	-0,006	-40,824	-86,881

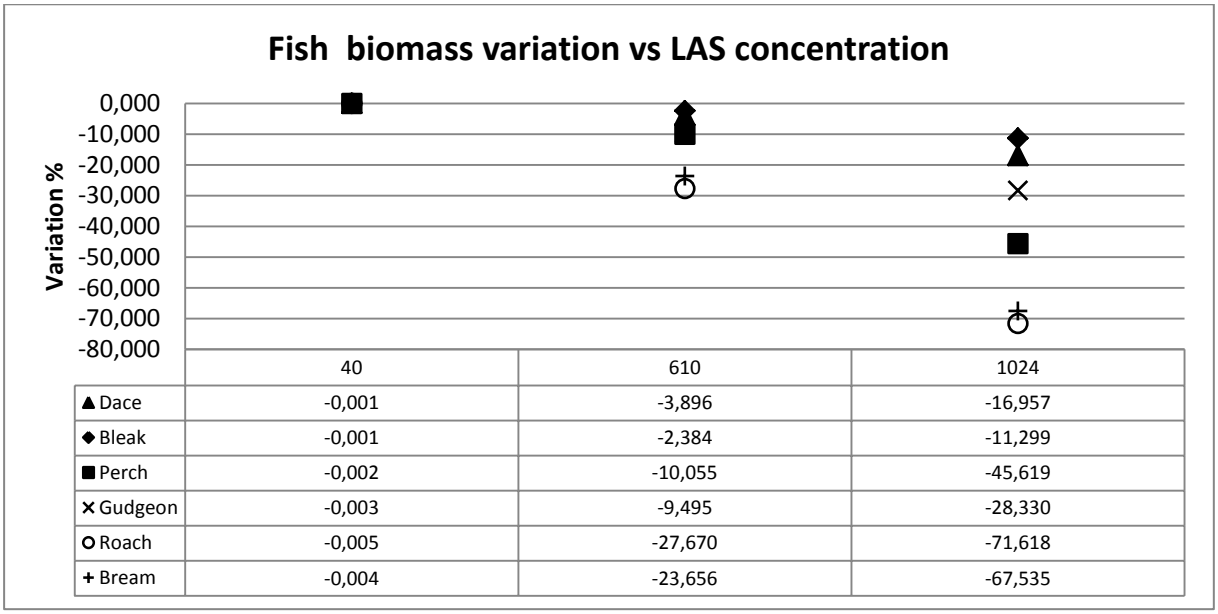
Figure 3.14 *Average relative variation for aquatic invertebrates subjected to LAS*

Periphyton biomass decrease with the increase of the pollutant concentration in water (- 20% ,C = 1024 μg/L) while Phytoplankton tends to have a small increase (Figure 3.13).

Zooplankton biomass increase during perturbation till a maximum of 40% for scenario of C = 1024 μg/L (Figure 3.14).

Chironomids group is the organism less sensible to the pollutant, its biomass change is lower than 5% in every scenario (Figure 3.14).

The highest decrease in biomass of aquatic invertebrates occurred to the Filter feeders and the Invertebrate predators. They have a respective decrease in biomass of about 90% and 86% in the scenario with the highest concentration (Figure 3.14). Fish biomasses tend to decrease from a minimum of 10% of Bleak to a maximum of 90 % of Roach (Figure 3.15).

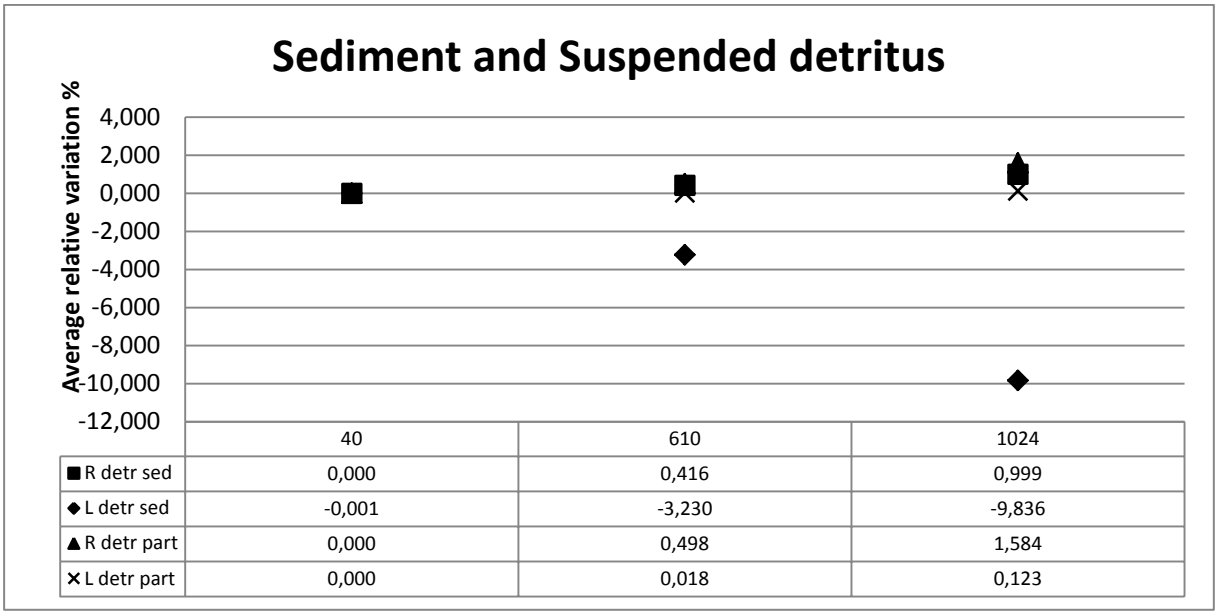


	40	610	1024
▲ Dace	-0,001	-3,896	-16,957
◆ Bleak	-0,001	-2,384	-11,299
■ Perch	-0,002	-10,055	-45,619
× Gudgeon	-0,003	-9,495	-28,330
O Roach	-0,005	-27,670	-71,618
+ Bream	-0,004	-23,656	-67,535

Figure 3.15 *Average relative variation for fishes subjected to LAS*

The average relative variation (Equation 40) is calculated also for sediment and suspended detritus. Instead of the organism biomass in [g/m2 dry], the mass of sediment detritus [g/m2 dry] and the mass of suspended detritus [mg/L dry] are used in the equation.

It is an interesting data because, even if detritus is not a living being, it is an important parameters of the food web, that could suffer of indirect effects due to ecosystem pollution. A decrease in labile detritus mass occurs in the second and third scenarios (C= 610 μg/L C = 1024 μg/L) (Figure 3.16).

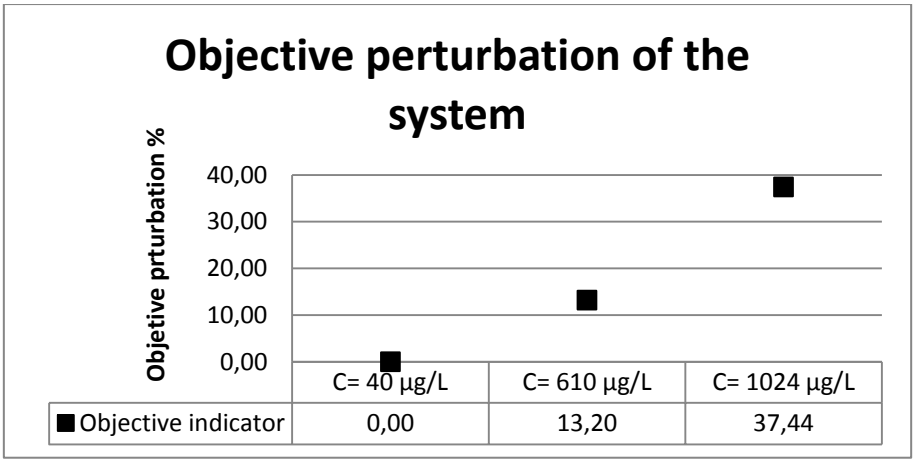


	40	610	1024
■ R detr sed	0,000	0,416	0,999
◆ L detr sed	-0,001	-3,230	-9,836
▲ R detr part	0,000	0,498	1,584
✕ L detr part	0,000	0,018	0,123

Figure 3.16 *Average relative variation for sediment and suspended detritus subjected to LAS*

Objective average perturbation

There is clearly an objective average perturbation of the ecosystem due to LAS (Equation 32 § 2.7). An increase of LAS concentration in water bring to an increase of objective average perturbation (Figure 3.17).



	C= 40 µg/L	C= 610 µg/L	C= 1024 µg/L
■ Objective indicator	0,00	13,20	37,44

Figure 3.17 *Objective perturbation of the system due to LAS pollution for the three different concentrations*

The Figure 3.18 tests if there is a relationship between the LC_{50} and the objective perturbation of the organism. Generally organisms with the lowest LC_{50} values are the ones with the

highest objective perturbation (Table 3.7) although data show a high variability suggesting that toxicity effects are mediated through ecological processes.

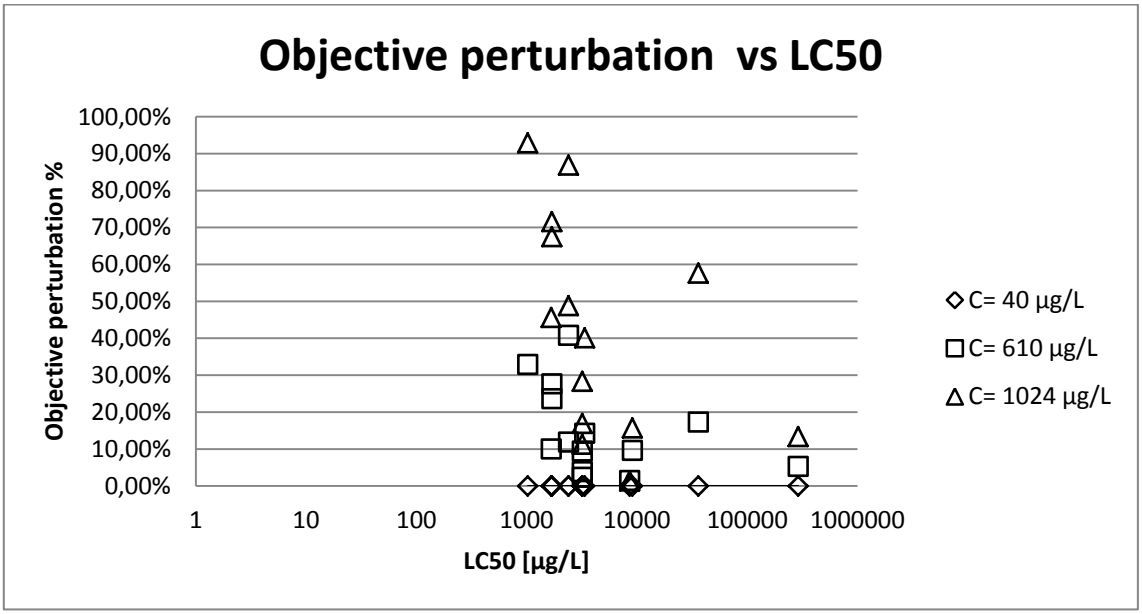


Figure 3.18 *Relationship between objective perturbation and LC_{50}*

Table 3.7 *Objective perturbation vs LC_{50}. The first column shows the LC_{50} of each organisms for LAS pollution. The second one contain the trophic level of the organism and the other three the objective perturbation for each scenario*

Organisms	LC50 (ug/L)	Trophic level	C= 40 µg/L	C= 610 µg/L	C= 1024 µg/L
Phytoplankton	290000	1	0,00%	5%	13%
Periphyton	9100	1	0,00%	10%	16%
Macrophyte	36000	1	0,00%	17%	58%
Chironomid	8600	2	0,00%	2%	1%
B.G.	2400	2	0,00%	12%	49%
Zooplankton	3357	2	0,00%	14%	40%
Filer feeder	1024	2	0,00%	33%	93%
Inv.predator	2400	3	0,01%	41%	87%
Dace	3200	2,621	0,00%	4%	17%
Bleak	3200	2,608	0,00%	2%	11%
Perch	1670	2,970	0,00%	10%	46%
Gudgeon	3200	2,428	0,00%	9%	28%
Roach	1695	2,335	0,00%	28%	72%
Bream	1695	2,397	0,00%	24%	68%

There are some organism where the link LC_{50} – Objective average perturbation is not so clear. Browsers and Grazeres category and Invertebrate predators category have the same LC_{50} but

in the scenario at the highest concentration of LAS in water (C = 1024 μg/L) objective perturbation of invertebrate predators is almost the double of the Browsers and Grazers one . The same is for the three fish Dace, Bleak and Gudgeon. Gudgeon objective perturbation in the scenario of C = 1024 μg/L is the double of the one of Bleak, that means probably there are also other processes that drive their population dynamics, in addition to the toxicity. In the scenario of C = 610 μg/L the effect on biomass variation is higher for Invertebrate predators than for Filter Feeders that is the category with the lower EC_{50} (EC_{50} = 610 μg/L).

Biological indicators

The production-respiration ratio (Equation 33 § Paragraph 2.7) of the control ecosystem is equal to 0,9. In the perturbed scenarios P/R increases until a maximum value of 1,05 for the third scenario (C = 1024 μg/L) (Figure 3.19) .

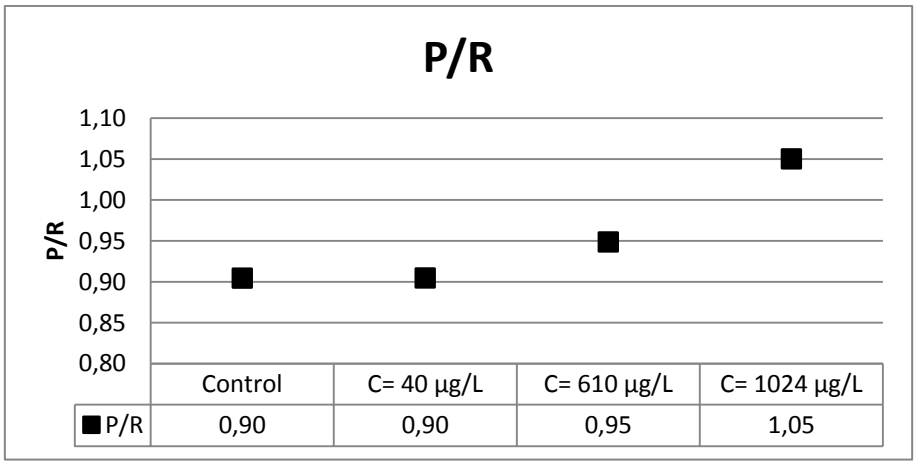


Figure 3.19 *P/R ratio for the control ecosystem and the three perturbed scenarios*

Shannon index (Equation 34) increases in the second perturbed scenario (C = 610 μg/L) but then it displays a strong decrease between second and third scenario (C = 1024 μg/L) (Figure 3.20), in agreement with the ecological theory stating the perturbations decrease the diversity of food webs.

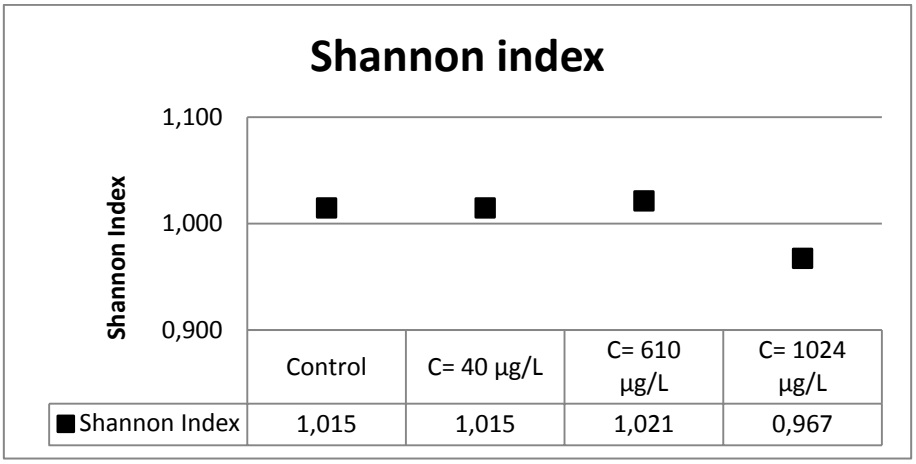


Figure 3.20 *Shannon index for the control ecosystem and the three perturbed scenarios*

Ecological perturbation and ecosystem services

Ecological perturbation of the different scenarios has been classified using Table 2.69 (§Paragraph 2.7).

The increase of pollutant concentration in water brings to an increase in Ecological perturbation (Table 3.8)

Table 3.8 *Ecological perturbation of the ecosystem subjected to LAS pollution in the three different scenarios*

Ecological perturbation	**C= 40 µg/L**	**Objective perturbation**	**C= 610 µg/L**	**Objective perturbation**	**C= 1024 µg/L**	**Objective perturbation**
		%		%		%
Phytoplankton	No visible perturbation	0	Low perturbation	5	Low perturbation	13
Macrophytes and phytobenthos	No visible perturbation	0	Low perturbation	15	Moderate-High perturbation	44
Benthic invertebrate fauna	No visible perturbation	0	Moderate perturbation	20	High perturbation	57
Fish fauna	No visible perturbation	0	Low perturbation	12	Moderate-High perturbation	37
Ecosystem	No visible perturbation	**0**	Low perturbation	**13**	Moderate-High perturbation	**37**

There is a change in water turbidity but it would be imperceptible to human eyes because these are changes of the order of millimeters. The possible reason is that the turbidity in AQUATOX depends on light extinction. This parameter is a sum of some coefficients that describe the extinction of light due to plants, suspended detritus, dissolved detritus, inorganic

solids and water. The River Thames at Reading during the 60's had a high detritus concentration. The suspended and dissolved detritus is not affected by LAS pollution at any concentration because there is a continuous constant input from upstream. For this reason light extinction depends mainly from detritus and inorganic solids and a variation in plants biomass do not create perceptible change to light extinction and indirectly also on turbidity.
Even if the change is not perceptible by human there is a decrease in turbidity for the scenario having C= 610 μg/L and then a low increase for the third scenario (C = 1024 μg/L) (Figure 3.21).

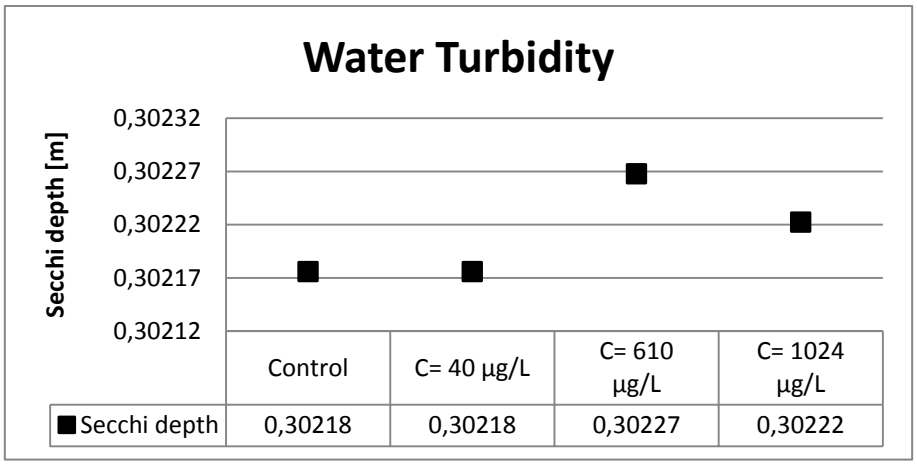


Figure 3.21 *Secchi depth (Turbidity measure) for the control ecosystem and the three perturbed scenarios*

The total fish biomass decreases with the increase of concentration of LAS in water (Figure 3.22)

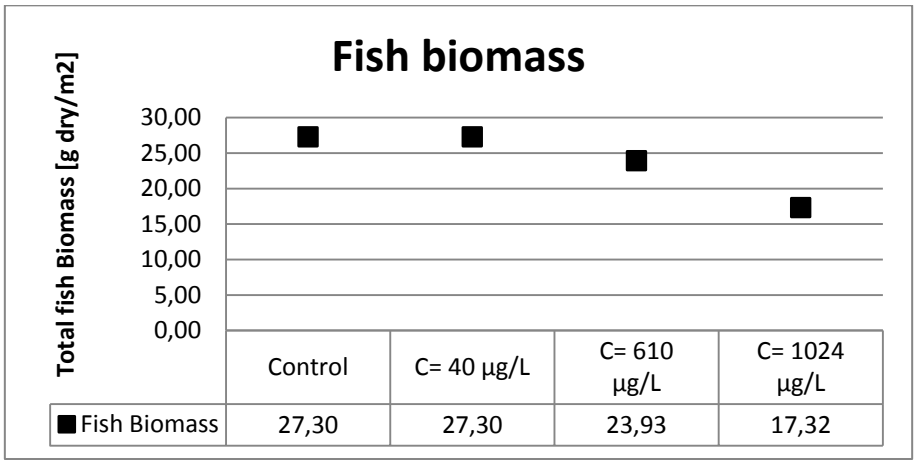


Figure 3.22 *Total fish biomass for the control ecosystem and the three perturbed scenarios*

3.2.1.2. TCS perturbation

Three scenarios of the perturbation have been created to estimate the effect of the pollutant in the environment. In the first one the TCS concentration in water is equal to its concentration actually presents in the river of UK nowadays. The second scenario has an input load from upstream and initial conditions equal to the EC_{50} for the most sensitive organism (i.e. Phytoplankton) while for the third one the concentration is equal to the LC_{50} of the most sensitive organism (Phytoplankton) (§ Paragraph 2.6).

