Republic of Serbia
Ministry of Energy, Development and Environmental Protection
ENVIRONMENTAL PROTECTION AGENCY

An improved system for assessment of water pollution from diffuse sources in Serbia - Case study for Kolubara river basin

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BELGRADE, 2013

„To work, to finish, to publish"

Michael Faraday (1791 – 1867), English scientist

AN IMPROVED SYSTEM FOR ASSESSMENT OF WATER POLLUTION FROM DIFFUSE SOURCES IN SERBIA – CASE STUDY FOR KOLUBARA RIVER BASIN

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FOREWORD

The present publication is an overview of the latest research related to diffuse pollution originating from runoff from various land use, agricultural surfaces, urban and rural areas and forest resources. These are all activities of a local character and with impacts on surface water quality in the more downstream section of the eco-region. Today diffuse pollution is usually connected with agriculture and runoff from urban surfaces, while waste water drainage from residential and industrial sites is a typical point source. In countries with under-developed waste water sewer and processing system, such as Serbia, most urban areas have no sewage systems with treatment of communal waste water. Likewise, rural waste waters are drained in septic tanks that are usually illegally built and not well maintained, or else they are released to the nearest stream. As the definition of diffuse pollution specifies that the source of this pollution is an area and not a precisely defined point, in may be assumed that the cases of release of waste waters from rural settlements without sewage systems can also be considered as diffuse sources. According to its nature, diffuse pollution can have diverse manifestations, such as suspended matter, nutrients, heavy metals, organic pollutants and also microbiological pollution.

In Serbian reference books there are few papers dealing with diffuse pollution and examples of using the model for load assessment are scarce. This is especially relevant as there is a legal obligation that the water management plans should contain an assessment of pollution from diffuse sources. This is why the present publication is intended for various interested users: ranging from those who have heard for the first time about diffuse pollution, down to experts in water protection who may find it useful in solving different problems and the local self-government and state officers performing various administration duties in the area of environmental protection.

The data relevant for the publication were obtained in the framework of the project An improved system for assessment of water pollution from diffuse sources in Serbia. The project was based on the Agreement on Cooperation between the Ministry of Environment and Spatial Planning, Republic of Serbia (MESP) and the Swedish Environmental Protection Agency - Swedish EPA (Cooperation Programme: Bilateral Program in the field of environment for the period 2010-2012). The implementing partners are Ministry of Energy, Development and Environmental Protection/Environmental Protection Agency, Ministry of Agriculture, Forestry, and Water Management /Republic Water Directorate and PE Srbijavode. The goal of the project is to establish and apply diffuse pollution management methodology based on the method used by the Swedish EPA. The objectives of the project are to establish and adopt diffuse pollution management methodology based on the experience of EU, to implement the Water Framework Directive and Nitrates Directive and to draft a proposal related to harmonization of national regulations. The project is also intended for coordination of the relevant authorities as regards management of diffuse pollution and improvement of technical skills in the area of diffuse pollution management.

The subject matter of diffuse pollution has been presented in five parts. The first part (chapter 1) includes background information about pollution from diffuse sources. The second part (chapter 2 and 3) describes main characteristics of the Kolubara Catchment, its climate, land use and hydrography and provides a brief overview of surface and ground water quality. The principles of assessment of diffuse source water pollution are given in the third part (chapter 4-8), together with quantification of the sources of diffuse pollution and methods of mathematical modelling of diffuse pollution. The fourth part (chapter 9.) deals with main input data required for diffuse pollution modelling by giving the example of the Kolubara Catchment. And finally, the fifth part (chapter 10.) provides recommendations derived from the project findings and related to institutional capacity building in the field of environmental and agricultural statistics and sub-legal regulations in the area of water protection.

We would like to thank the „Ministry of Environmental Protection, Mining and Spatial Planning – Department for Protection from Water Pollution and Fishery", the Republic Hydrometeorological Service and the Agricultural Technical Service „Valjevo" for the submitting data for the project.

Stockholm, March 2013. Authors

Belgrade, March 2013.

CONTENT

1. MAIN OF DIFFUSE POLLUTION

1.1. CHARACTERISTICS OF DIFFUSE POLLUTION

Reference books dealing with the quality and protection of surface and ground waters classify the main sources of pollution into two main categories, according to the spatial origins of its generation and release:

(1) point sources and

(2) non-point (diffuse) pollution sources.

Research conducted so-far in the field of pollution control has mostly focused on point sources, the site of which is usually well-known and visible, and their pollution is quantified by routine laboratory procedures. Examples of these pollution sources are dumping of industrial waste, effluent from public sewerage system and sewage and waste water treatment facilities, as well as other sources which directly release polluted waste waters into the recipient by means of a sewage collection system, thus generating a multitude of point releases. On the other hand, diffuse pollution is caused by diffuse (non-point) sources which have a wide spatial distribution (Figure 1.).