The effect of TCS on organisms biomasses at the actual concentration (C= 0,05 µg/L) are so low that the organisms biomass trends hide entirely the control ones (Figure 3.23). The organisms that change highly their biomass due to perturbation of TCS are Phytoplankton, Periphyton and Zooplankton (Figure 3.23 – a,b,f). The biomass of these three organisms is close to zero for the second and third scenarios (C= 1,6 µg/L and C= 16 µg/L).

Macrophytes are the only organisms that maintain values close to the control biomass for all the simulations (Figure 3.23 – c).For the other living beings the main changes in biomass occurs in the second part of the year, from the end of July (figure 3.23).

The values of the biomass change between the second scenario and the third scenario (C= 1,6 µg/L and C= 16 µg/L) are similar because the pollutant water concentration of the third scenario remains far from most of the organisms LC_{50}, except for Phytoplankton and Periphyton.

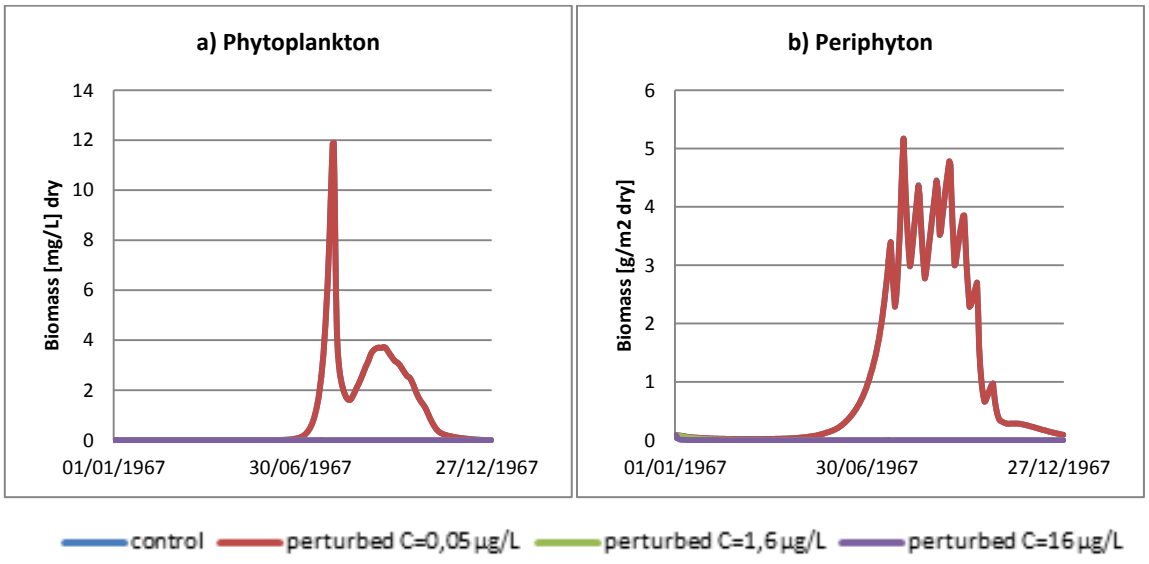


Figure 3.23- part 1 *Biomass trends of the ecosystem organisms subjected to different TCS concentrations in water. a) Phytoplankton, b) Periphyton*

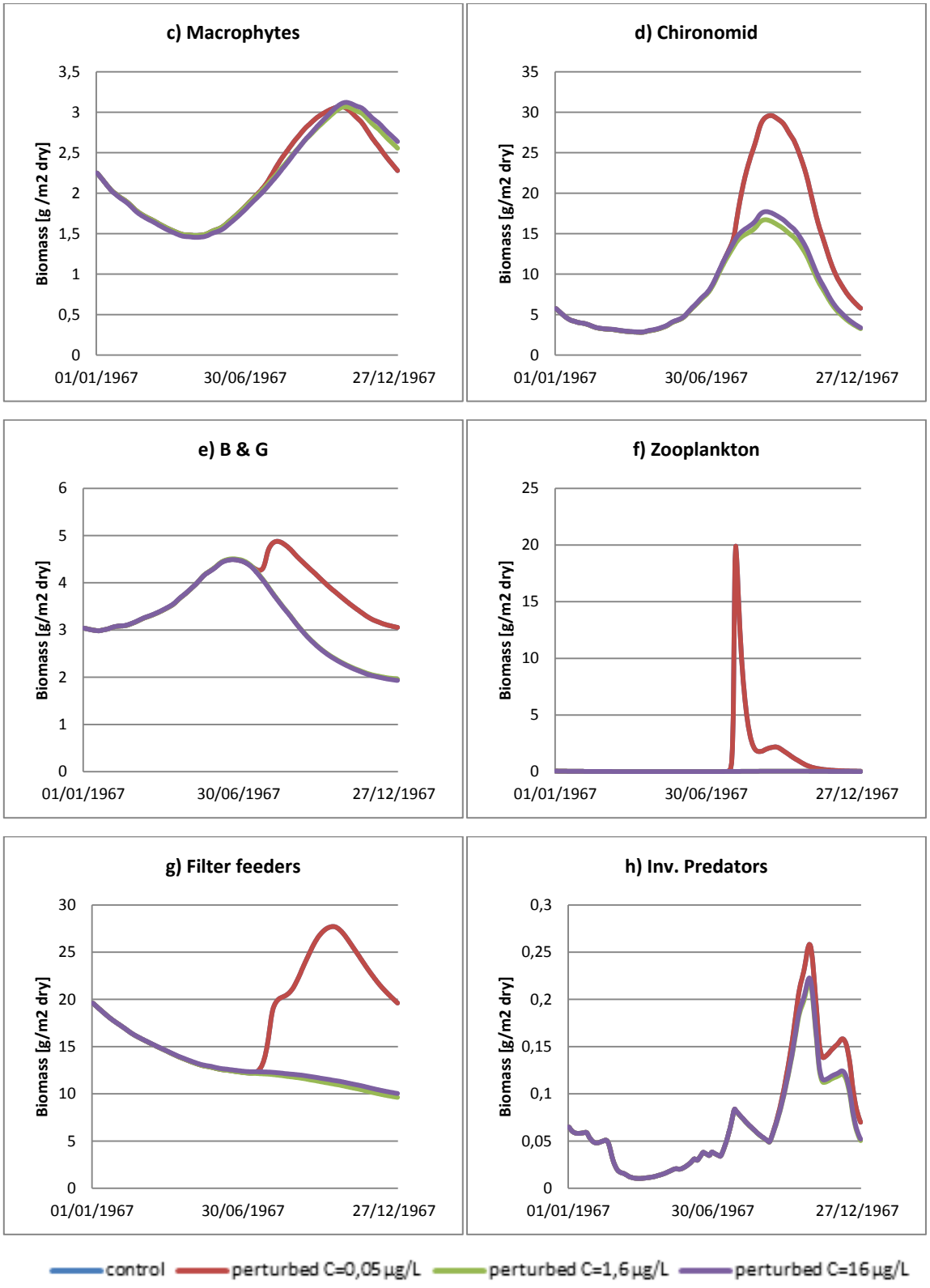


Figure 3.23- part 2 *Biomoass trend of ecosystem organisms subjected to different TCS concentrations in water. c) Macrophites, d) Chironomids, e)Browsers and grazers, f) Zooplankton, g) Filter feeders, h) Inv. predators*

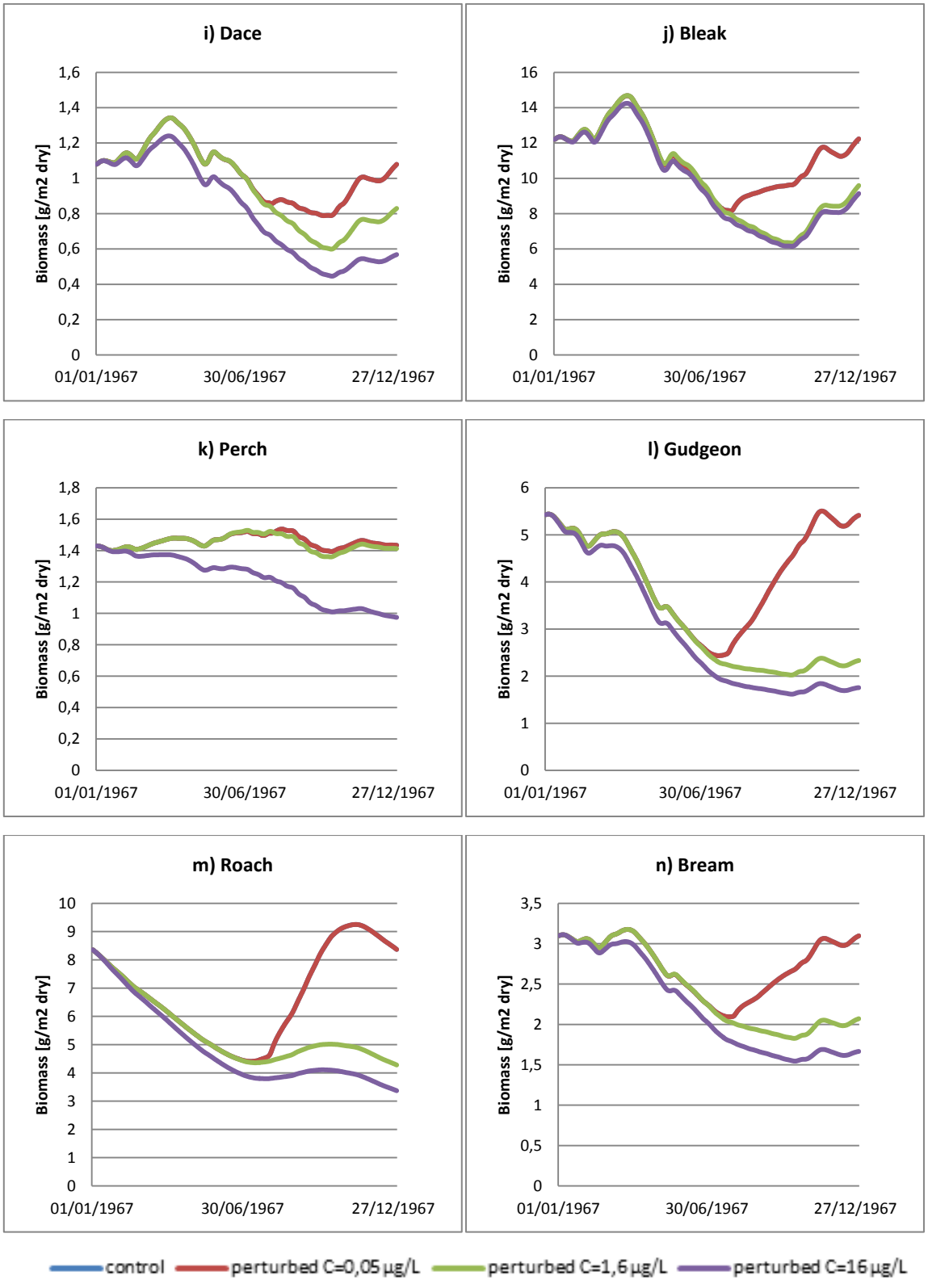


Figure 3.23- part 3 *Biomass trends of the ecosystem organisms subjected to different TCS concentrations in water. i) Dace, j) Bleak, k)Perch, l) Gudgeon, m) Roach, n) Bream*

The relative variations of organisms biomasses for TCS pollution have been calculated (Equation 40).

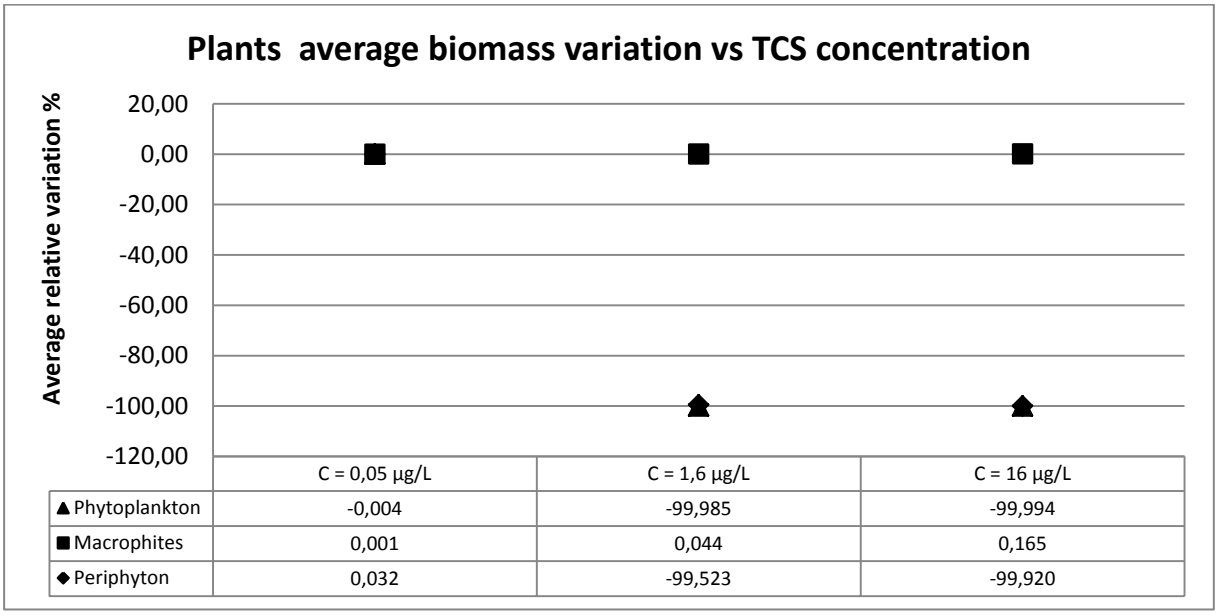
Except for Macrophites, the biomasses of all the organisms of the ecosystem tend to decrease. Phytoplankton and Periphyton biomass decrease almost of 100% in the second scenario (C= 1,6 µg/L) (Figure 3.24). Zooplankton has a similar behavior of Phytoplankton, it is close to extinction in the second (C= 1,6 µg/L) and third scenario (C= 16 µg/L) (Figure 3.25).

The other aquatic invertebrates show the maximum decrease of biomass in the second scenario (C= 1,6 µg/L), between 10% and 40% (Figure 3.25).

Fishes biomass decrease both in the second (C= 1,6 µg/L) and third scenario (C= 16 µg/L) (Figure 3.26). Bream and Roach are the two fish with the highest decrease in biomass.

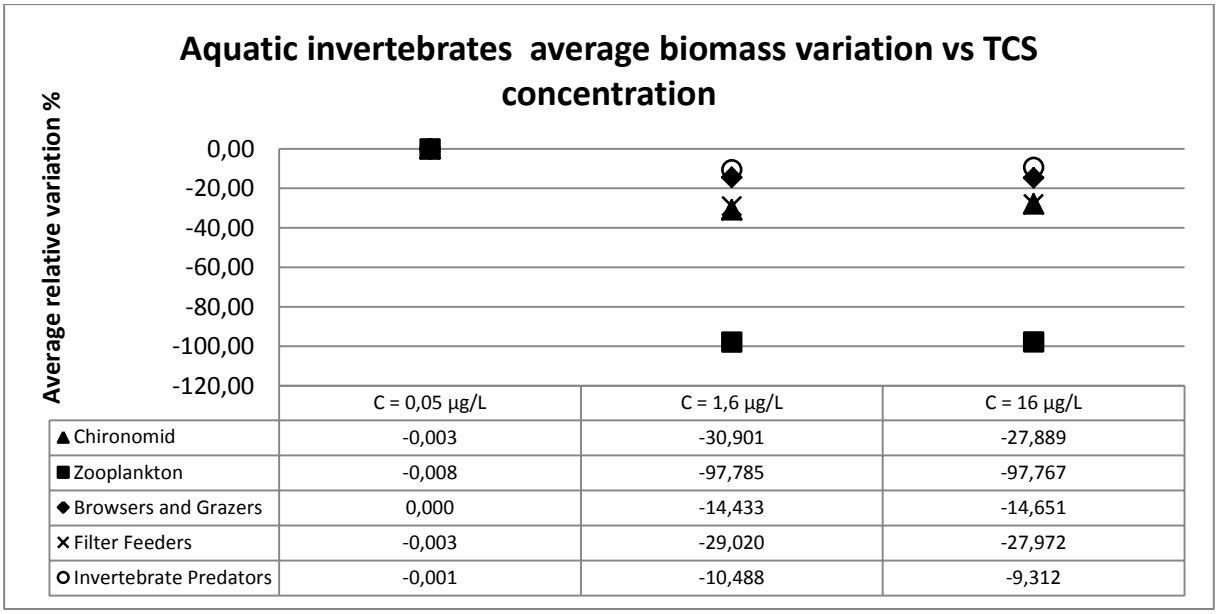
Perch and Dace have high different behaviors between the second (C= 1,6 µg/L) and third scenarios (C= 16 µg/L) while Bleak and Gudgeon average relative variations remain similar in the scenarios having concentrations equal to C= 1,6 µg/L and C= 16 µg/L .

Average relative variation of refractory suspended detritus increase in the second and third perturbed scenarios (C= 1,6 µg/L, C= 16 µg/L) while labile suspended detritus and the two fraction of sediment detritus tend to have a mass decrease (Figure 3.27).