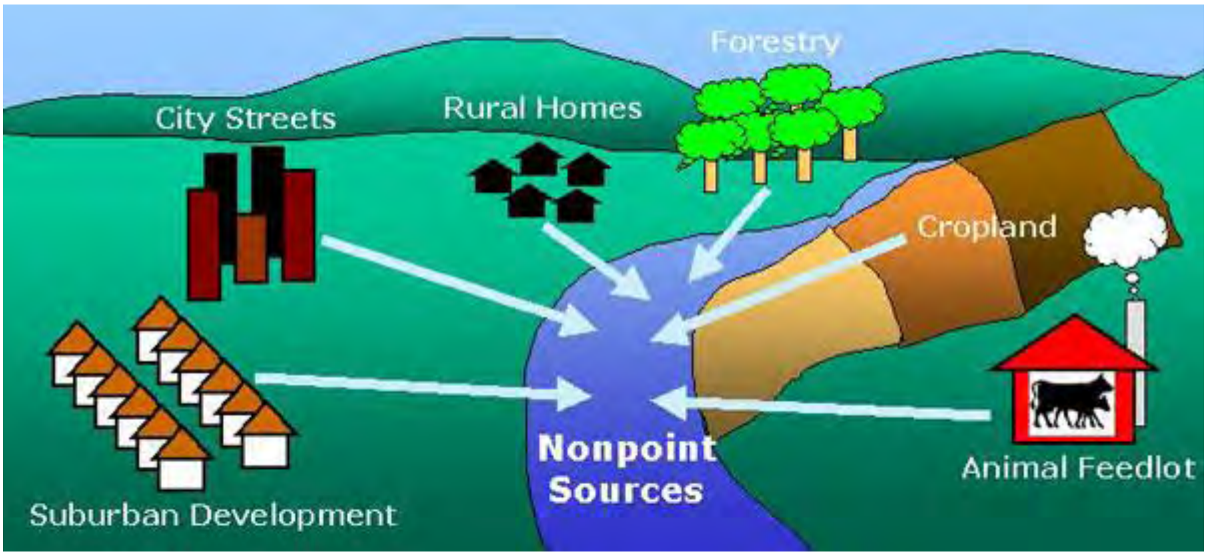

Figure 1. Spatial distribution of non-point/diffuse sources of water pollution

Diffuse pollution is a common problem affecting the quality of surface and ground water. It is of spatial nature and in major part it has not been included by reduction measures. Typically, this pollution occurs in shorter time intervals than the point source pollution. Diffuse pollution occurs with rain and melted snow runoff from the soil, which spreads the pollution and directs it to the nearest surface water, i.e. lakes, rivers, canals and/or causes its leaching into ground water. Diffuse pollution may originate from sediments deposited in the lakes, water bodies, marsh land, and from atmospheric depositions. It is also caused by runoff from urban surfaces (streets, parking space, roofs, lawns, house gardens etc), by runoff and leaching water from agricultural land, village yards, cattle farms, from mining sites and from surfaces with hotbeds or woodcutting.

In short, diffuse pollution is caused by different sources, and most of them are directly connected with a specific manner of land use. The two types of pollution can be compared in the following manner:

A) Point source pollution

a. Measured in terms of quality and quantity, mostly human-induced.

b. Major serious impacts on water quality usually occur in the summer periods, with low flow of water bodies.

c. Waste water releases are located at well-known points, and they are released by pipes or channels.

d. They may be quantified by standard hydraulic engineering techniques and by available equipment.

e. The main parameters of water quality are biochemical oxygen consumption (BOC), nutrients, suspended matter, and in case of industry heavy metals and other hazardous organic and non-organic substances.

f. Control programmes are implemented by state authorities and local self-government.

B) Diffuse pollution

a. Very dynamic, occurs at random, closely connected to the hydraulical cycle.

b. Variability of values may include more orders of magnitude, one order of magnitude or values may vary within an area.

c. Most serious impacts on water quality occur during or after atmospheric precipitation.

d. In general, release of waste waters may not be identifiable, it usually occurs in a broader area.

e. It is difficult to quantify pollution according to standard hydraulic engineering techniques.

f. Main parameters of water quality are suspended matter, nutrients, heavy metals and hazardous organic and non-organic substances.

1.2. DIFFUSE POLLUTION BY AGRICULTURAL NUTRIENTS

Diffuse pollution and its sources may vary, and they are usually divided into six main categories:

- Nutrients
- Suspended matter
- Acids and salts
- Heavy metals
- Hazardous and harmful substances and
- Pathogenic microorganisms.

Besides runoff from urban surfaces (streets, parking space, roofs, lawns, gardens and so on) which contain nutrients, heavy metals, salts, suspended (mineral) matter, poisonous chemicals and microbiological organisms, an important source of diffuse pollution is agricultural production. Runoff and leaching water from agricultural surfaces, as well as waste dumps from exploitation of mineral ores and forested land, contribute to the content of nutrients, sediments, pesticides, herbicides, microbiological agents and heavy metals.

Agricultural activities causing diffuse pollution are cultivation and harvest of crops, fertilization, use of pesticides, irrigation and drainage of arable land. Cattle raising and livestock grazing also contribute towards diffuse pollution, by reduction of leaky (permeable) layers of soil. Excessive grazing causes depletion of protective vegetation cover, together with over-production of natural fertilizers and their inadequate control and use. Finally, direct approach of cattle to surface water bodies also contributes to this phenomenon.

Nutrients, which are absorbed in agricultural land in several different forms, originate from a number of sources, such as:

- artificial fertilizers in a dry of liquid form, containing biogene elements such as nitrogen (N), phosphorus (P), potassium (K), secondary elements and micro-elements;
- animal (natural) fertilizers, containing N, P, K, secondary elements, microelements, salts, some metals and organic substances;
- harvest residual containing N, P, K, secondary elements and microelements;
- irrigation water that is drained from the soil; and
- nutrients from atmospheric depositions.

Nitrogen and phosphorus are two main biogene elements influencing the deterioration of water quality. They are important nutrients for agricultural crops, but they also cause pollution from the use of agricultural land.

Nitrogen is the main component of proteins and other macro-molecules in plants and animals. It is necessary for photo-synthesis of plants and growth of crops. Nitrogen in the soil and water helps the growth of plants and is one of the most important limiting factors for the production of agricultural crops. Plants may take in large amounts of nitrates without this harming them. In order to increase crop yield, farmers add nitrogen and other nutrients in the form of artificial or natural (organic) fertilizers/manure. Depending on the type, in their growth crops take in up to 5 kg of nitrogen per hectare a day, or else 20−70% of nitrogen (from fertilizers) applied on the soil. The rest of nitrous nitrogen remains in the soil after the harvest has been completed.

Besides being absorbed by the crops and weed, the nitrogen from fertilizers may disappear from the soil by surface runoff, through assimilation by soil micro-organisms and by its subsequent transformation into humus, or by leaching from the soil in the form of nitrates, and finally by denitrification and conversion of nitrate into atmospheric forms. Nitrogen in the soil does not originate only from fertilizers, but also from decomposition of the soil's organic matter. This is why it is difficult to estimate the amount of nitrogen in surface and ground water which originates from artificial fertilizers and the quantity which originates from the soil organic matter and numerous other sources.

Eliminating the nitrogen from applied fertilizers through surface runoff is especially common in sloping land. The runoff is more intense if the fertilizers have been left on the surface, than if they have been incorporated in the soil by agricultural tools. The nitrogen leaches from the surface layer of the soil (into which fertilizers are introduced) to deeper layers, where it can remain or further leach into ground and surface water. The intensity of nitrogen leaching depends on a number of factors, such as the type and angle of inclination of the soil, climate, type and quantity of fertilizers, time and manner of application, type and phase of crops, height of plant cover and so on. It is most difficult to determine which part of the nitrogen introduced by fertilizers is disposed in one of the mentioned ways. These processes usually take place in the soil, but they are prevalent in agricultural land, where both natural and artificial fertilizers are applied.

Phosphorus is an element naturally occurring in the soil. It may be present in numerous different forms, most of which are not accessible to plants. Phosphorus is a biogene element, which has an essential role and is very important for agricultural production and natural eco-systems. It is necessary for development of plant and animal life, which take it within specific limit values. Phosphorus reaches the soil by applying artificial and natural fertilizers. As opposed to nitrogen compounds, it is relatively insoluble and is usually found in suspended form. Phosphorus leaches to a lesser extent from the fertilizers than nitrogen does. It is eliminated from the soil by harvest, except on sloping land, where it leaches in contact with water (erosion), together with land particles or without them, in the form of particles or granules of an artificial fertilizer. It is widely accepted that in the soil scarce of phosphorus, the crops will take in 20% of the applied phosphorus fertilizers in the first year of growth, only it the fertilizers are applied near the plant.

1.3. THE PROBLEM OF QUANTIFICATION OF DIFFUSE POLLUTION

Diffuse pollution is inherently complex and its management is closely connected to land users, primarily in rural areas. This very fact shows that local self-government, state authorities and organizations, research institutions and individuals should get involved in its reduction. Diffuse pollution sources in rural areas have the largest spatial distribution, and relevant information about these sources is the least available. (Figure 2.)

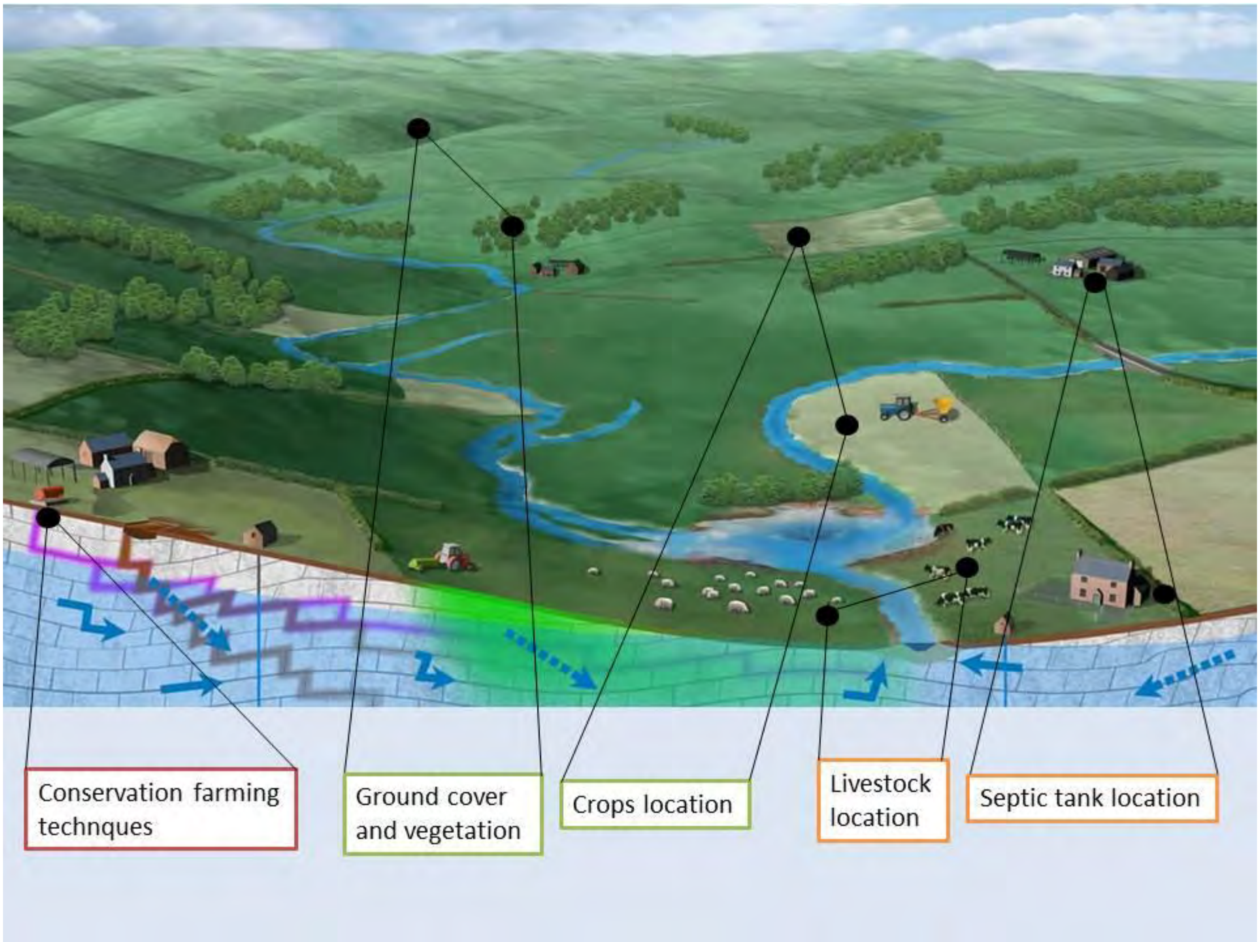

Figure 2. Sources of diffuse pollution in rural areas

Apart from the quantification of the sites of diffuse water pollution, another problem is to determine *mass flow* of the pollution in a specific time interval resulting from the runoff from a defined localized area. The best way to identify the mass flow is to continually measure the flow and pollution concentrations in the water body in question, as the product of these measured values will show the exact magnitude of pollution load. There are limitations of such an approach, first of all of financial nature; this is why a contemporary approach to modelling is to estimate *mass flow*.

With natural science development, and first of all with improvements of computer technology, models are usually defined as mathematical formulations used to simulate dynamic processes in an area of research, on the basis of the same or different premises, or different scenarios. Development and application of mathematical models, especially in the field of environment, includes the use of the geographic information system (GIS), as its integral part.

An example of such an approach is the use of mathematical model for the Kolubara River Catchment diffuse pollution management, which has been presented in this report together with the research findings.

2. MAIN CHARACTERISTICS OF THE KOLUBARA CATCHMENT

2.1. GEOSPATIAL AND DEMOGRAPHIC CHARACTERISTICS

The Kolubara catchment is situated in the west of Serbia and occupies 4.12% of the total surface of the country. It is shaped in the form of an irregular rectangular, with the distance between the most westerly point (19° $30^{'}$ east longitude) and the most easterly point (20° $35^{'}$ east longitude), i.e. in the west-east direction, being 81.2 km. The distance between the most northerly (44° $40^{'}$ north latitude) and the most southerly point (44° $05^{'}$ north latitude), or else in the north-south direction is 64 km. The highest point in the catchment is at 1346 m, and the lowest point is at 73 m altitude. The height difference between these two points is 1273 m.

The Kolubara is the last right tributary of the Sava River and it joins the Sava at 28^{th} kilometre from the point where the Sava flows into the Danube. It originates from the Obnica and Jablanica streams which meet at around 195 m altitude. According to its length (86.4 km) and the surface of its catchment (3,638.47 km^2), the Kolubara ranks among medium-size rivers of Serbia.