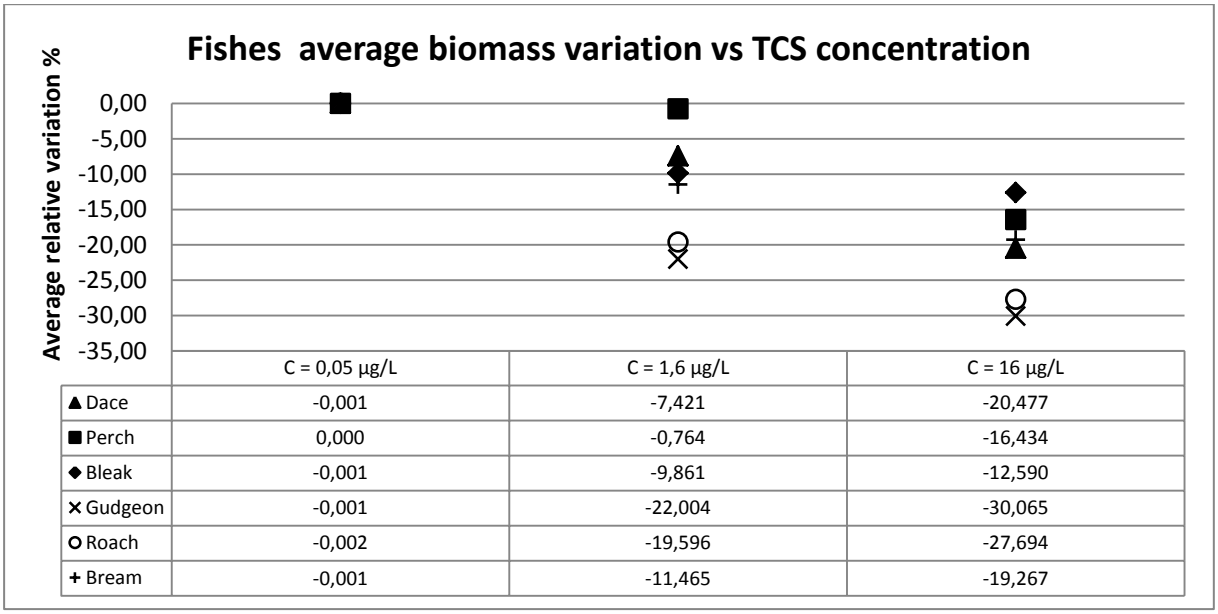
	C = 0,05 µg/L	C = 1,6 µg/L	C = 16 µg/L
▲ Phytoplankton	-0,004	-99,985	-99,994
■ Macrophites	0,001	0,044	0,165
◆ Periphyton	0,032	-99,523	-99,920

Figure 3.24 *Average relative variation for plants subjected to TCS*



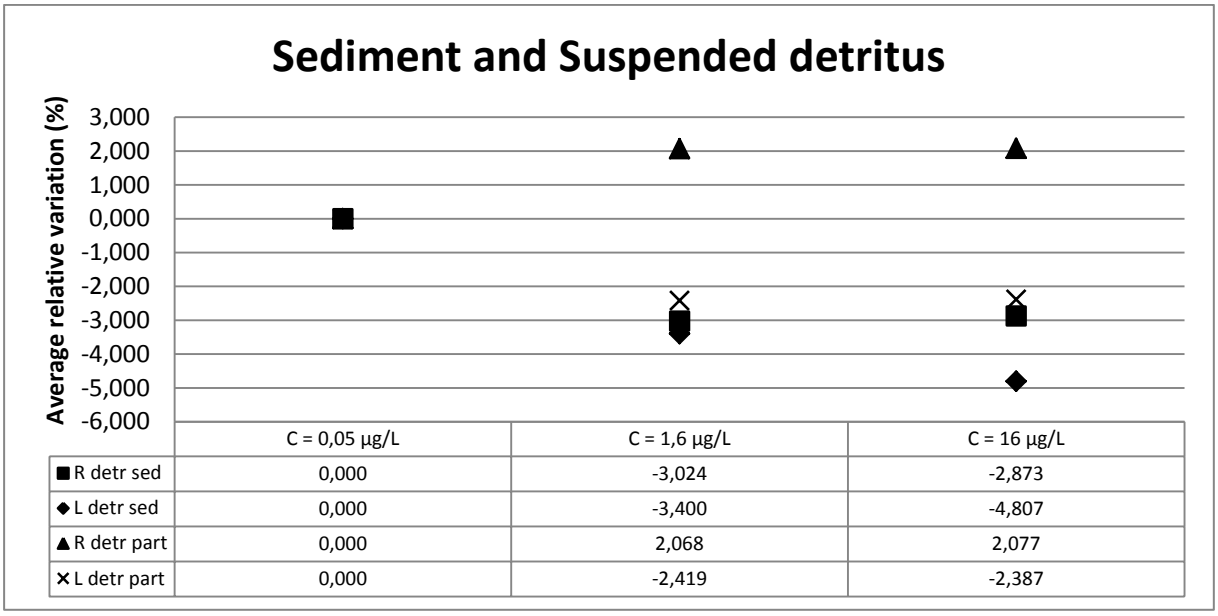
	C = 0,05 µg/L	C = 1,6 µg/L	C = 16 µg/L
▲ Chironomid	-0,003	-30,901	-27,889
■ Zooplankton	-0,008	-97,785	-97,767
◆ Browsers and Grazers	0,000	-14,433	-14,651
✕ Filter Feeders	-0,003	-29,020	-27,972
○ Invertebrate Predators	-0,001	-10,488	-9,312

Figure 3.25 *Average relative variation for aquatic invertebrates subjected to TCS*



	C = 0,05 µg/L	C = 1,6 µg/L	C = 16 µg/L
▲ Dace	-0,001	-7,421	-20,477
■ Perch	0,000	-0,764	-16,434
◆ Bleak	-0,001	-9,861	-12,590
✕ Gudgeon	-0,001	-22,004	-30,065
○ Roach	-0,002	-19,596	-27,694
+ Bream	-0,001	-11,465	-19,267

Figure 3.26 *Average relative variation for fishes subjected to TCS*

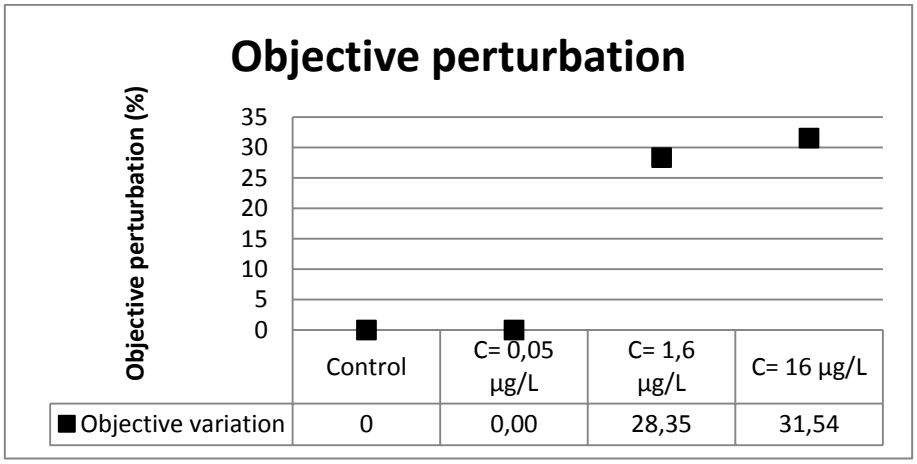


	C = 0,05 µg/L	C = 1,6 µg/L	C = 16 µg/L
■ R detr sed	0,000	-3,024	-2,873
◆ L detr sed	0,000	-3,400	-4,807
▲ R detr part	0,000	2,068	2,077
✕ L detr part	0,000	-2,419	-2,387

Figure 3.27 *Average relative variation for sediment and suspended detritus subjected to LAS*

Objective perturbation

The ecosystem is subjected to a variation due to TCS pollution (Equation 32 § 2.7) (Figure 3.28).



	Control	C= 0,05 µg/L	C= 1,6 µg/L	C= 16 µg/L
■ Objective variation	0	0,00	28,35	31,54

Figure 3.28 *Objective perturbation of the system due to TCS pollution for the three different concentrations*

In Figure 3.29 is plotted the Objective perturbation vs the LC_{50} of the organisms for the TCS. Some living beings that has high LC_{50} show an high objective perturbation. The most representative case is the one of Zooplankton, which objective perturbation is almost 100% (scenarios C= 1,6 µg/L, C= 16 µg/L) even if it has the highest LC_{50}. This is clearly the result

of a trophic interaction (zooplankton feeds on micro-algae which are heavily impacted by TCS).

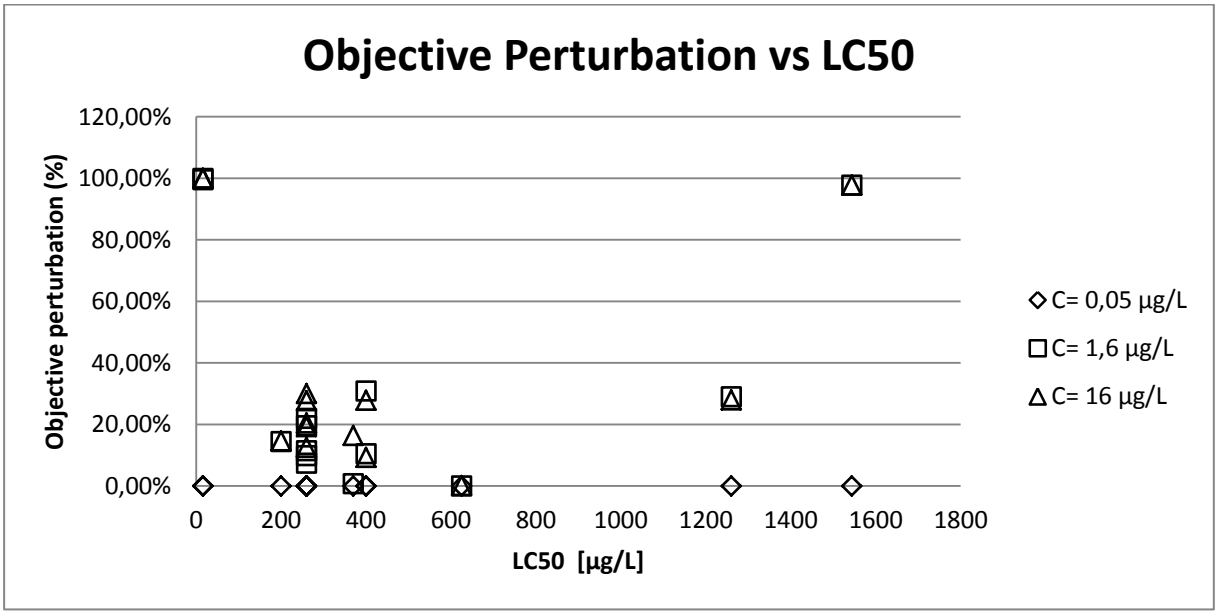


Figure 3.29 *Relationship between objective perturbation and LC_{50}*

Chironomids LC_{50} for TCS is equal to one third of the Filter feeders one but they have the similar objective variation for all the three scenarios (Table 3.9).

Table 3.9 *Objective perturbation vs LC_{50}. The first column shows the LC_{50} of each organisms for TCS pollution. The second one contain the trophic level of the organism and the other three the objective perturbation for each scenario*

Organisms	LC50 (ug/L)	Trophic level	C= 0,05 µg/L	C= 1,6 µg/L	C= 16 µg/L
Phytoplankton	16,1	1	0,00%	99,99%	99,99%
Periphyton	16	1	0,03%	99,52%	99,92%
Macrophyte	625	1	0,00%	0,04%	0,16%
Chironomid	400	2	0,00%	30,90%	27,89%
B.G.	200	2	0,00%	14,43%	14,65%
Zooplankton	1544	2	0,01%	97,79%	97,77%
Filer feeder	1260	2	0,00%	29,02%	27,97%
Inv.predator	400	3	0,00%	10,49%	9,31%
Dace	260	2,621	0,00%	7,42%	20,48%
Bleak	260	2,608	0,00%	9,86%	12,59%
Perch	370	2,97	0,00%	0,76%	16,43%
Gudgeon	260	2,428	0,00%	22,00%	30,06%
Roach	260	2,335	0,00%	19,60%	27,69%
Bream	260	2,397	0,00%	11,47%	19,27%

Biological indicators

The production-respiration ratio (Equation 33 § Paragraph 2.7) of the control ecosystem is equal to 0,9. In the first perturbed scenario (C = 0,05 µg/L) P/R remains close to the control value and decrease to a value close to zero for the other two scenarios (Figure 3.30). The biodiversity of the ecosystem decreases with the increase of TCS concentration in water. The Shannon index (Equation 34) of the control simulation is about 1,02 and decrease until about 0,95 for the scenario with the highest pollutant concentration in water (Figure 3.31).

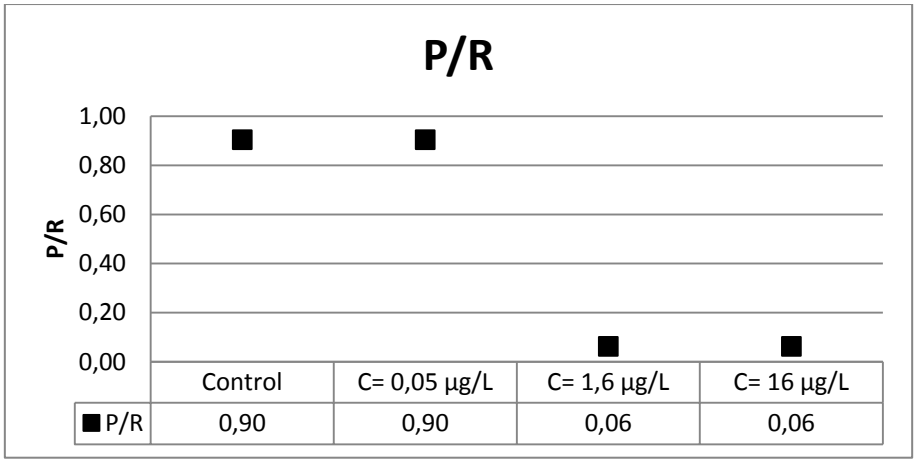


Figure 3.30 *P/R ratio for the control ecosystem and the three perturbed scenarios*

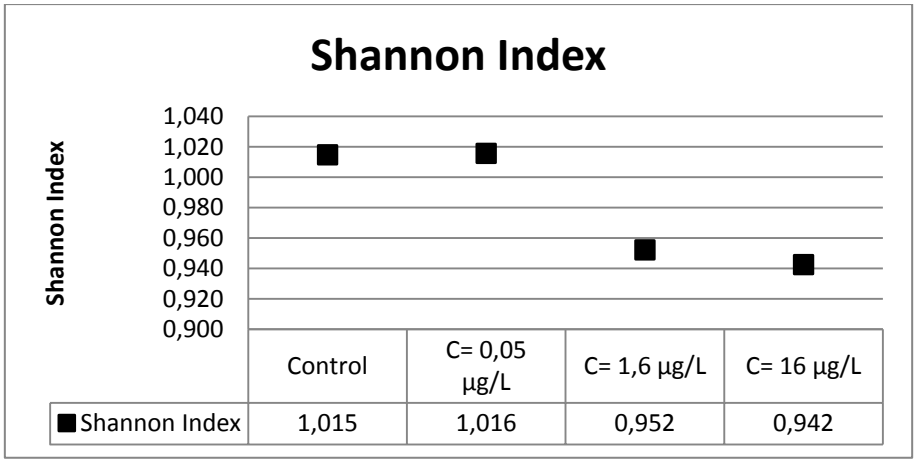


Figure 3.31 *Shannon index for the control ecosystem and the three perturbed scenarios*

Ecological perturbation and ecosystem services

Ecological perturbation of the different scenarios has been classified using Table 2.69 (§Paragraph 2.7).The increase of pollutant concentration in water brings to an increase in Ecological perturbation (Table 3.10).

The perturbation of Phytoplankton reach easily a level of "high perturbation" in the second and third simulation (C= 1,6 µg/L and C= 16 µg/l) (Table 3.10)

Table 3.10 *Ecological perturbation of the ecosystem subjected to TCS pollution in the three different scenarios*

Ecological perturbation	C= 0,05 µg/L	Objective perturbation	C= 1,6 µg/L	Objective perturbation	C= 16 µg/L	Objective perturbation
		%		%		%
Phytoplankton	No visible perturbation	0,004	High perturbation	99,985	High perturbation	99,994
Macrophytes and phytobenthos	No visible perturbation	0,011	Moderate-High perturbation	32,379	Moderate-High perturbation	32,589
Benthic invertebrate fauna	No visible perturbation	0,003	Moderate-High perturbation	29,858	Moderate-High perturbation	28,340
Fish fauna	No visible perturbation	0,001	Low perturbation	13,726	Moderate perturbation	20,196
Global	No visible perturbation	0,004	Moderate Perturbation	28,347	Moderate-High perturbation	31,545

For the same reason explained for LAS the changes in turbidity, i.e. in the Secchi depth are of the order of millimeters (Paragraph 3.2.1.1).

For TCS perturbations there is an increase in turbidity (a decrease in Secchi depth) for the scenarios having pollutant concentration equal to C = 1,6 µg/L and C = 16 µg/L (Figure 3.32).

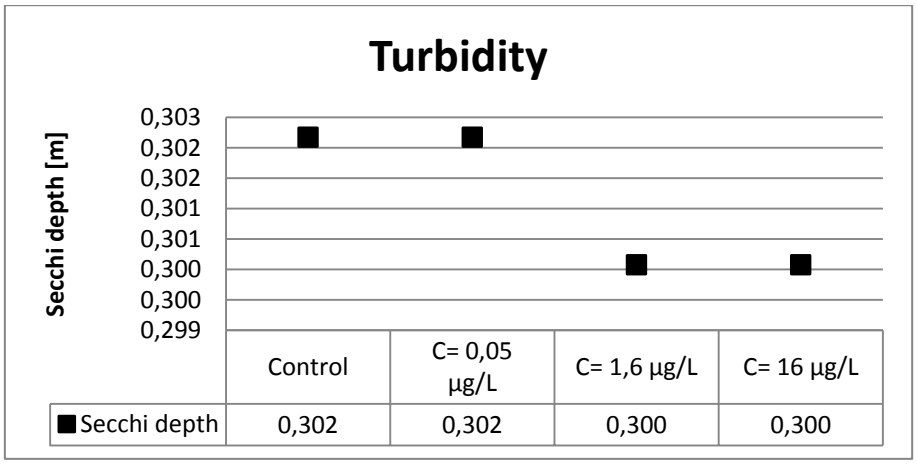


Figure 3.32 *Secchi depth (Turbidity measure) for the control ecosystem and the three perturbed scenarios*

The scenarios having an high concentration of TCS in water (C = 1,6 µg/L and C = 16 µg/L) show a decrease in catchable species. The total biomass of fish reaches a minimum of 21,8 [g/m^2 dry] in the third scenario (Figure 3.33).

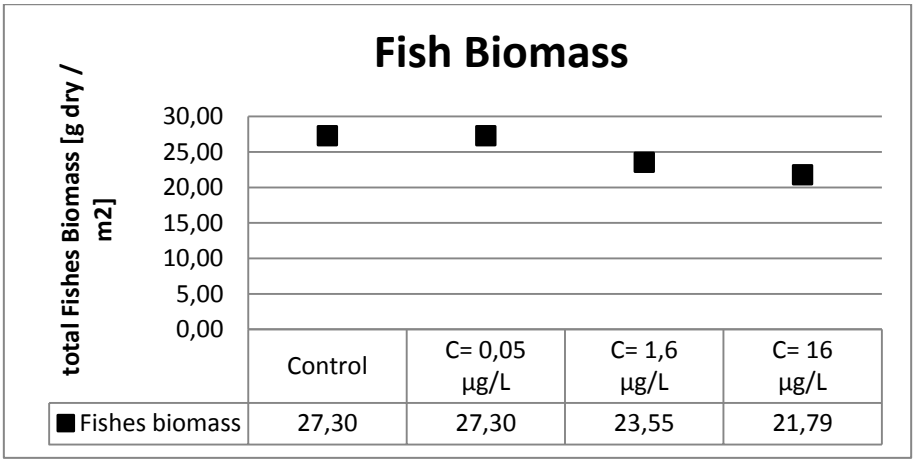


Figure 3.33 *Total fish biomass for the control ecosystem and the three perturbed scenarios*

3.2.2. The perturbed ecosystem in 3 and 6 years of simulation

The perturbed scenarios of LAS and TCS were run for two different period of time, three years and six years.

These scenarios could be useful to understand how the reactions of ecosystem to pollution varies over a relative long-scale perturbation.

Unfortunately it has still not been found a reason to the behavior of the biomass trend of an organism (Macrophyte) of the ecosystem. In an ecosystem model, where the organisms are continuously linked, an errors in a variable could generate a cascade of errors in the entire trophic network.

For this reason in this paragraph only an overview on the perturbed ecosystem is given. The two scenarios for LAS and TCS with the actual pollutant concentration in the rivers water are not analyzed because the effect are so low that is difficult to show them using a chart (biomass relative variation is lower than 1%) .

Only the figure about the six years simulations are shown because they contains also the three years simulations.

3.2.2.1. LAS perturbation

LAS perturbed scenario C= 610 µg/L 3- 6 years

Phytoplankton has an increase of biomass in the three years perturbation and still increase for the one of six years. The first peak increase its magnitude every year and the second peak become larger (Figure 3.34 – a). Periphyton biomass has its maximum value on the fourth year (Figure 3.34 – b).

Macrophytes show an exponential growth until the fourth year when it reaches a peak of 30 [g/m2 dry], then its biomass decreases(Figure 3.34 – c).

The concentration of pollutant input from upstream is equal to the EC_{50} of Filter feeders. Their biomass decrease from the first year and remain mainly stable in this new equilibrium situation both in the three-year and six-year simulations (Figure 3.34 – d). Chironomids is the animal with the highest peak of biomass, 40 [g/m2 dry] (Figure 3.34 – d).

Zooplankton biomass increases in a way similar to phytoplankton every year while Browsers and Grazers biomass shows a low decrease and then it stabilizes in the new perturbed equilibrium trend after one year (Figure 3.34 – e).

Invertebrate Predators is still present in the ecosystem in three-year simulation of but it is almost extinct in the fourth year (Figure 3.34 – f).

Bleak shows a low decrease of biomass in the three-year simulation and then from the fourth year has a low increase. It is one of the animal with the lowest change in biomass (Figure 3.34 – g). Roach presence in the ecosystem decreases in the first three years and from the fourth year shows an exponential biomass increase (Figure 3.34 – g). Gudgeon shows a similar biomass trend to the one of Roach while Bream biomass decreases slowly and stabilizes in the new perturbed situation (Figure 3.34 – h).

The biomass of Perch decreases from the first year till the sixth. On the contrary Dace has a decrease in biomass from the first to the third year where its biomass starts to rise until the end of the sixth year (Figure 3.34 – i).

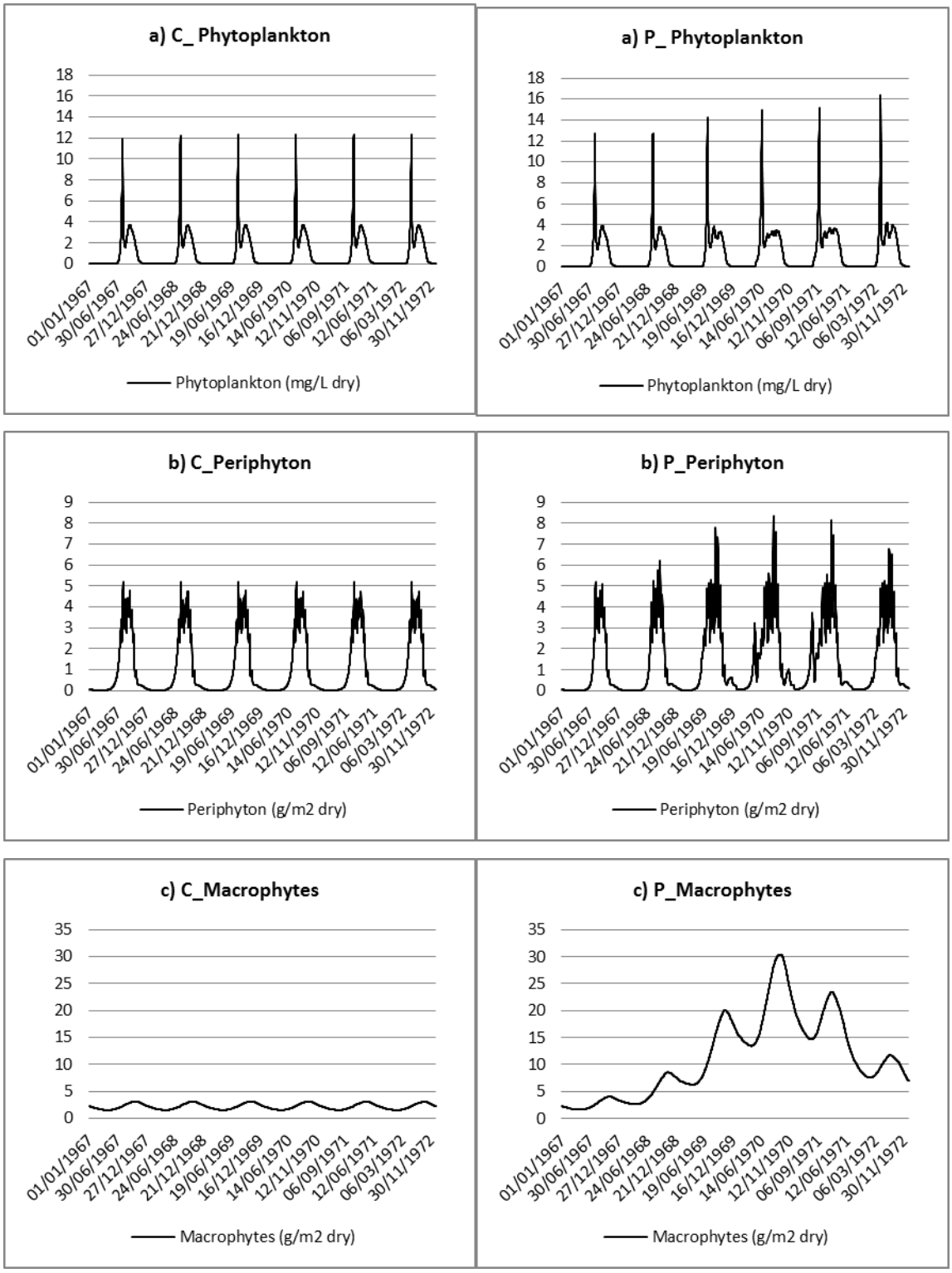


Figure 3.34- part 1 *Biomass trends of the ecosystem organisms subjected to a concentration of LAS of 610 µg/L for a period of simulation of six years . C means "control simulation" while P means "perturbed simulation". a) Phytoplankton, b) Periphyton c)Macrophytes*

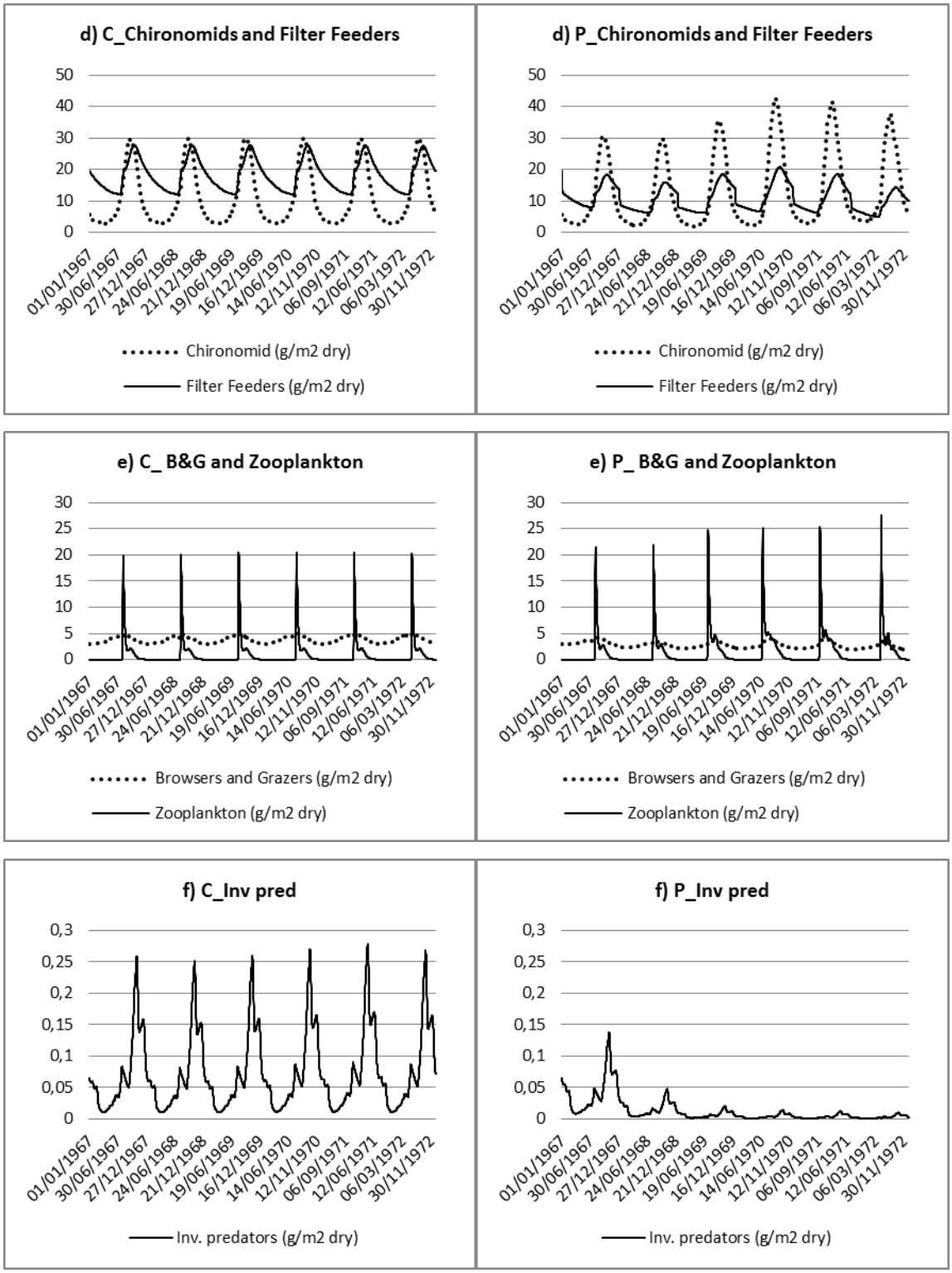


Figure 3.34- part 2 *Biomass trend of the ecosystem organisms subjected to a concentration of LAS of 610 µg/L for a period of simulation of six years . C means "control simulation" while P means "perturbed simulation".d) Chironomids and Filter feeders, e) Browsers and Grazers and Zooplankton, f) Invertebrate predators*

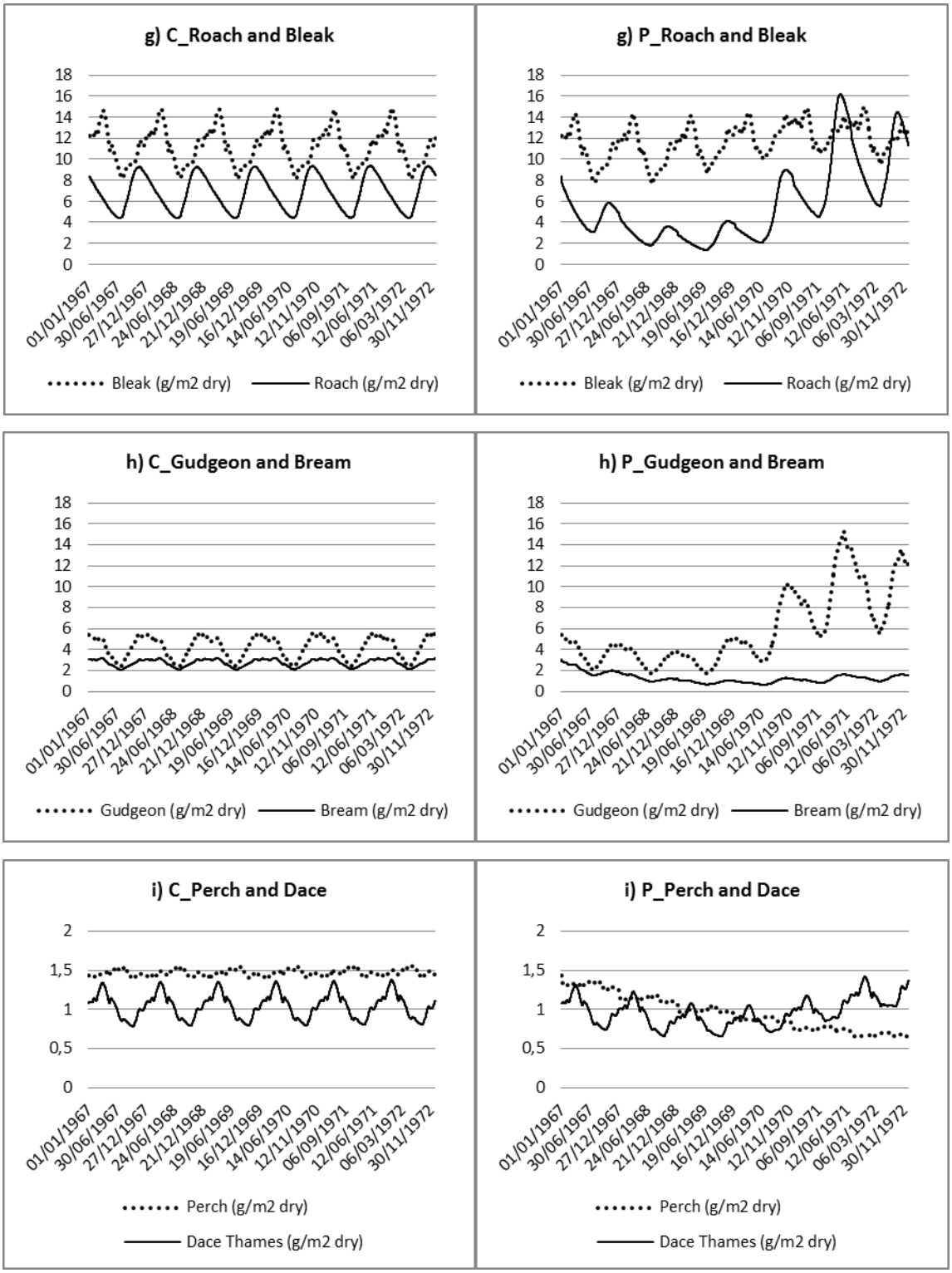


Figure 3.34- part 3 *Biomass trends of the ecosystem organisms subjected to a concentration of LAS of 610 µg/L for a period of simulation of six years . C means "control simulation" while P means "perturbed simulation". f) Inv. Predators, g) Roach and Bleak, h) Gudgeon and Bream, i) Perch and Dace*

LAS perturbed scenario C= 1024 µg/L 3- 6 years

In this scenario phytoplankton bloom peak of July rises from a value of about 12 [mg/L dry] to 15 [mg/L dry]. This behavior starts from the first year of simulation and fluctuates around this value for the entire six years (Figure 3.35 – a). The increase of periphyton biomass is faster than in scenario C= 610 µg/L (Figure 3.35 – b).

Macrophytes have an exponential increase in biomass, similar to the one of the simulation having concentration of LAS C= 610 µg/L. In the LAS simulation of C=1024 µg/L Macrophytes show an higher peak at fourth year [80 g/m^2 dry] than for the previous simulation (Figure 3.35 – c).

Filter feeders disappear from the ecosystem in two years while Chironomids biomass trend is similar to the one of scenario C= 610 µg/L (Figure 3.35 – d). Zooplankton behavior is similar to the one of phytoplankton. Browsers and Grazers biomass decrease to a value close to zero in few years (Figure 3.35 – e). Invertebrate predators are the class of organism that shows the highest biomass variation together with the Filter feeders(Figure 3.35 – f). Roach and Bream die after two years while the effect of the pollutant on Gudgeon and Bleak is similar to the scenario of C= 610 µg/L(Figure 3.35 – g,h).

Perch biomass reaches slowly a value close to zero in six years while Dace biomass trend stabilizes at value lower than the control one (Figure 3.35 – i).

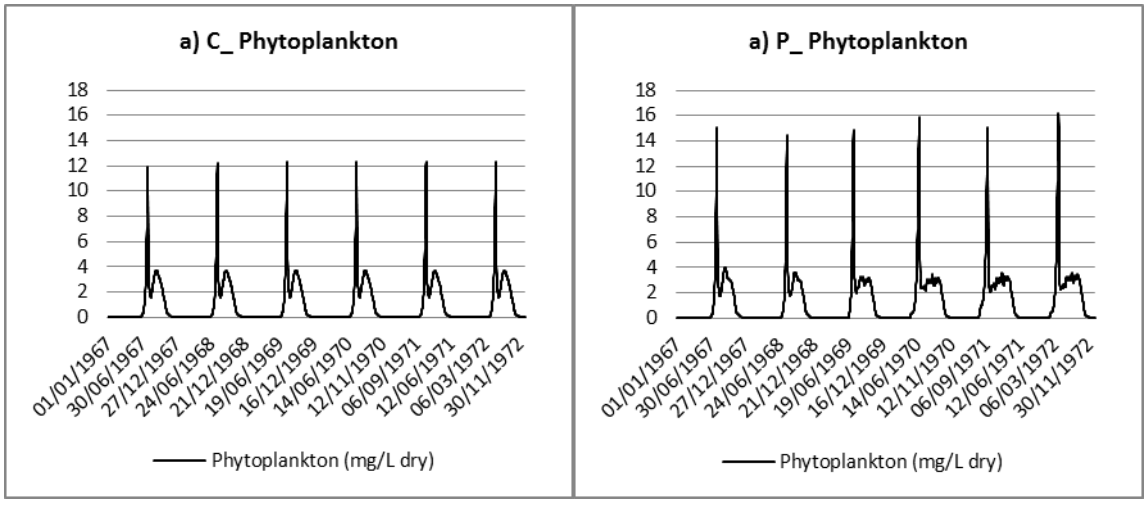


Figure 3.35- part 1 *Biomass trends of the ecosystem organisms subjected to a concentration of LAS of 1024 µg/L for a period of simulation of six years . C means "control simulation" while P means "perturbed simulation".a) Phytoplankton*