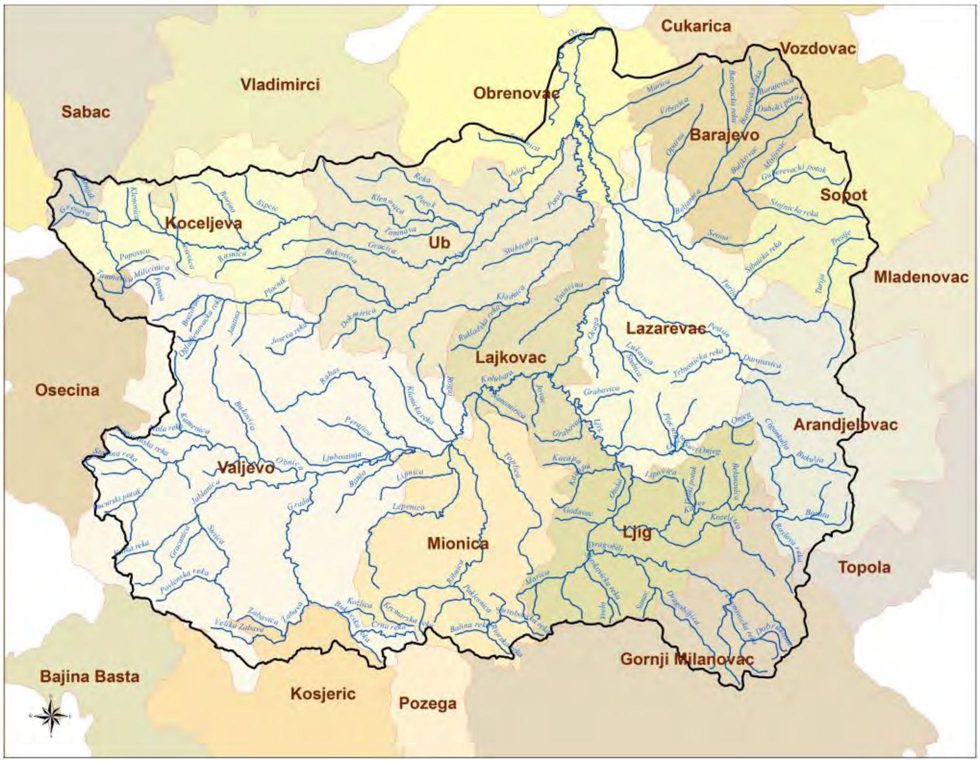

Figure 3. Geospatial distribution of the Kolubara catchment and the related municipalities

The Kolubara catchment includes parts or entire areas of the following municipalities: Obrenovac, Barajevo, Sopot, Lazarevac, Koceljeva, Ub, Valjevo, Lajkovac, Mionica, Ljig, Arandjelovac, Gornji Milanovac and Kosjeric. In terms of regional distribution, the catchment spreads across the territory of the Kolubara, Macva, Morava, Sumadija and Zlatibor districts and covers a part of the Belgrade City area. (Figure 3.)

The major part of the catchment is densely populated, with 325,000 inhabitants. Most population is concentrated in Valjevo, Lazarevac and Obrenovac. Urbanization and industrialization processes initiated after the Second World War had a major impact on population migrations in the Kolubara catchment, as regards both the mechanical and biological component of migration, and eventually they caused deagrarization. The geographical position of the catchment, as well as the socio-economic position of the inhabitants also affected the size of population.

The landscape of the Kolubara catchment is of polygenetic and polyphase nature. It originated under the influence of polyphase tectonic movement, multiple transgressions and regressions during the neogene period, and by sequence of erosion-accumulation processes. The medium altitude of the Kolubara catchment landscape is 276.4 m. The catchment consists of two clearly distinguished basins: Upper Kolubara basin in the south and Lower Kolubara basin in the north; the basins are separated by Pridvorica village.

In the area of Upper Kolubara basin there are three valleys: Valjevo, Toplice and Ljig valley. The Valjevo Kolubara is the western section of the Upper Kolubara and the following streams flow towards its centre, i.e. the Valjevo valley: Obnica, Jablanica, Gradac and Ribnica. The eastern section of the Upper Kolubara is the valley system of Ljig, and the Dragobilj stream, Boljkovacka River, Paleznicka River and Onjeg flow towards the Ljig valley. The middle part of the Upper Kolubara Basin hosts the valley system of Toplice. The Tamnava River together with the Ub tributary flows on the left towards the Upper Kolubara basin, and the Pestan and Turija streams flow on the right towards the same basin.

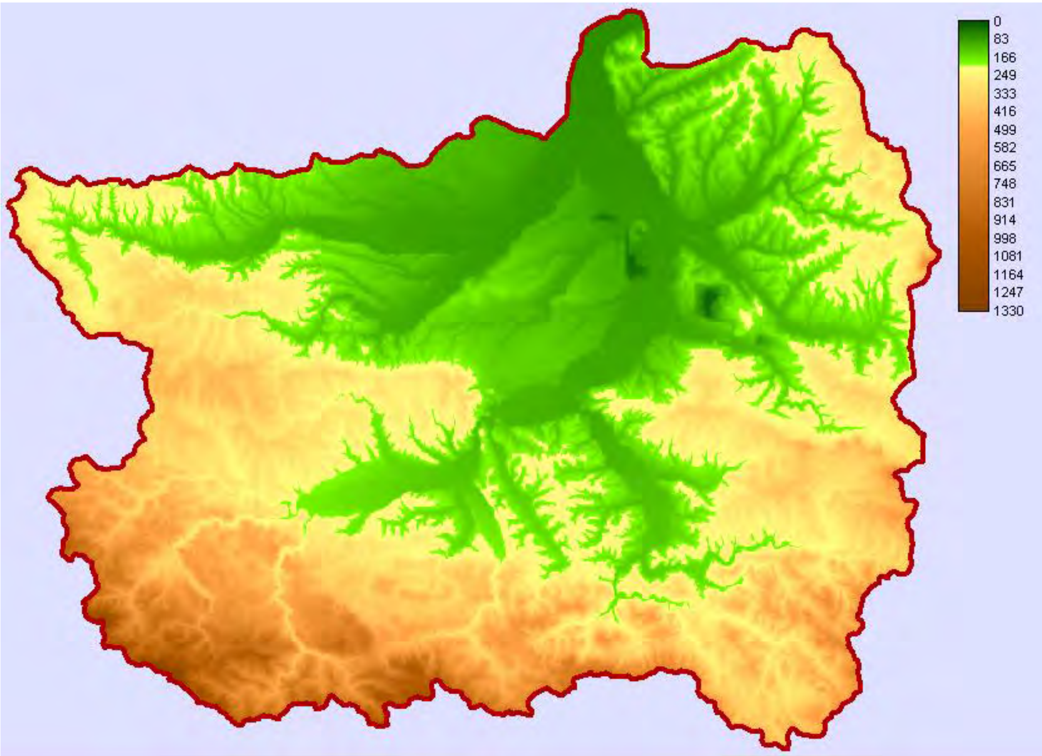

Figure 4. Hypsometric chart of the Kolubara catchment.