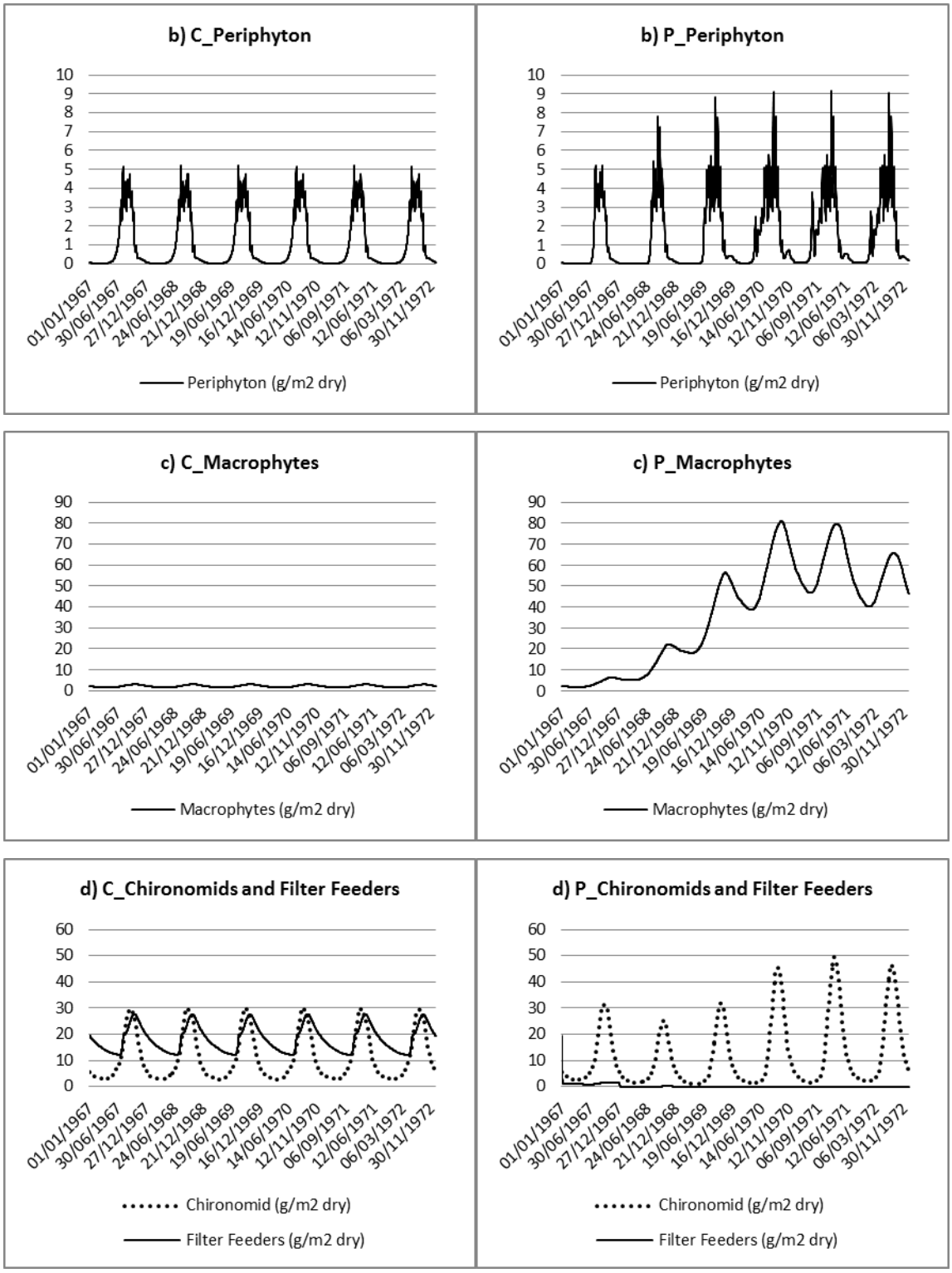


Figure 3.35- part 2 *Biomass trends of the ecosystem organisms subjected to a concentration of LAS of 1024 µg/L for a period of simulation of six years . C means "control simulation" while P means "perturbed simulation". b)Periphyton, c) Macrophytes, d) Chironomids and Filter feeders*

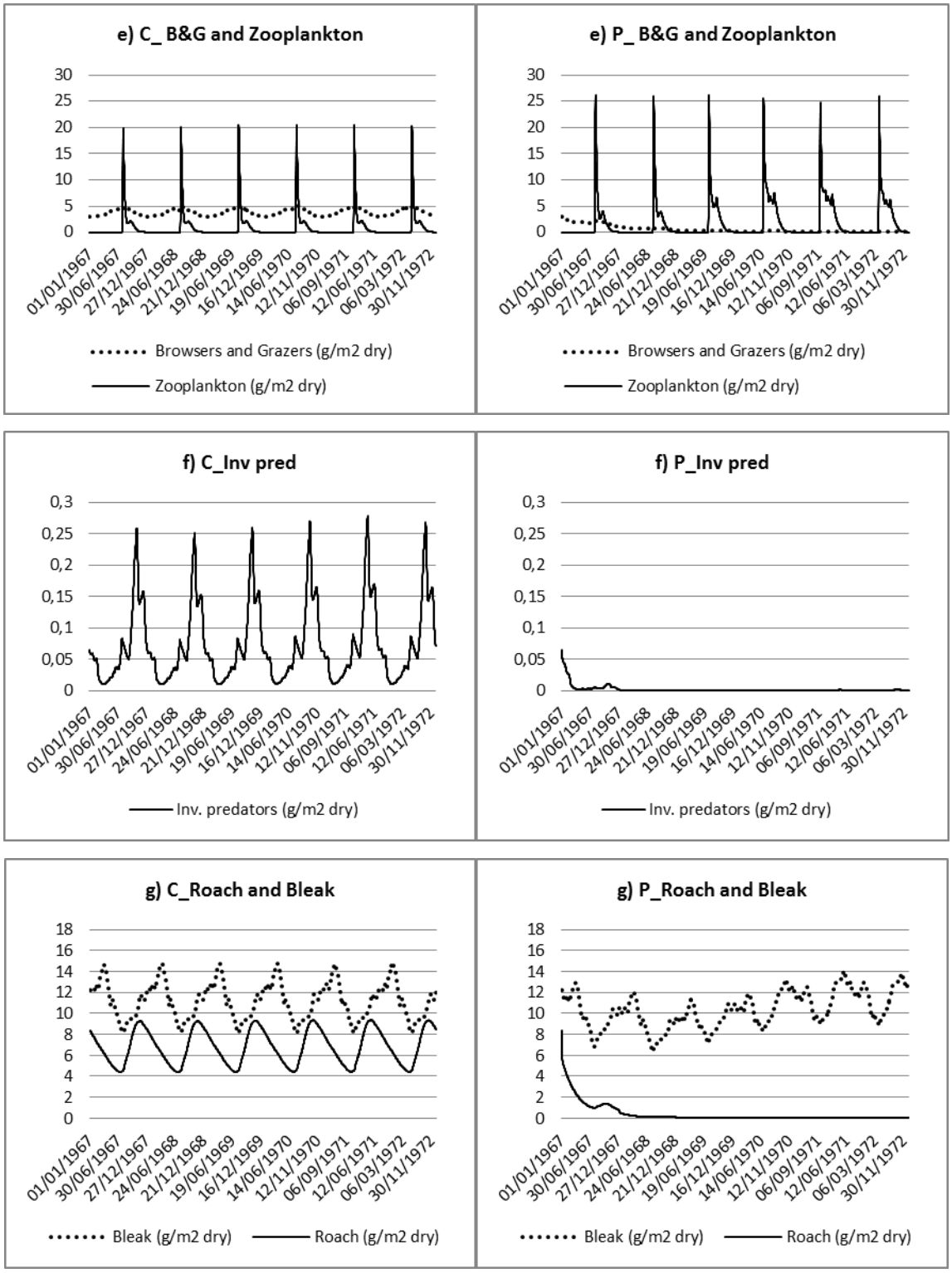


Figure 3.35- part 3 *Biomass trends of the ecosystem organisms subjected to a concentration of LAS of 1024 µg/L for a period of simulation of six years . C means "control simulation" while P means "perturbed simulation". e)Browsers and Grazers f) Inv. Predators, g)Roach and Bleak*

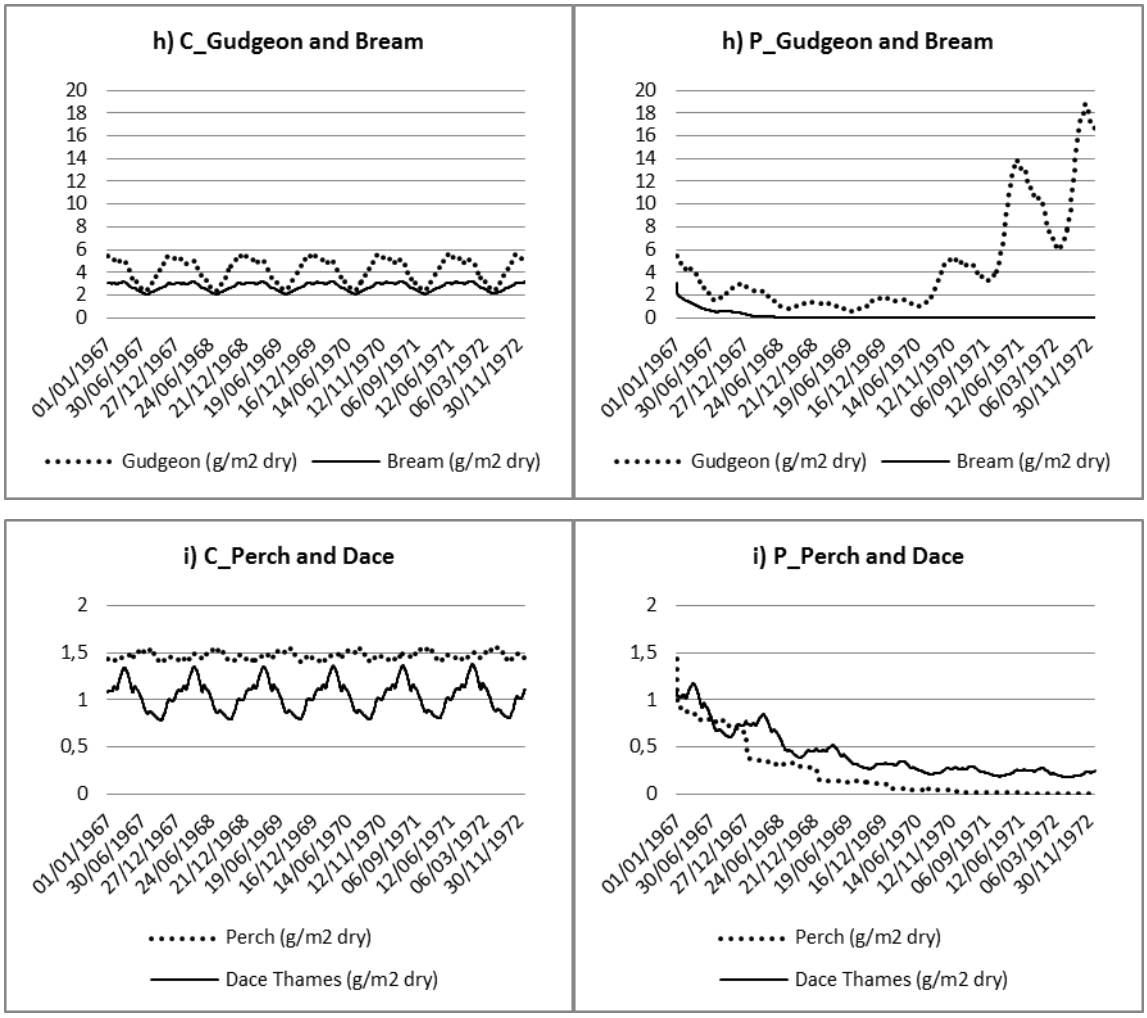


Figure 3.35- part 4 *Biomass trends of the ecosystem organisms subjected to a concentration of LAS of 1024 µg/L for a period of simulation of six years . C means "control simulation" while P means "perturbed simulation".h) Gudgeon and Bream i) Perch and Dace*

TCS perturbed scenario C= 1,6 µg/L 3- 6 years

Phytoplankton biomass disappears in the first three years of simulation but it shows small peaks in the bloom season for the last three years that reach a maximum value of about 4 [mg/L dry]. This is four time lower than the biomass of the bloom in control ecosystem (Figure 3.36 – a). Periphyton has similar behavior (Figure 3.36 – b).

Macrophytes biomass has an exponential increase until the fifth year where it has the maximum peak and starts to decrease (Figure 3.36 – c).

Filter feeders biomass decreases until a value close to 10 [g/m^2 dry] at the end of spring in the second year of simulation. From the second to the fifth years the trend remains stable in this new equilibrium reached in the perturbed simulation whereas the biomass starts to increase

again (Figure 3.35 – d). Zooplankton, as for LAS, demonstrates its close link with phytoplankton. It has a biomass value close to zero for the entire period of simulation. Browsers and grazers have a low decrease in biomass (Figure 3.35 – e).

Invertebrates predators biomass becomes close to zero after three years of simulation (Figure 3.35 – f). Bleak biomass decreases at the beginning and then it stabilizes after three years while Roach behavior shows a decrease in biomass for four years and then in the last two years a zone of exponential increase (Figure 3.35 – g).

Bream and Gudgeon biomasses decrease in the same way from the first till the sixth years (Figure 3.35 – h). The same fate occurs to Dace and Perch (Figure 3.35 – i).

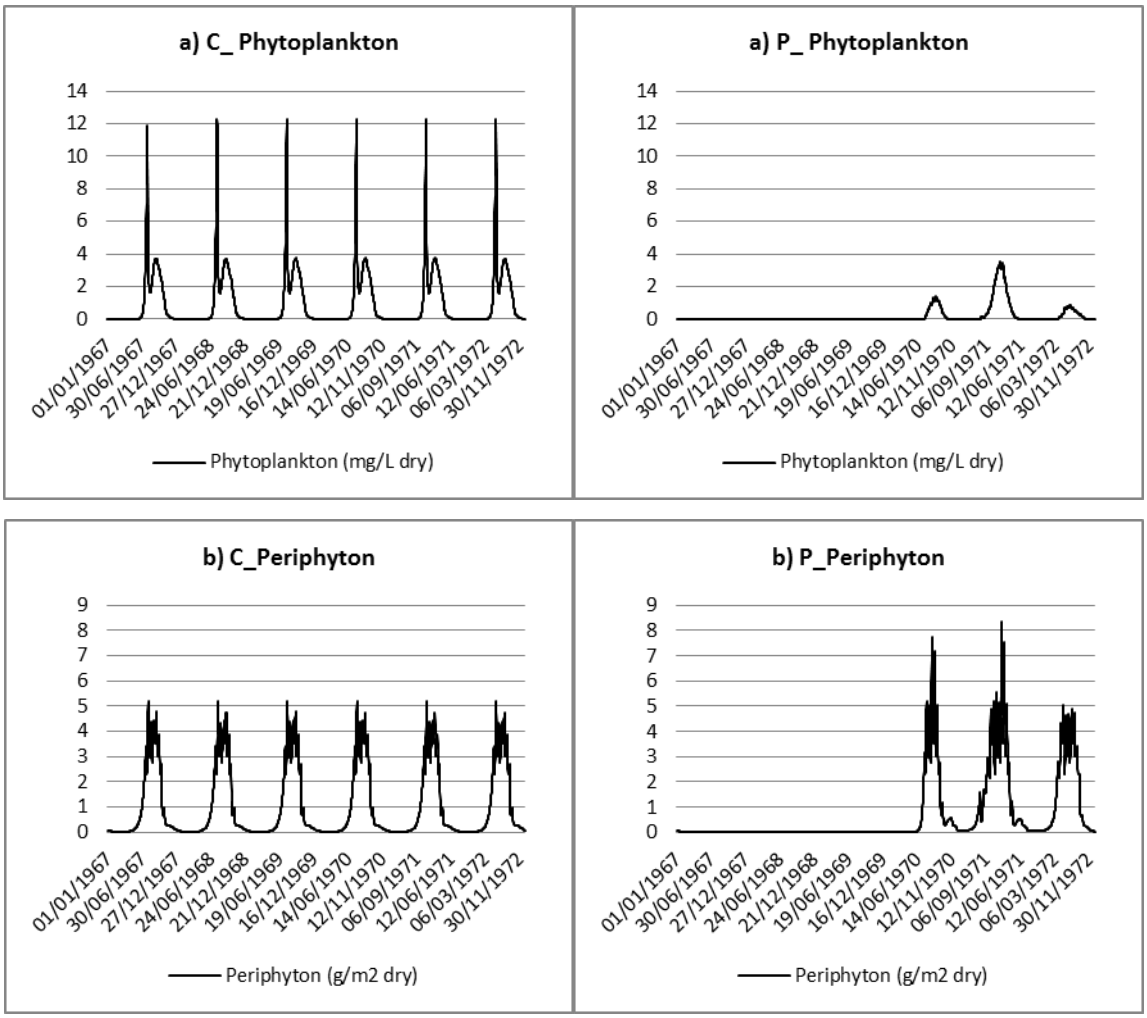


Figure 3.36- part 1 *Biomass trends of the ecosystem organisms subjected to a concentration of TCS of 1,6 µg/L for a period of simulation of six years . C means "control simulation" while P means "perturbed simulation". a) Phytoplankton, b) Periphyton*

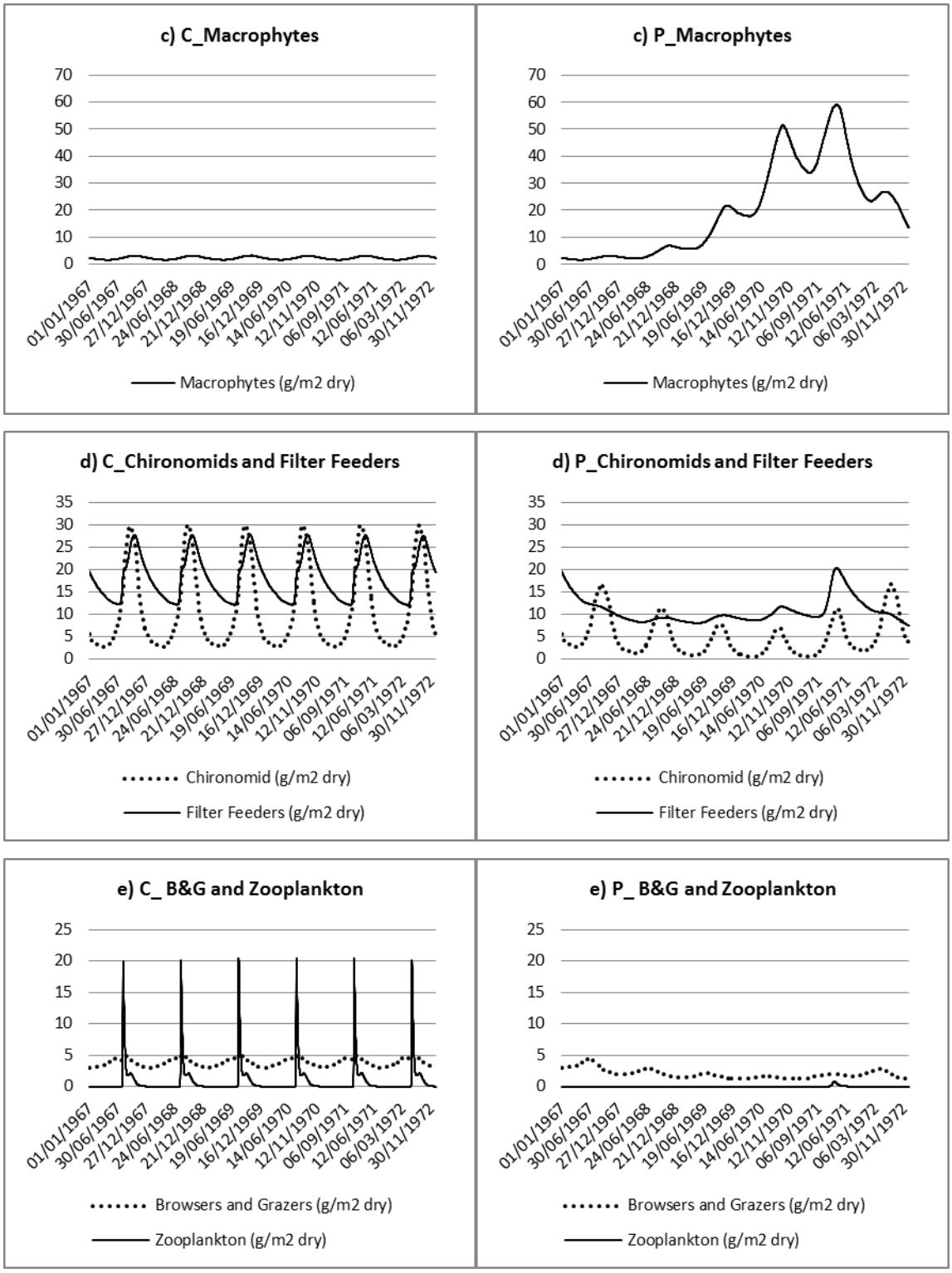


Figure 3.36- part 2 *Biomass trends of the ecosystem organisms subjected to a concentration of TCS of 1,6 µg/L for a period of simulation of six years . C means "control simulation" while P means "perturbed simulation". c) Macrophytes, d)Chironomids and Filter Feeders, e) Browsers and Grazers and Zooplankton*