Out of the entire surface of the catchment of 3,638.5km^2, a zone up to 300 m altitude takes up the share of about 68%. (Table 1.)

Table 1. Distribution and surface of upper zones in the Kolubara catchment

Upper zone [m]	Surface [km^2]	Share in total surface [%]
0-100	260.06	7.15
100-200	1261.32	34.67
200-300	938.22	25.79
300-400	534.61	14.69
400-500	263.95	7.25
500-600	134.23	3.69
600-700	82.21	2.26
700-800	70.45	1.94
800-900	46.28	1.27
900-1000	29.73	0.82
1000-1100	11.72	0.32
1100-1200	3.53	0.10
1200-1300	2.06	0.06
1300-1400	0.08	0.002
Total	**3638.47**	**100.00**

The Kolubara catchment rivers flow through various sections of landscape. The diversity is reflected in the geological composition and the age of specific sections of the catchment, as well as in geo-tectonic diversity of the terrains that the Kolubara river flows through. The catchment is made of versatile metamorphic, magmatic and sediment rocks from Palaeozoic, Mesozoic or age.

2.2. CLIMATE

The climate of Serbia may be generally described as being moderate continental climate (with more or less prominent local features). Its main characteristic is double maximum precipitation, with frequent and abundant rains in the summer half of the year and with relatively dry winters. Specific local conditions of the Kolubara catchment as regards precipitation may be observed by an analysis of precipitation data taken from rain gauge stations from this area; it shows that maximum precipitation occurs in June (only two stations show maximum in May). The Kolubara catchment has the so-called continental pluviometric regime, with typically one maximum precipitation round in early summer and one minimum precipitation round during the winter months. Mean precipitation amount in the Kolubara catchment for the period 1925-2000 is 814.7 mm.

Data for rain gauge stations have been shown in GIS as spot elements.

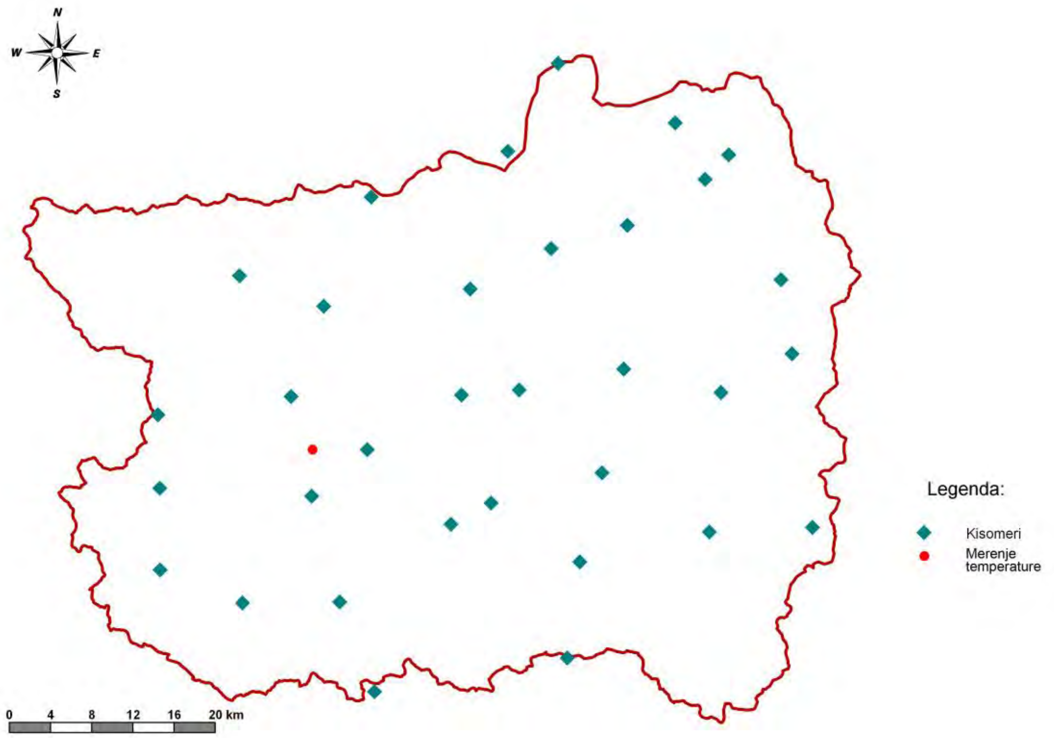

Figure 5. Distribution of precipitation and temperature measurement stations in the Kolubara catchment

Figure 6. Isohyet chart of the Kolubara catchment for the period 1925-2000

Table 2. Surfaces with different precipitation amounts in the Kolubara catchment

Amount of precipitation [mm]	Surface [km²]	Share in total area [%]
500-600	2.41	0.07
600-700	195.18	5.36
700-800	1410.05	38.75
800-900	1546.29	42.50
900-1000	464.19	12.76
1000-1100	20.34	0.56
Total	**3638.47**	**100.00**

Local characteristics of the Kolubara catchment may be observed through meteorological parameters from the Valjevo station, located at 176 m altitude, which ranks among the lowest parts of this area. (Table 3.) and (Figure 7.) show average monthly and annual precipitation amounts in Valjevo; apparently, most precipitation occurs in June and the least in February. The figure also shows comparative average in the last decade, which was obviously marked by more rains, especially in the spring and fall.[1]

[1] Source: Republic Hydrometeorological Service (www.hidmet.gov.rs)

Table 3. Average amounts of precipitation for the period 1946-2010 in Valjevo

Meteorological station of Valjevo	Month												Year
	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	
Average precipitation amount in mm	47.0	43.8	52.7	54.8	66.3	106.4	75.1	69.7	70.7	66.3	58.8	61.3	781

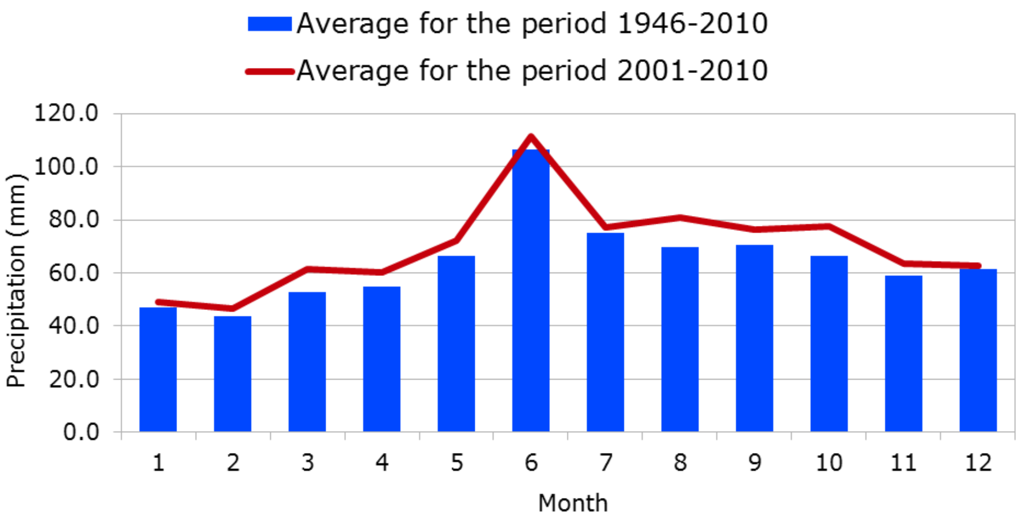

Figure 7. Average monthly amounts of precipitation for the periods 1946-2010 and 2001-2010

(Table 4.) and (Figure 8.) show average monthly and annual air temperatures in Valjevo. Namely, the hottest month is July and the coldest is January. The figure shows a comparative average of temperatures in the last decade, which was apparently hotter, especially in the summer.

Table 4. Average air temperatures for the period 1946-2010 in Valjevo

Meteorological station of Valjevo	Month												Year
	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	
Average temperature in ºC	0.8	2.5	6.4	11.3	16.4	19.5	21.2	20.8	15.8	11.3	6.3	1.8	11.2

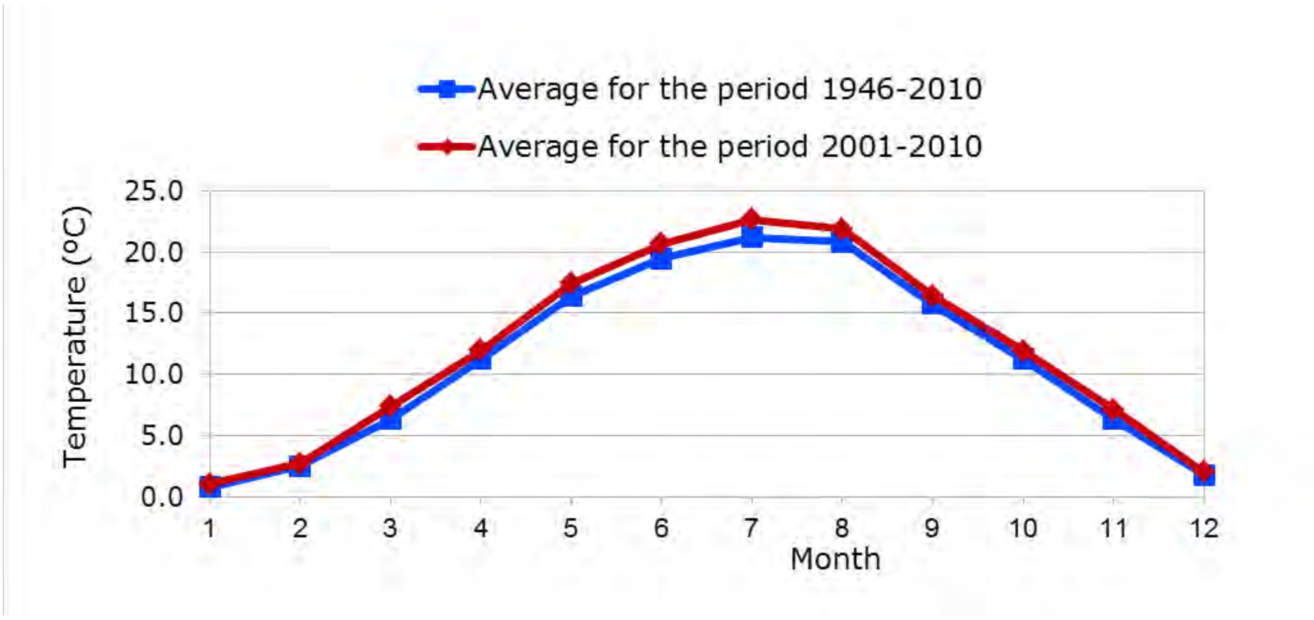

Figure 8. Average monthly temperatures in Valjevo for the periods 1946-2010 and 2001-2010

Both in this area and across Serbia there are air currents of different directions, but there are two distinctive periods: the winter period with dominant east and south-western air currents and the summer period, with dominant south-western air currents. In terms of frequency of occurrence at the meteorological station of Valjevo, west-southwest, west to north-northwest are the most frequent, followed by the less frequent northeast-east-southeast winds. Wind speeds are usually below 20 m/s.

2.3. THE SOIL

2.3.1. GEOLOGICAL CHARACTERISTICS AND PEDOLOGICAL COMPOSITION OF THE KOLUBARA CATCHMENT

The Kolubara River Catchment includes sections of landscape with high diversity in terms of geological composition and age. As a whole, it demonstrates a high geotectonic diversity. The catchment was made of most diverse metamorphic, magmatic and sediment rocks of Palaeozoic, Mesozoic or Quarter Age. Neogene sediments are prevalent, with a total share of 35.75%, followed by quarter sediments (23.09%) and a complex of fliss and related clastic rocks (11.72%), as shown in (Table 5.).