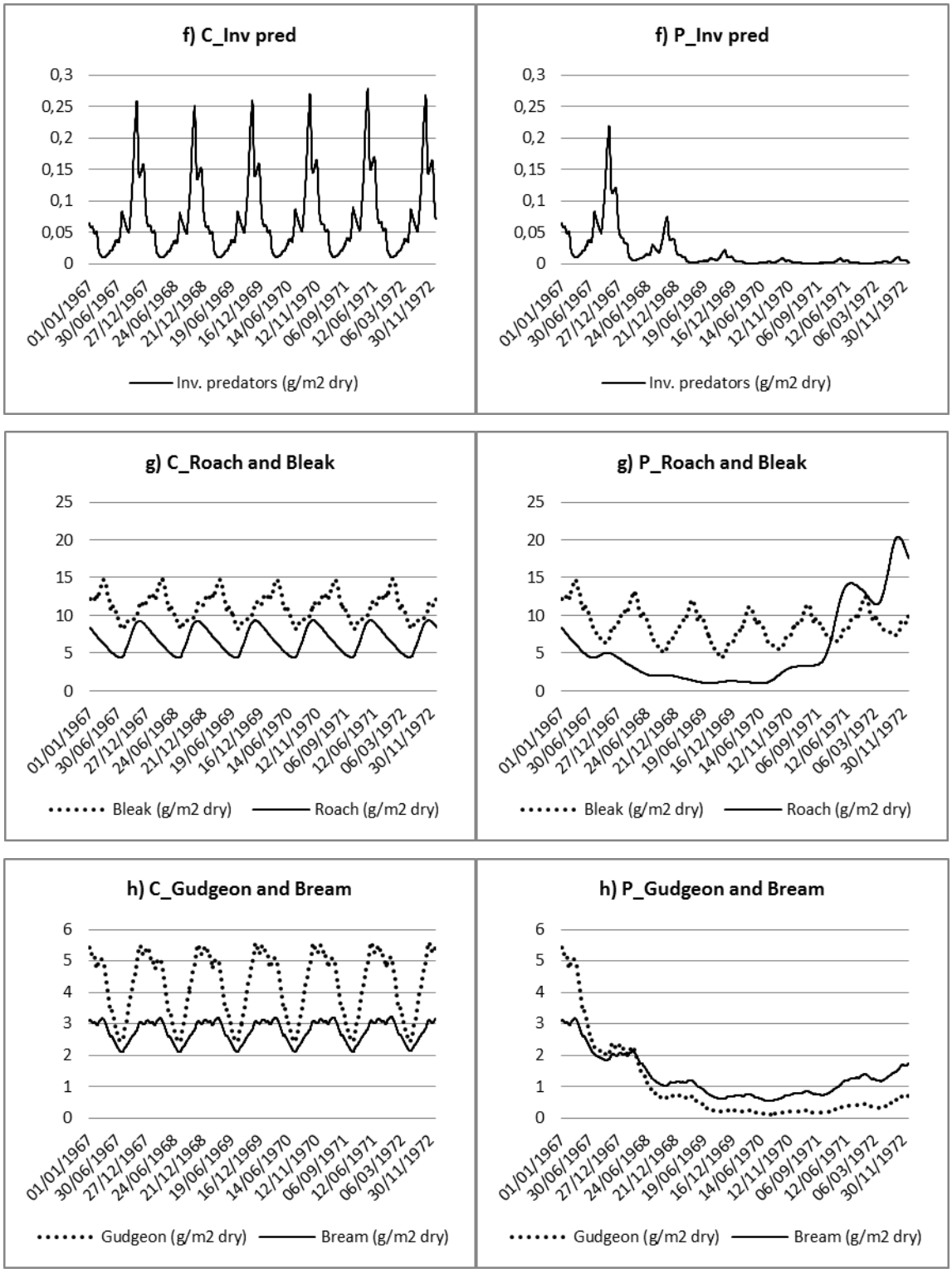


Figure 3.36- part 3 *Biomass trends of the ecosystem organisms subjected to a concentration of TCS of 1,6 µg/L for a period of simulation of six years . C means "control simulation" while P means "perturbed simulation". f)Inv. Predators, g) Roach and Bleak, h) Gudgeon and Bream,*

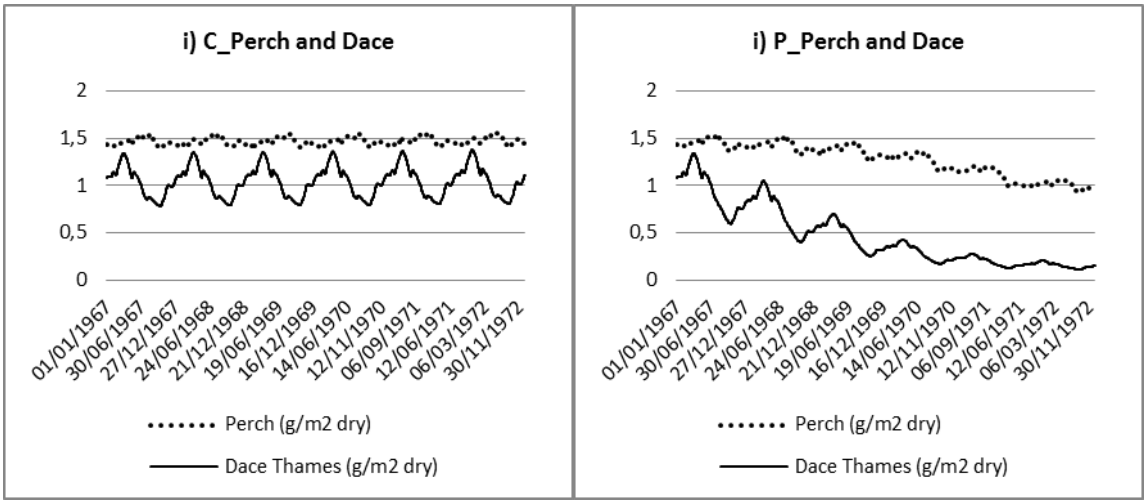


Figure 3.36- part 4 *Biomass trends of the ecosystem organisms subjected to a concentration of TCS of 1,6 µg/L for a period of simulation of six years . C means "control simulation" while P means "perturbed simulation". i) Perch and Dace*

TCS perturbed scenario C= 16 µg/L 3- 6 years

Phytoplankton disappears since the first years differently from the scenario of TCS concentration C= 1,6 µg/L has not any peak in the further years (Figure 3.37 – a). The same fate occurs to Periphyton (Figure 3.35 – b).

Macrophites have and higher increase than the scenario of concentration equal to C= 1,6 µg/L. This increase still express an exponential behavior from the first year until the fourth year (Figure 3.35 – c). Zooplankton biomass remains close to zero for the entire period of simulation (Figure 3.35 – d)

The other aquatic invertebrates behaviors remain the same of the scenario having a TCS concentration in water of 1,6 µg/L (Figure 3.35 – d, e, f).

Bleak biomass decreases and stabilize and reach a new equilibrium trend at lower values of biomass.

Roach shows a decrease in biomass until the fourth year but from the fifth year its biomass rises showing an exponential trend (Figure 3.35 – g).

At the end of the third year Gudgeon and Bream biomasses are close to zero while it takes a longer time for Dace and Bream to disappear (Figure 3.35 – h,i).

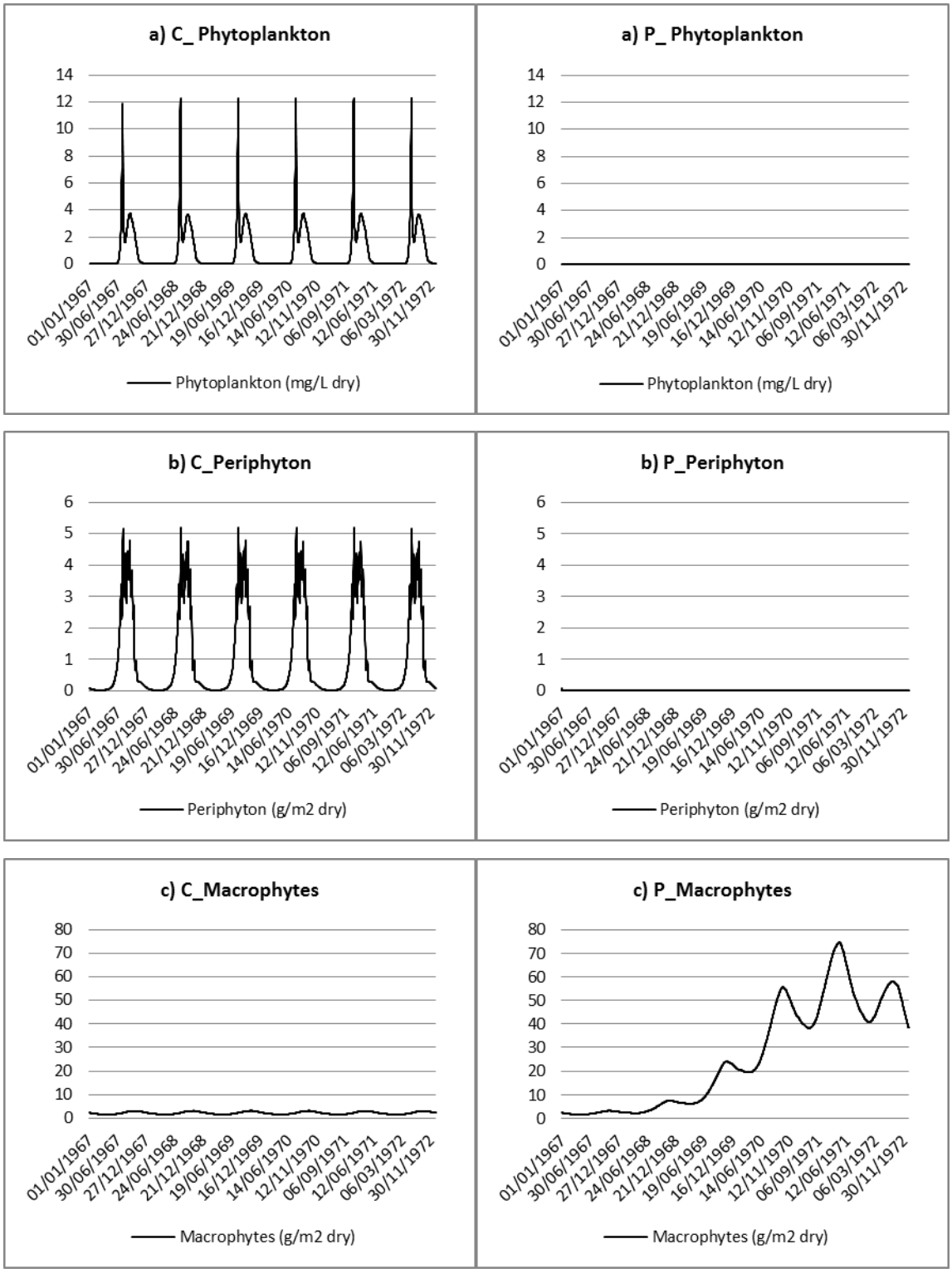


Figure 3.37- part 1 *Biomass trends of the ecosystem organisms subjected to a concentration of TCS of 16 µg/L for a period of simulation of six years . C means "control simulation" while P means "perturbed simulation". a) Phytoplankton, b) Periphyton, c)Macrophytes*

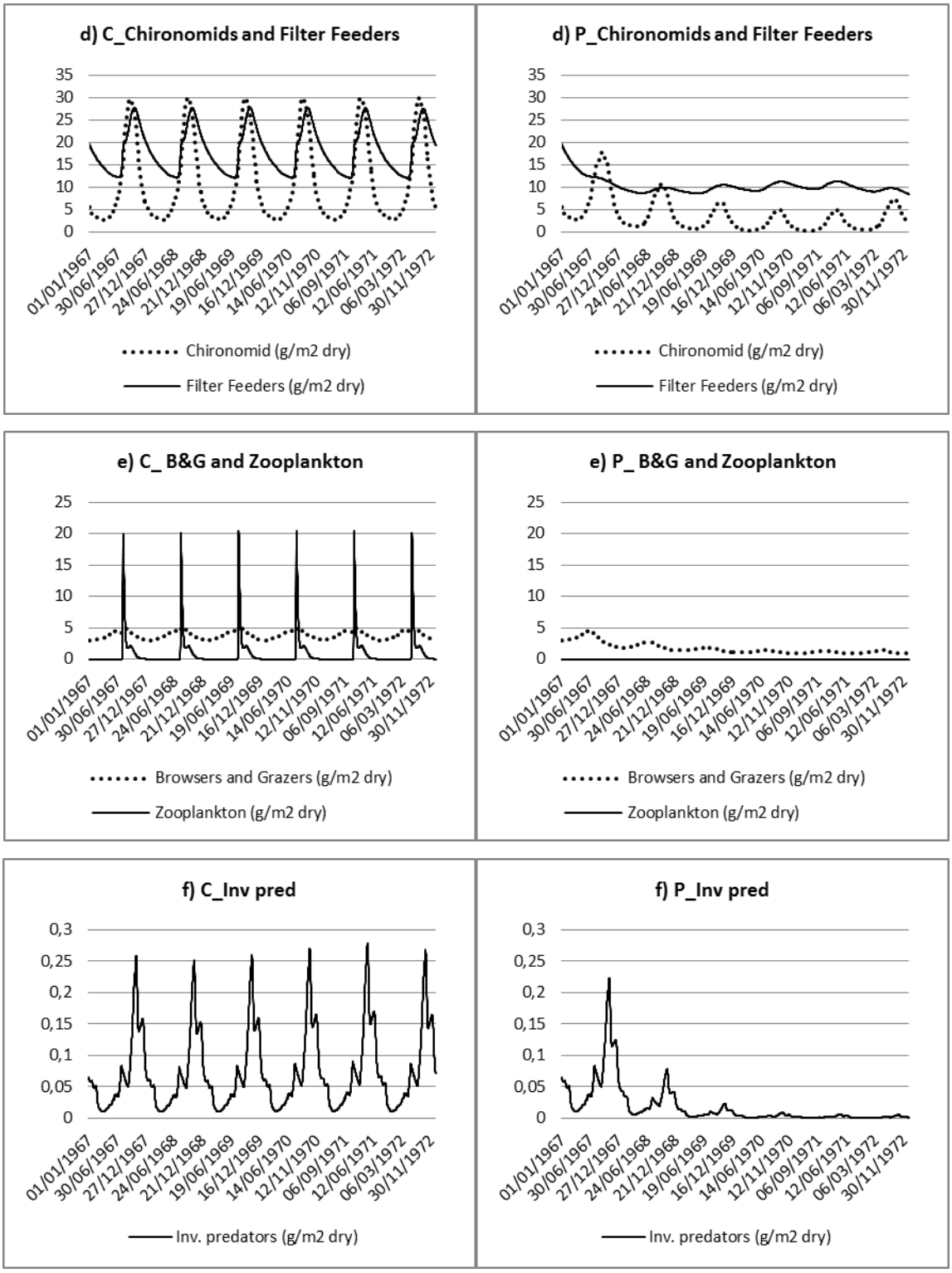


Figure 3.37- part 2 *Biomass trends of the ecosystem organisms subjected to a concentration of TCS of 16 µg/L for a period of simulation of six years . C means "control simulation" while P means "perturbed simulation". d) Chironomids and Filter feeders, e) Browsers and Grazers and Zooplankton, f) Inv.Predators*

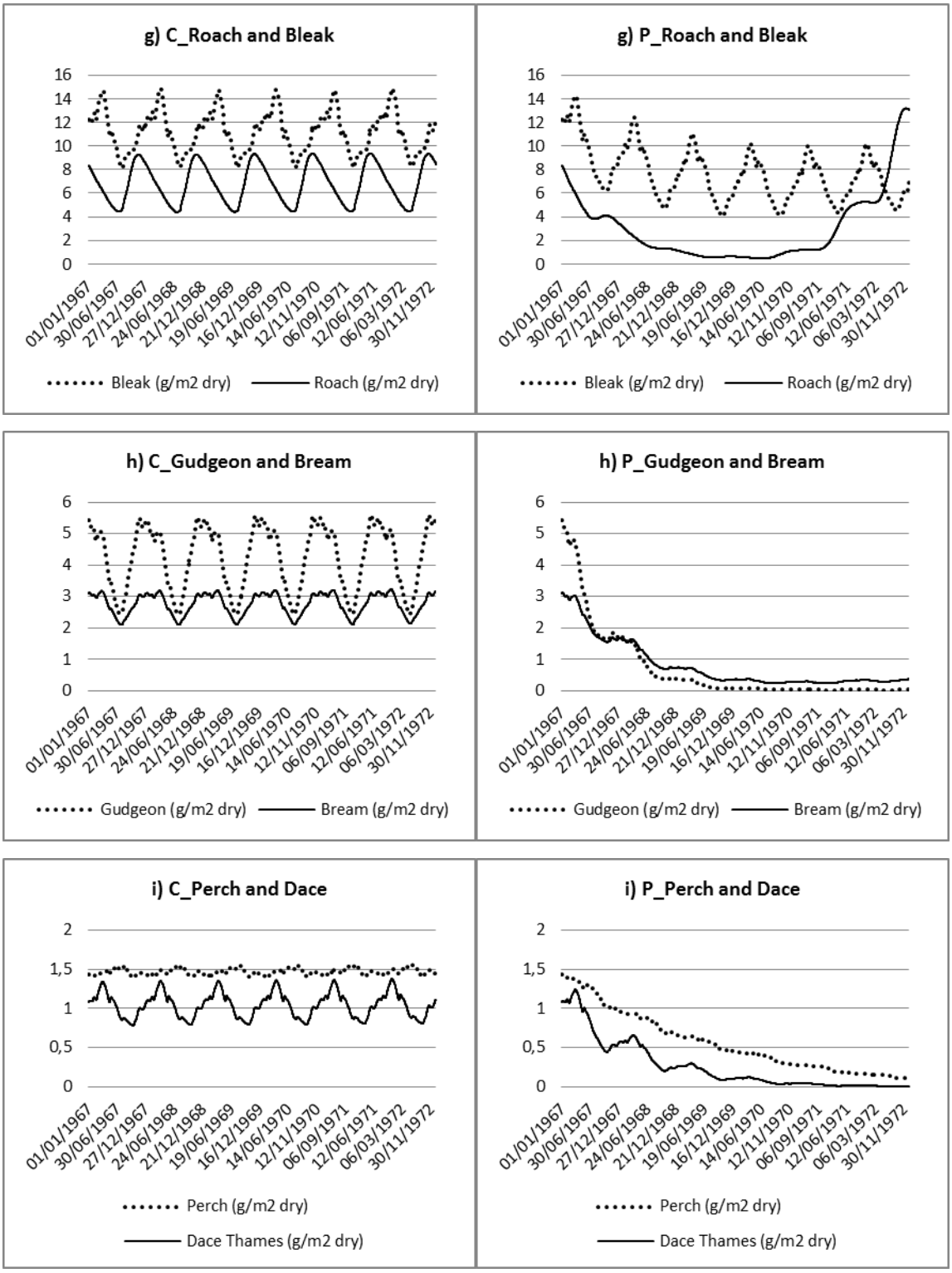


Figure 3.37- part 3 *Biomass trends of the ecosystem organisms subjected to a concentration of TCS of 16 µg/L for a period of simulation of six years . C means "control simulation" while P means "perturbed simulation". f) Invertebrate Predators g) Roach and Bleak, h) Gudgeon and Bream, i) Perch and Dace*

Chapter 4

4. Discussion

The stabilized ecosystem can be considered as a good representation of the actual River Thames between Coversham and Sonning locks although with some uncertainties due to assumptions taken and the lack of data. In this section the model outputs are discussed in relation to observed measurements of other case studies present in available literature.

Phytoplankton has a peak of chlorophyll equal to 240 μg/L between July and August. The trend of chlorophyll has the same shape of the one of phytoplankton (Figure 3.5).