Table 5. Prevalence of related lithological complexes in the Kolubara Catchment

Name of lithological complex	Surface (km^2)	Share in the total surface of catchment (%)
Quarter sediments	840.10	23.09
Neogene sediments	1300.16	35.75
Complex of fliss and related clastic rocks	426.49	11.72
Complex of carbonate rocks	343.57	9.44
Complex of magmatic rocks	135.65	3.73
Diabase-horn formation	102.93	2.83
Complex of ultramaphites and serpentinites	58.05	1.60
Complex of metamorphic and shale rocks	431.05	11.85
Total	**3638.47**	**100.0**

There are various genetic types of soil in the area now occupied by the Kolubara Catchment, and their distribution was conditioned by the effects of main pedo-genetic factors, such as geological basis, landscape, climate and vegetation. The combined inter-action of these factors has led towards formation of various types of soil, which have been presented by a surface (polygonal) element (Figure 9.). Pseudo-gleyed soils (parapodozol) occupy the major part of the surface in the Kolubara Catchment (around 25%) and are present in flat or gently undulating terrains (mostly on the old river alluvial terraces) (Dragicevic, 2007). They are most present at 150-350m altitude. These are extremely acid soils, scarce of clay, humus and nutrients. They have unfavourable chemical and water-air conditions and are less permeable. In the Kolubara River Catchment another prevalent group of soils are brown soils (dystric cambisol) formed on various geological platforms. Within the group of cambisols there are three sub-groups: brown soils on shale, magmatic and sediment rocks. Large parts of river valleys in the Kolubara Catchment are covered by meadows (semi-gley). They were formed in middle parts of the alluvial plane, by transformation of alluvial deposits with a high level of ground water. Due to large humidity, they have a developed grass and forest vegetation. As regards the content of nutrients, they rank among very rich soils. Due to the vicinity of water, heavy mechanical content, excessive humidity in winter and a lack of biological activity, the quality of meadow soils is very low.

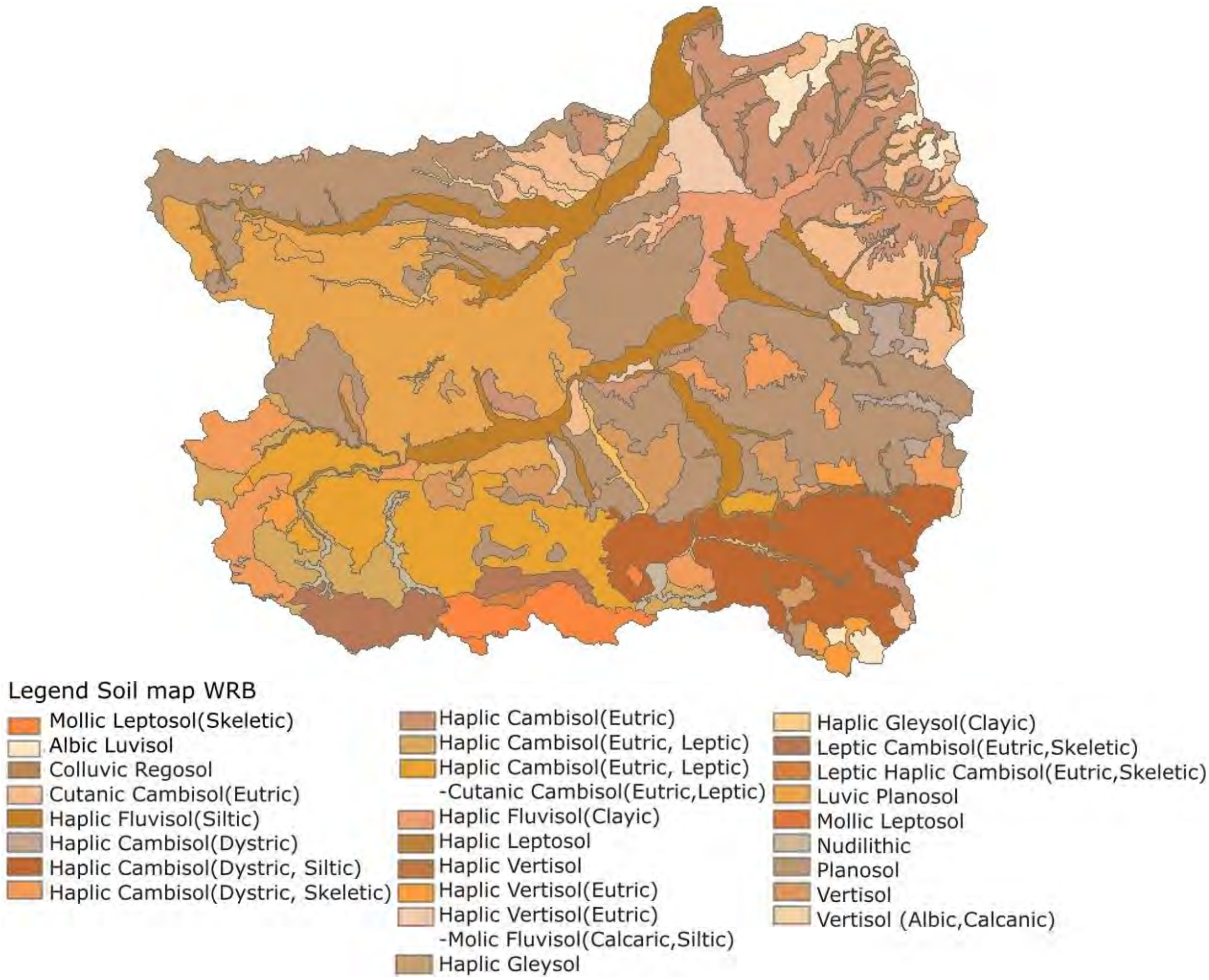

Figure 9. Soil map of Kolubara catchment

The soil map of Kolubara catchment was made according to WRB classification due to incomplete harmonization of national classification and cartographic names from different periods of Soil mapping of Serbia.

2.3.2. Quality of the soil

The quality of the soil of the Kolubara catchment was determined on the basis of systematic fertility control data obtained from 5783 samples at 0-30cm depth. The analysis of the content of easily accessible Phosphorus (P_2O_5 – mg/100g) shows that 43.3% samples from the Kolubara Catchment have a very low content of phosphorus, 25.3% have a low content; 9.7% have an optimum content, while 1% of samples have a harmful and toxic content of phosphorus in the soil (Figure 10.) (Systematic Control of Fertility of Agricultural Land , 2011.).