The peak value of chlorophyll simulated by the AQUATOX model is similar to the peak value of chlorophyll of Figure 8 in the paper by Bowes (Bowes et al, 2012). This figure shows the chlorophyll trend in the River Thames at Sonning. There are two chlorophyll peaks of 250 μg/L between April and June. The difference in the peaks period between the chlorophyll trend of the AQUATOX model and Bowes' same trend is probably due to the assumption taken to model the light in AQUATOX. Because a lack of data the default light series of AQUATOX was chosen to simulate the light dynamic which depends mainly on altitude and latitude. Temperature and light are two of the main important forcing functions in biological models. The dynamics of primary producers depend on light and, as a cascade effect, also the dynamics of animals.

The difference in the trend shapes between chlorophyll in the Bowes paper (Bowes et al, 2012) and the one plotted by AQUATOX model of the River Thames could be also due to the different species considered as phytoplankton.

Chlorophyll values in Bowes (Bowes et al, 2012) take into account all the species of phytoplankton present in the river. Different species have biomass blooms in different periods of the year. In the River Thames model of AQUATOX only the *Diatom* species was considered to simplify the ecosystem. A similar trend of *Diatom* was found in the paper of M. Ü. Taner (Taner at al, 2011). In the Taner study AQUATOX is parameterized to model the ecosystem of Onondaga lake, where temperature at epilimnion is similar to the temperature of the Thames.

In Figure 9-c of Taner's paper the *Diatom* trend is shown. The algal bloom occurs in June while in the River Thames AQUATOX model in August (Figure 3.5).

Experimental macrophytes and periphyton trends were found for the Upper Kennet river, a tributary of the Thames.

Results of the articles by Flynn (Flynn et al, 2002) show the Macrophytes cover of the stream channel (surface area occupied by each specie (Flynn et al, 2002)) increases from annual lows during winter to maximum in late summer (August-September). The Macropytes cover exhibits very similar trends to the Macrophytes biomass [g/m2 dry] (Flynn et al, 2002).

In Figure 3 of Flynn the trends of the macrophytes cover percentage for a year are shown and some of them are similar to the biomass trend of the macrophytes in the River Thames study in AQUATOX (Figure 3.6). Both trends are characterized by the start of the growing season in April. Some Macrophytes have cover peaks (i.e. biomass) until November (Figure 3 – d (Flynn et al, 2002). This peaks period is similar to the AQUATOX simulation (Figure 3.6).

In Figure 4 – a of Flynn's paper (Flynn et al, 2002) Periphyton biomass [g/m2 dry] for the Kennet river between October 1998 and August 2000 is shown. In 1999 the growing season started in June (even if there were some isolated peaks in May) and continued until the maximum value of biomass between September and October and decreased in the winter season. Peaks of Periphyton biomass occurs in the AQUATOX River Thames model from July to October (Figure 3.6).

Zooplankton behavior modelled by AQUATOX for the River Thames has its peaks in August (Figure 3.7). It is represented by *Rotifers.* Orcutt shows in their paper the seasonal population dynamics for planktonic rotifers in lake Ogletorpe between December 1978 and December 1979 (Figure 1) (Orcutt & Pace, 1984). Four of the five taxa of *Rotifers* studied by Orcutt exhibit highest population peaks between July and October.

The Chironomid annual biomass trend in Lake Onondaga (Figure 10 – d (Taner at al, 2011)) shows a biomass peak in September, similar to the one of the AQUATOX River Thames model (Figure 3.7).

Data on biomass trends of aquatic worms (Oligocheta) living in an alkaline bog stream in Wisconsin (USA) have been found (Smith, 1986). These can be analyzed to evaluate biomass trends of invertebrate predators in the River Thames model.

Four aquatic worms of the five species studied by Smith (Smith, 1986) present the main peaks between September and November (Figure 3 (Smith, 1986)).

Invertebrate predator category in the River Thames model has its main peak in October (Figure 3.8).

4.1. LAS perturbation

River Thames ecosystem results to be resistant to LAS pollution at the actual concentration, at least for six years. Biomass variation of organisms does not exceed 1% as regards the perturbed scenario of LAS concentration in water of 40 μg/L. River flood over a year could cause higher variation to the river ecosystem. A river flood can provoke an increase in the washout of many organisms and can cause the death of animals and plants (e.g. the increase in detritus concentration could decrease the primary production or the phenomena of macrophytes breakage can increase in importance in the plant mass balance).
Perturbed scenarios with higher concentrations (C= 610 μg/L, C= 1024 μg/L) change drastically the ecosystem. The organisms subjected to a higher impact are animals while plants are not sensible to LAS at these concentrations even if their biomasses change because of their relationship with the ecosystem groups.
Only the results of one-year simulation are discussed because of the uncertain results of the three-year and six-year simulations due to macrophytes behavior (§ Paragraph 3.2).

4.1.1. Perturbed scenario LAS C= 610 μg/L

Phytoplankton behavior mainly depends on the effect of the pollutant on the Filter Feeders category that is one of its two predators. Filter feeder biomass decreases due to the pollutant concentration in water that is equal to its EC_{50} (Figure 3.12 – g). The decrease in Filter Feeders biomass causes an increase in Phytoplankton (Figure 3.12 – a) because the amount of phytoplankton predated decrease.
The increase in defecation (together with the decrease in consumption) is one of the main causes responsible for animals' biomass variation (more detailed information are shown in Appendix C). They are the main components in the animals' mass balance, that means that the effect of increase in defecation due to toxicant could be one of the main causes of biomass decrease for the fauna. Normally consumption and defecation have similar trends because they both depend from ingestion. If the alimentary regime of the animal does not change a

decrease in ingestion due to a decrease in a food source should cause an equal decrease in defecation (Equation 97 AQUATOX Technical report 3.1 (Park & Clough, 2012)).

Sometimes this two parameters behave in a different manner. If there are a decrease in consumption (or if it does not change) and an increase in defecation two possible situations could happen. In the first case the animal starts to feed with a more accessible source of food which has anyway an higher egestion rate thus generating an increase in defecation whereas in the second case the increase in defecation is due to an effect of the pollutant on the animal metabolism. The increase of defecation due to toxicant is modelled by AQUATOX using the equation 379 of the AQUATOX Technical report 3.1 (Park & Clough, 2012). This aspect is the main cause of Inv. Predator biomass decrease as well as the decrease in Filter feeders biomass, one of its source of food (Appendix C).

The phytoplankton biomass increase generates an increase in Zooplankton biomass (which is together with Filter feeders the other phytoplankton predator (3.12 – f)). Zooplankton biomass peaks coincide with the ones of Phytoplankton. Two other organisms which are quite sensible to chemical toxicity are Roach and Bream (EC_{50} = 1010 μg/L), in fact their biomasses decrease (Figure 3.12 m, n). Periphyton biomass has a decrease (Figure 3.12 – b) as shown by the average relative variation that is equal to about 10% (Figure 3.13); this is due to the effect of the pollutant on Periphyton photosynthesis (EC_{50} (910 μg/L)). A decrease in Periphyton (Figure 3.12 – b) and labile detritus (Figure 3.16) cause a change in Browsers and Grazers food preference moving to sediment refractory detritus that is more abundant because Bream and Roach biomasses (their main competitors for refractory detritus) are decreasing (Figure 3.12 – m,n) . Browsers and Grazers' egestion factor for the refractory detritus is higher than the one for Periphyton and labile detritus. For this reason B&G defecation increases and decreases the assimilated amount of food used for the animal metabolism (mechanism described in Appendix C). The decrease in B&G biomass accelerates the drop of invertebrate predators' biomass. The decrease of Roach and Bream biomass causes a growth of Macrophytes biomass because there is a reduction in the one of its main predators (Figure 3.12 – c). Furthermore macrophytes are resistant to pollutant. Chironomid biomass remains mainly the same (Figure 3.12 – d). Like Macrophytes, Chironomids are resistant to pollutant at this simulated concentration (EC_{50} = 8000 μg/L) and they feed on detritus. Detritus fractions, except for labile sediment detritus, do not show significant mass changes in LAS pollution scenario (Figure 3.16). Suspended detritus is an input from upstream; the detritus

that changes in more proportion is the labile sediment fraction that is highly dependent on ecosystem biomass dynamics and does not have an input from upstream.

Dace and Bleak are the fish having the lowest decrease in biomass (Figure 3.12 – i,j) because they depend mainly on adult chironomids and external insects that do not suffer from the toxicant contamination. Their biomass drop depends on the increase in defecation. This could be due to a change in the food preference to the detritus fraction that now is more abundant because of the decrease of some animal biomass (e.g. Filter Feeders) or to the effect of toxicant to the organism (Appendix C).

Perch biomass drops because of direct toxicity (Figure 3.12 – k) .

Gudgeon presence decreases (Figure 3.12 – l) because of an increase in egestion rate due to the changes in the food source (The decrease of periphyton availability could move the diet to detritus) or to the toxicant effects (refers to Appendix C).

4.1.2. Perturbed scenario LAS C= 1024 μg/L

The ecosystem behaves mainly in the same way as the perturbed scenario having LAS concentration in water equal to 610 μg/L . The main difference between the two scenarios is that the effects of the pollutant are amplified. Filter feeders, Roach and Bream biomasses reach values lower than 1 [g/m^2 dry] at the end of the year (Figure 3.12 – g,m,n). The concentration of LAS in water is close to their LC_{50} (F.F. LC_{50}= 1024 μg/L , R. and Br. LC_{50} =1695 μg/L). The same observation can be made for Perch (LC_{50} = 1670 μg/L) as shown in the Figure 3.12 - k.

4.1.3. Ecological indicators

Objective perturbation of the system increases with the increase of LAS concentration in water (Figure 3.17). Biomass changes are mainly due to the direct toxicity of the pollutant. Nevertheless some organisms have the same LC_{50} but show highly different objective perturbation (Figure 3.18, Table 3.7). These results can be interpreted as a demonstration of the indirect effects of toxicity due to food web interactions.

The decrease in animal biomass and the growth of the plant biomass cause an increase of the P/R ratio (Figure 3.19). P/R growth is higher in the case of higher simulated concentration of

LAS in water. Theoretically P/R = 1 represents a mature ecosystem (Odum, 1983). At LAS simulation having C= 610 μg/L there is an increase of P/R from 0,9 (control and C= 40 μg/L) to 0,95 (Figure 3.19). This could seem a value that tends to be close to the maturation but the following observation is to be made: this value is calculated only on one year simulation. If the behavior of macrophytes at pollutant concentration of C= 610 μg/L in the long term were realistic (Figure 3.34), the P/R ratio would reach in the sixth year a value of 1,6, which is far away from the maturation.

The same discussion can be done for the perturbed simulation having C= 1024 μg/L. Over a period of one year P/R ratio has already surpassed the maturation value (P/R = 1,05) (Figure 3.19).

The Ecosystem biodiversity measures an increase in the simulation of LAS concentration equal to 610 μg/L. This is the result of the biomass decrease of Filter feeders. They are the organisms with the highest biomass and Shannon index increases when the organisms of the ecosystem tend to have the same biomasses (Figure 3.20).

At the concentration of 1024 μg/L there is a clear decrease in biodiversity due to the high decrease of some species and the increase of others. These two events tend to distance the biomass value of each organism from the average organisms biomass (Figure 3.20).

The ecological perturbation of the system passes from the "no visible perturbation " category in case of the LAS concentration equal to 40 μg/L, to the "moderate- high perturbation" in case of C=1024 μg/L (Table 3.8).

The total biomass of fish catchable in the system decreases with the increase of the pollutant concentration (Figure 3.22). There is a decrease in the ecosystem service provided to human activities (fishing).

A special observation is needed as regards turbidity. An increase in Phytoplankton, Macrophytes and suspended detritus should create an increase in turbidity, i.e. a decrease in Secchi depth. On the contrary there is an increase in Secchi depth in LAS simulations (Figure 3.19).

The hypothesis is that a similar result is due to how the suspended inorganic sediments are modelled in AQUATOX. They are the fraction of suspended material in water with the highest light attenuation coefficient (Table 2.2) so that a change in their concentration could generate changes in water turbidity.

Suspended inorganic sediment mass in the system, when the option to insert the input from upstream of suspended solid is set on TSS (total suspended solids), is calculated using Equation 244 of AQUATOX Technical Report 3.1 (Park & Clough, 2012).
This equation describes the concentration of suspended inorganic sediments as the difference between the TSS (observed concentration of total suspended solids) and the predicted phytoplankton and suspended detritus concentrations in the system.
This way to model the sediment inorganic detritus brings to a decrease of its concentration when both plant biomass and suspended detritus concentration increase because the TSS input from upstream is constant.
This option is useful because it guarantees that the composition of the upstream input of TSS (inorganic suspended sediment, suspended detritus, phytoplankton) takes into consideration the effect of the pollutant also in the section immediately upstream of the volume modelled but in the case of turbidity it can generates some incongruences.

4.2. TCS perturbation

River Thames ecosystem results resistant to Triclosan pollution at the actual concentration (C = 0,05 μg/L). The biomass variations in this simulation are under 1% for every organism of the ecosystem.
With an increase in pollutant concentration (at least 100 times more than the actual concentration) the ecosystem is inevitably compromised and the organisms most affected by direct toxicity are micro-algae (Phytoplankton and Periphyton).
Only the results of one-year simulation are discussed because of the uncertain results of the three-year and six-year simulations due to the macrophytes behavior (§ Paragraph 3.2).

4.2.1. Perturbed scenario TCS C= 1,6 μg/L

Phytoplankton and Periphyton biomass disappear at the very beginning of the year of the simulation when the pollutant is input into the ecosystem (Figure 3.23 – a,b) . The causes of this result are the direct toxicity of TCS for micro-algae. Their EC_{50} is equal to the pollutant concentration in water C= 1,6 μg/L.

The phytoplankton extinction causes the disappearance of Zooplankton (Figure 3.23 – f) and a reduction of the Filter Feeders biomass (Figure 3.23 – g). Zooplankton biomass peak in July depends on the phytoplankton bloom. The decrease of Filter feeders biomass is due to the drop of consumption rate and the increase in defecation rate. Their diet might have moved to a preference in suspended particulate detritus (mechanism explained in Appendix C).

Browsers and Grazers ingestion decreases because of the effect of the pollutant on the Periphyton (Figure 3.23 – e).

The disappearance of algae and some invertebrates causes a decrease in detritus formation of the ecosystem, except for refractory suspended detritus that depends mainly on input from upstream (Figure 3.27). The fractions of organism mortality and egestion that contribute to the detritus in the ecosystem are shown in Table 11 of AQUATOX Technical report 3.1. Furthermore detritus fractions are modelled in AQUATOX to be continuously linked one each other (Figure 3.5).

The increase in refractory suspended detritus concentration and the decrease of the other food sources generate a change in animal diets. Most animals show a decrease in consumption and at the same time an increase in defecation. This could happen if alimentary behaviors are changed moving into food sources with higher egestion factors (refractory detritus) or there are some toxicant effects (refer to Appendix C).

Aquatic invertebrates have EC_{50} relatively higher than the TCS concentration in water (like 100 times more than 1,6 μg/L). That means that the increase in egestion is due mainly to a change in food source. This is the case of Chironomids: their biomass decreases in perturbed simulation (Figure 3.23 – d) because of an increase in defecation even if consumption remains similar to the one of control ecosystem (refer to Appendix C).

Fish show a decrease in biomass in the second part of the year (Figure 3.23 – i,j,k,l,m,n) due to an increase in defecation for the toxicant effect (their EC_{50} is only 10 times higher than the pollutant concentration in water) and alimentary regime changes (refer to Appendix C).

In Appendix C is described the case of Roach: Zooplankton and Periphyton cover about 28% of its diet and they disappear but there is not a decrease in consumption. This means that Roach has found another source of food but at the same time there is an increase in defecation meaning that it has changed its diet in favor of a new food source with a higher egestion rate.

Invertebrate predators show a similar decrease in consumption and egestion and a consequent decrease in biomass (Figure 3.23 - h). The meaning of this is that there is a decrease in their sources of food (Filter Feeders, Browsers and Grazers and Chironomid biomass decrease)

without any choice to change its diet into something more abundant in the ecosystem because they feed only on these three groups of invertebrates.
Macrophytes are resistant to TCS pollution, their biomass remain close to the one of the control ecosystem (Figure 3.23 – c).

4.2.2. Perturbed scenario TCS C= 16 μg/L

The results of this scenario are very similar to the one of TCS C= 1,6 μg/L. There is only an amplification of the effect. In this case the increase in the input concentration from 1,6 μg/L to 16 μg/L shows fewer changes in the ecosystem than the increase for LAS from 610 μg/L to 1024 μg/L. As a matter of fact this concentration is still lower than the LC_{50} for the animals and because plants' existence was already compromised in the previous simulation.
The only animal that present a high change is Perch (Figure 3.23 – k). It shows a high decrease in biomass considering the low decrease in its biomass as a result in the simulation with TCS concentration in water equal to 1,6 μg/L.

4.2.3. Ecological indicators

The TCS input in the ecosystem causes a visible objective perturbation when the TCS concentration in water is equal to 1,6 μg/L (Figure 3.28). The scenario having the highest TCS concentration simulated (16 μg/L) has a similar objective variation to the one with C = 1,6 μg/L.
In this case the importance of food web in studying the effect of pollutants in the ecosystem is clear (Figure 3.29).
Zooplankton is the most resistant organism for TCS (It has the highest LC_{50} = 1544 μg/L). A laboratory test could have as a result that TCS at this concentration would not have any threat for its survival. The ecosystem model of River Thames in AQUATOX demonstrates that it would disappear easily due to the effect of the pollutant on its main source of food (Phytoplankton) (Table 3.9).
The P/R ratio decreases drastically in the second and third scenarios (respectively C= 1,6 μg/L and C= 16 μg/L) because the micro-algae decrease to a value close to zero. GPP (i.e. the

fraction numerator) assume a value close to zero as well as consequently the ratio P/R (Figure 3.30).

The biodiversity of the system decreases because the micro-algae and zooplankton tend to move away from the average organism biomass of the system. Shannon index tends to decrease (Figure 3.31).

The ecological perturbation of the system increases with the increase of the TCS concentration in water (Table 3.10).

Fish total biomass drops with the increase of pollutant concentration in water (Figure 3.33) . TCS deteriorates the ecosystem service the system offers to humans.

The behavior of turbidity seems to confirm the hypothesis supposed for LAS (§ Paragraph 4.1.3).

In this case the micro-algae and the most fractions of detritus decrease (Figure 3.32). The result expected for turbidity is a decrease, i.e. an increase in Secchi depth. The plotted results of AQUATOX show instead a decrease in Secchi depth.

4.3. Future developments and AQUATOX criticism

From the beginning of this work it has been clear that there was a lack of data on river ecosystem dynamics and the relative organisms composing the riverine ecosystem.

There is the need for some investments in the collection of data on species biological parameters and the physic characteristics of the most important rivers in Europe, taking also into account the increasing importance of ecological modelling in ecological risk assessment.

Moreover the European Community should take the responsibility to create a database with these data that should be accessible for the entire Science Community. This improvement would create a more efficient system decreasing the time invested by researchers to find out the data and the model would improve their accuracy.

The model here proposed uses data from different sites and periods and many assumptions have been taken to overcome the high scarcity of data.

The model could be improved as follows:

- creating a multi-segments linked simulation taking into consideration also the presence of the Kennet river, a River Thames tributary;

- more detailed data on the organisms' biological parameters and ecotoxicity tests are needed for the organisms actually present in the ecosystem;
- studies on macrophytes should be carried out to evaluate if the long term results of this research (3 – 6 years) regarding the LAS and TCS pollution could be a good representation of the reality. Long term models could show a wider picture of the scenario underlying also some aspects that are not visible in a one-year simulation.

AQUATOX demonstrated to be a useful instrument for the ecological and ecotoxicological food web modelling. An improvement that should be added in the new version is the possibility to model external organisms dynamically as a source of food while, in the last version (version 3.1), the external organisms considered are only aquatic dependent vertebrates.

In this study two of the main sources of food for some fish come from outside the system (External insects and Adult chironomids).

The best way found to insert this animals in the ecosystem has been to create fictitious animals having all biological parameters equal to zero. Their survival depends only on the input from upstream. The input concentration is set as a constant value but the input biomass changes during the year depending on the water flow. This choice has guaranteed the maintenance of the original trophic web but the biomass trends of those animals that feed on adult chironomids and external insects (the major part of the fish) are strongly influenced by this assumption. They show peaks of biomass in positions similar to flow peaks (Figure 2.3, Figure 3.10 and Figure 3.11).

Macrophyte biomass trend, in the study, has always been the most difficult to be balanced. A review on Macrophyte mass balance parameters could be done to evaluate if the equations used create instability in the organism biomass with exponential behaviors such as biomass growth or biomass drop periods (Figure 3.34 - c, Figure 3.35 - c, Figures 3.36 – c and Figure 3.37 - c)

Chapter 5

5. Conclusion

The River Thames food web model demonstrates the importance of the development of ecosystem models that ought to be used in risk assessment.

The evaluation of the risk assessment based only on a ratio between two concentration (PEC /PNEC) cannot describe the enormous complex relationships that occur between organisms in an ecosystem. The results of this work show that the biomass variations of the ecosystem groups due to the presence of toxicants in the system cannot be attributed only to singular toxicity effects (expressed using acute toxicity parameters: EC_{50}, LC_{50} values). Many organisms express similar biomass variations having highly different LC_{50}. Furthermore, some organisms biomasses increase with the presence of pollutants (for example Zooplankton and Macrophytes groups in LAS perturbations). Indirect ecological interactions clearly play a role here. The main direct effect of the pollutants on animals is the deterioration of the fragile equilibrium between some biological functions of the fauna (e.g. Ingestion - Egestion variation) while for plants the decrease in the photosynthesis efficiency causes a rapid decrease of the biomasses of these organisms.

The simulations having an input concentration of the pollutant similar to the actual concentration present in the river (LAS C = 40 μg/L, TCS C = 0,05 μg/L) give a positive message. It seems that the actual concentration of the pollutants does not pose a high risk for the ecosystem. The highest biomass variation remains under 1% of the controlled one, which is a small value with respect to natural sources of variability in the ecosystem. For instance, the river ecosystem is characterized by large annual changes due to flooding. With the increase of the concentration of pollutants in water the ecosystem perturbation reaches unsustainable levels.

The TCS simulation demonstrates that concentrations in the order of 1 μg/L are enough to extinguish the micro-algae community of the river and, through a cascade process, reduce the biomass of all the animals present in the ecosystem.

The ecosystem is more resistant to LAS. A 10 fold increase in the actual water concentration of LAS in the river ecosystem generates visible changes in the ecosystem like the biomass

decrease of the most sensible organisms (Filter feeders, invertebrate predators and some fishes).

Appendices

Appendix A

Table A.1 *Flow Data*

Date	Flow m3/d
03/01/1967	5875200
10/01/1967	3456000
17/01/1967	3196800
24/01/1967	7344000
31/01/1967	5875200
07/02/1967	2678400
14/02/1967	1987200
21/02/1967	11059200
28/02/1967	10281600
07/03/1967	5875200
14/03/1967	8121600
21/01/1967	3715200
04/04/1967	2419200
11/04/1967	2678400
18/04/1967	1900800
25/04/1967	1555200
02/05/1967	1123200
09/05/1967	1728000
16/05/1967	7344000
23/05/1967	1987200
06/06/1967	2419200
13/06/1967	1728000
20/06/1967	1382400
27/06/1967	1814400
04/07/1967	864000
11/07/1967	1209600
18/07/1967	864000
25/07/1967	1728000
01/08/1967	777600
08/08/1967	1382400
15/08/1967	864000
22/08/1967	1468800
29/08/1967	518400
05/09/1967	1209600
12/09/1967	604800
19/09/1967	1382400
26/09/1967	864000
03/10/1967	1728000
10/10/1967	1468800
17/10/1967	4924800
24/10/1967	2678400
31/10/1967	8380800
07/11/1967	9849600
14/11/1967	4320000
21/11/1967	2419200
28/11/1967	2937600
05/12/1967	2764800
12/12/1967	5961600
19/12/1967	9590400

Table A.2 *Temperature Data*

Date	Temperature (°C)
03/01/1967	4,2
10/01/1967	2,5
17/01/1967	5,5
24/01/1967	6,5
31/01/1967	8,5
07/02/1967	7
14/02/1967	5
21/02/1967	6,5
28/02/1967	7,2
07/03/1967	8,2
14/03/1967	6,6
21/01/1967	8,7
04/04/1967	8,5
11/04/1967	8,5
18/04/1967	11,1
25/04/1967	10,2
02/05/1967	11,4
09/05/1967	11,6
16/05/1967	13
23/05/1967	12
30/05/1967	13,2
06/06/1967	16,4
13/06/1967	15,6
20/06/1967	16,5
27/06/1967	15,7
04/07/1967	18
11/07/1967	19,7
18/07/1967	19
25/07/1967	19
01/08/1967	18,5
08/08/1967	17,5
15/08/1967	16,5
22/08/1967	17
29/08/1967	17,5
05/09/1967	16,5
12/09/1967	15
19/09/1967	15
26/09/1967	14,5
03/10/1967	14
10/10/1967	14
17/10/1967	12,5
24/10/1967	11,5
31/10/1967	8,7
07/11/1967	7,5
14/11/1967	9
21/11/1967	6
28/11/1967	6
05/12/1967	7,5
12/12/1967	3,5
19/12/1967	5

Appendix B

Chironomid		
Chironomidae chirinominae	4,500	kcal/g dry
Chironomidae Orthocladinae	4,896	kcal/g dry
Inv. Predators		
Eropbdella octoculata	5,442	kcal/g dry
Eropbdella testacea	5,440	kcal/g dry
Glossiphonia clompanata	5,442	kcal/g dry
Glossiphonia heteroclita	5,443	kcal/g dry
Helobdella Stagnalis	5,442	kcal/g dry
Filter Feeders		
Anodonta cygnea	5,052	kcal/g dry
Anodonta anatina	5,052	kcal/g dry
Unio	5,052	kcal/g dry
Spahaerium Corneum	2,488	kcal/g dry
Sphaerium rivicola	2,488	kcal/g dry
Spongilla	4,000	kcal/g dry
Plumatella	4,000	kcal/g dry
Browsers and Grazers		
Viviparus	3,142	kcal/g dry
Bithynia	3,555	kcal/g dry
Bithynia	3,584	kcal/g dry
Asellus	6,024	kcal/g dry
Tuficidae	7,603	kcal/g dry
Caenis	11,083	kcal/g dry

Appendix C

Some of the charts in this appendix, which are not present in the results, can be useful to the reader to understand some results shown in the discussion chapter.

The effect of toxicants on the consumption and defecation rates in the animals present in the ecosystem

Figure C.1 shows how a toxicant interacts with the consumption-defecation activity of animals.

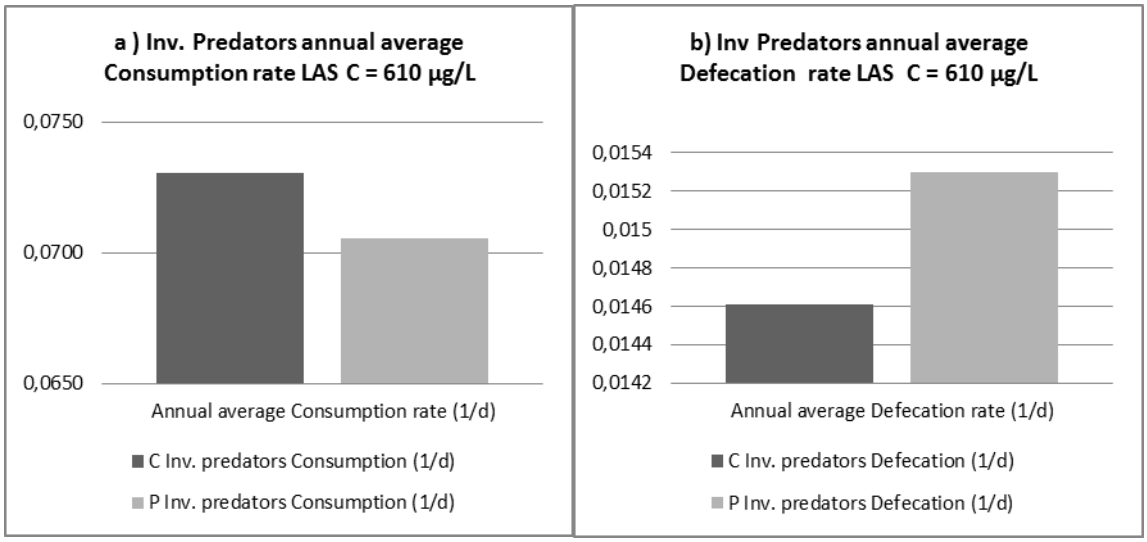


Figure C.1 *The average annual consumption rate (a) and defecation rate (b) for Inv. Predators are shown for perturbed (P) and control simulation (C). The consumption rate decreases in perturbed simulation but the egestion rate increase.*

Effect of pollutants on the photosynthetic rate of plants

Pollutants interact with plants in different manners, increasing the mortality or changing the efficiency of photosynthesis.

Figure C.2 details the effect of LAS on periphyton for the former's concentration in water equal to C = 610 µg/L. In this figure the variation of photosynthetic rate and the variation of the reduction factor of photosyntesys due to toxicant for periphyton are shown. The term "variation" means how the parameter value changes from the control to the perturbed

simulation. This parameter is expressed in percentage. A negative value expresses a decrease of the parameter in the perturbed simulation. On the other hand, a positive value means an increase of the parameter value in the perturbed simulation.

The reduction factor is a parameter that could have values from 0 to 1. It is equal to 1 when there is no effect of toxicants on photosynthesis while there is a decrease when the pollutant concentration increases (equation 37 AQUATOX Technical documentation 3.1 (Park & Clough, 2012)). Figure 3.2 shows clearly the relationship between the two parameters. The LAS presence is the main cause of the periphyton decrease (Figure 3.12 – b).

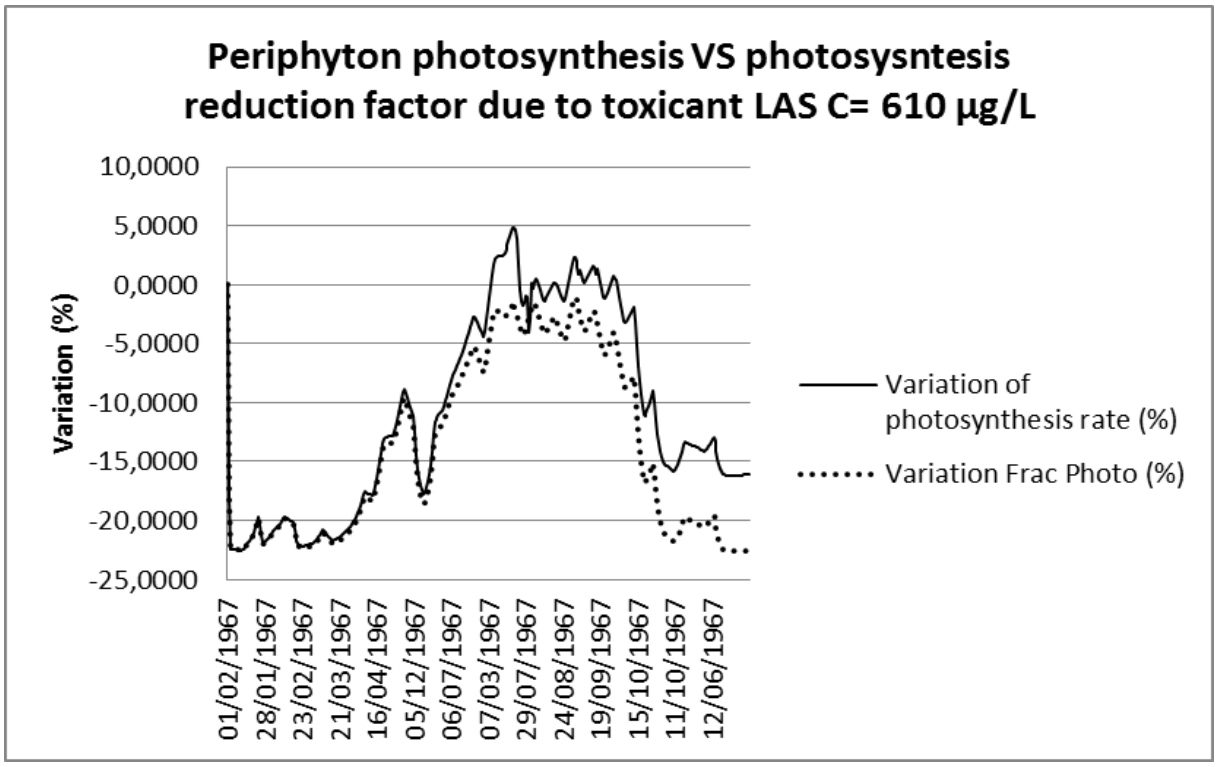


Figure C.2 *The variation of photosynthesis rate and the photosynthesis reduction factor due to toxicant*

The effect of a diet change on the consumption and defecation rates in the animals due to a decrease in the presence of some preys

Figure C.3 illustrates the consequences of a diet change due to a decrease in the availability of some preys. In this chart the behavior of the Roach is shown when there is a TCS concentration equal to 1,6 µg/L.

In this case the consumption rate does not show a high variation between perturbed and control simulation while there is a high increase in the defecation rate.

The assumption that justifies this behavior is that the alimentary regime of Roach, due to the decrease or disappearance of the biomass of some preys, switches to food items having a higher egestion rate (e.g. refractory detritus) because they are easier to be found in these conditions.

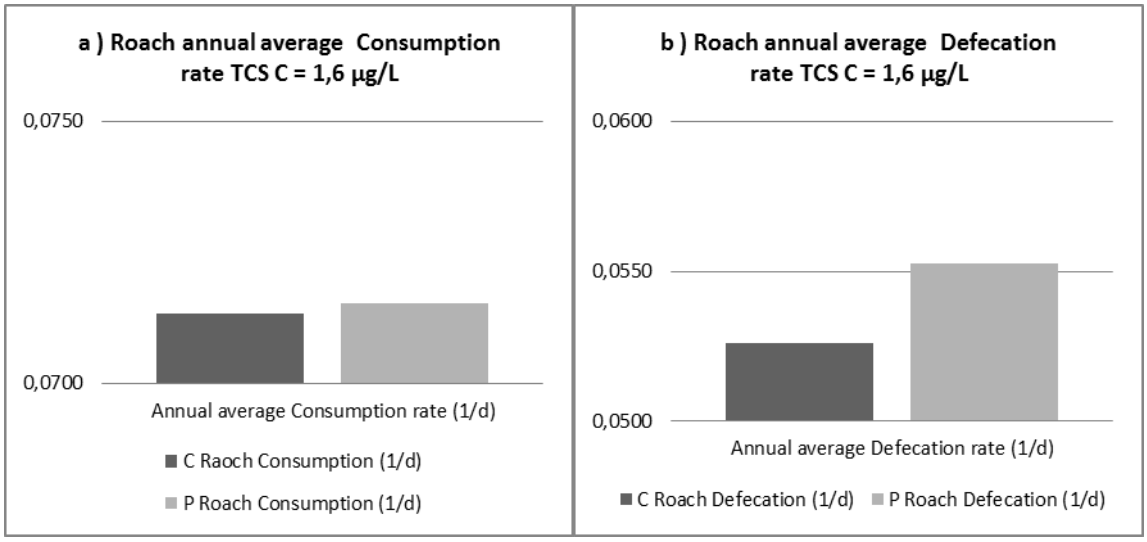


Figure C.3 *The average annual consumption rate (a) and defecation rate (b) for Roach are shown for perturbed (P) and control simulation (C). The consumption rate remains mainly the same in perturbed simulation but the egestion rate increase.*

Effect of the decrease of detritus fractions due to a drop in plant and animal biomasses

The activities of organisms have an influence on detritus formation. The detritus presence in the ecosystem can decrease due to an increase in consumption or can decrease because of the disappearance of some organisms. Mortality, Excretion and Defecation (the latter only for animals) are the three main processes of organisms that influence the detritus formation. The defecated substance forms the sediment detritus while fractions of dead organisms and excreted materials contribute to form suspended and dissolved detritus (AQUATOX Technical Report 3.1 (Park & Clough, 2012)).

The example of the disappearance of micro-algae and some organisms from the ecosystem during the perturbed simulation having a concentration of TCS equal to 1,6 µg/L was chosen.

The peak in decrease in the detrital formation is in July, when micro-algae disappear and generate the extinction of some organisms (e.g. Zooplankton) (Figure C.4). This fact causes a decrease in Suspended labile detritus. The disappearance of animals decreases the sediment

detritus. The effect on sediment detritus is more visible than the one on suspended detritus because it does not have a constant input from upstream.

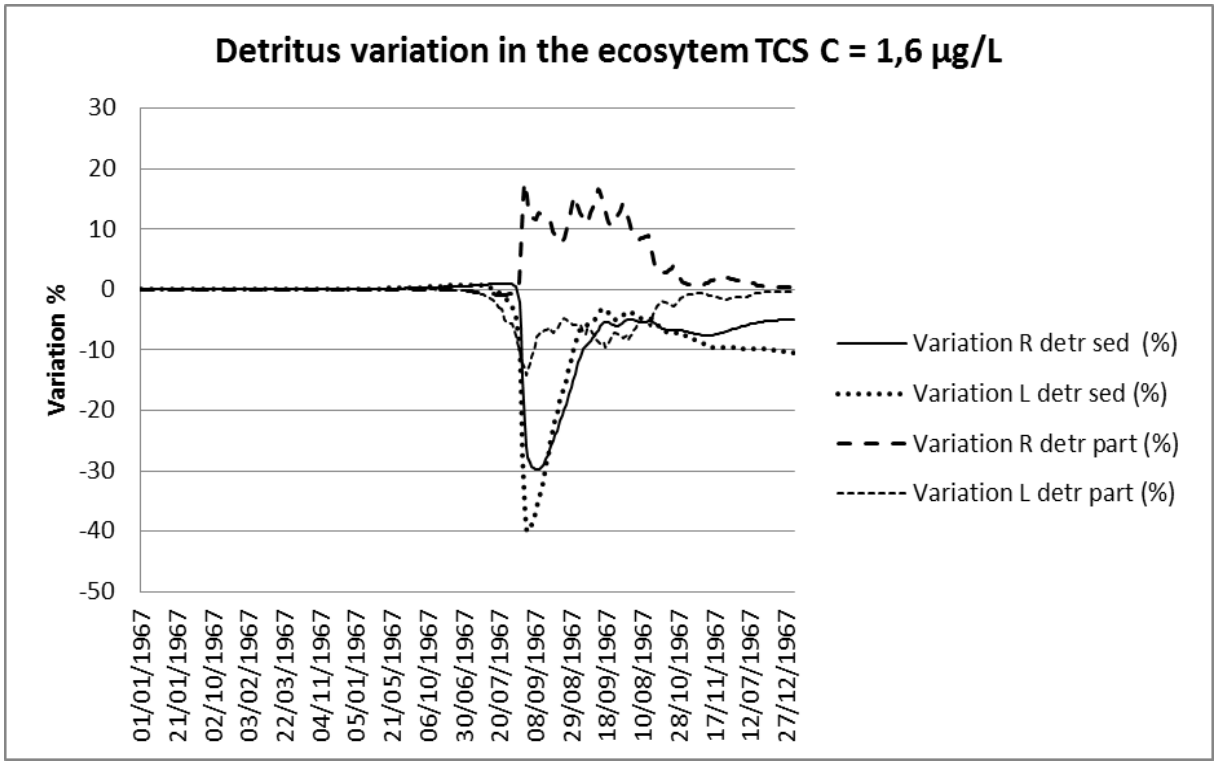


Figure C.2 *The variation of suspended and sediment detritus due to the disappearance of the organisms*

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