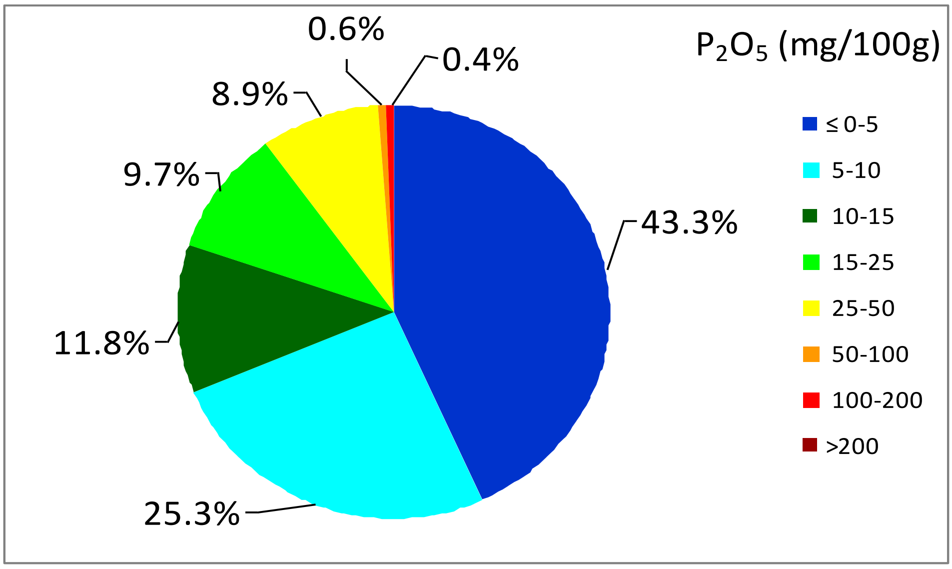

Figure 10. The content of accessible forms of phosphorus in the soils of the Kolubara Catchment (P_2O_5 – mg/100g)

2.3.3. Land use

Land use has been shown on the basis of the CORINE land cover 2006. Corine Land Cover is a data base of the European Environmental Agency (EEA) and its member countries in the framework of the European Information and Observation Network (EIONET). By photographic interpretation of satellite images national registers of land cover were obtained; they are fundamental maps of the land cover of Europe. CLC meta-data, in addition to the CLC data bases provide basic information about the composition of the shown surfaces in the Kolubara Catchment. Meta-data have been produced according to a standard structure prescribed by CLC TT (Nestorov I., Protic D., 2009), and CLC data sets are a valuable source of information for environmental monitoring, spatial planning, water management etc.

Analysis of the land cover data base has shown that out of 29 CLC classes that are typical of the land cover in Serbia, there are 17 CLC classes in the Kolubara Catchment. Agricultural surfaces are dominant, with 71.39% (class 211 – non-irrigated arable fields, 222 orchards, 231 pastures, 242 arable lot complexes, 243 prevalently agricultural land with a considerable surface under natural vegetation), followed by forests and semi-natural areas with 25.81% (class 311 broad-leaves forests, 312 conifer forests, 313 mixed forests, 321 natural grass regions, 324 transitory forest/bushy areas), artificial surfaces with 2.73% (class

112 discontinued urban areas, 121 industrial or commercial units, 123 airports, 131 mines, 132 waste dumps, 141 urban green areas); finally, water basins take up 0.07% of the surface of the Catchment (class 512 water basins). (Figure 11., Table 6.).

Statistical data obtained show that in the Kolubara Catchment area there are 35.64%, surfaces under grain fields, followed by 16.59% fields under fodder, 7.03% under vegetable fields, while industrial plants occupy 0.79% surface of the Catchment. Meadows and pastures occupy 26.52% of the surface, orchards 9.6% and vineyards 0.15%. Other surfaces occupy 3.68% of the Catchment.

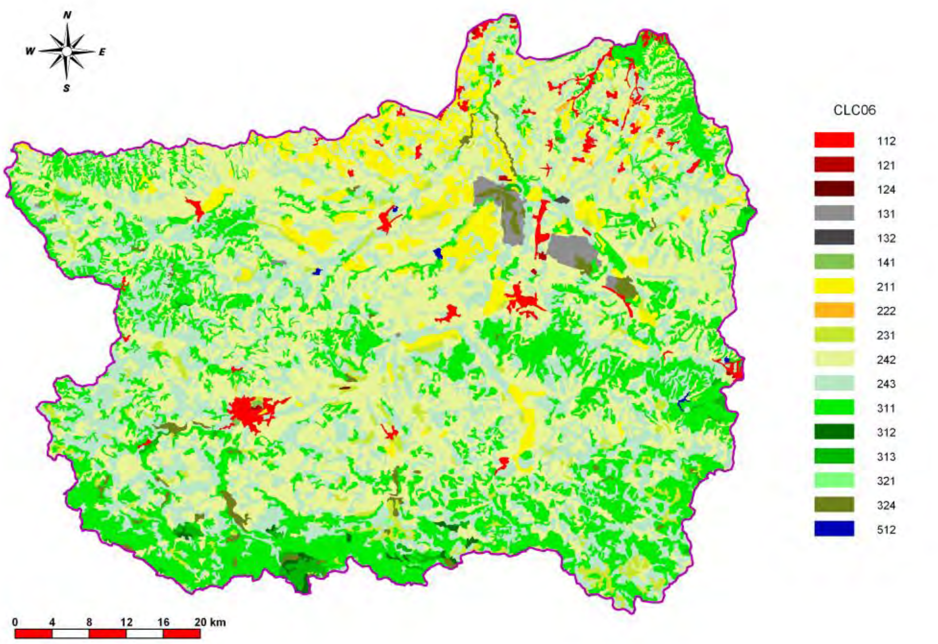

Figure 11. Land use of the Kolubara catchment surfaces

Table 6. Presence of CLC classes in the Kolubara Catchment

CLC 2006	Surface [km²]	Share in total surface [%]
ARTIFICIAL SURFACES (112,121,124,131,132,141)	99.42	2.73
AGRICULTURAL SURFACES (211,222,231,242,243)	2597.33	71.39
FORESTS AND SEMI-NATURAL AREAS (311,312,313,321,324)	939.32	25.81
WATER BASINS (512)	2.40	0.07
Total	**3638.47**	**100.00**

2.4. HYDROGRAPHY

Hydrological measurements and observations in the Kolubara catchment were initiated in 1923 by the installation of the water level staffs in Obrenovac. Other water measurement stations were installed after 1950, and the two most recent ones – Junkovac and Cemanov Bridge have been operational since 1970. In the Kolubara catchment, water level is observed at 14 measurement stations. At the main course of the Kolubara Catchment water level is observed at 4 profiles. The water measurement station of Valjevo is situated on the Kolubara River at 80.3 km distance from its juncture with the Sava River. The station was established in 1951, while the limnigraph was installed in 1951. The water measurement station of Slovac, on the Kolubara River, is at 54.7 km from the river source. This station was established in 1953, and the limnigraph was installed in 1958, and from this moment onwards deposit measurements have been performed, while water temperature has been measured since 1959. The water measurement station of Beli Brod, on the Kolubara River, is located at 39.2 km distance from the river source. It was established in 1950, and the limnigraph was installed in 1976. The water measurement station of Drazevac, on the Kolubara River, is located at 12 km distance from the point where it meets the Sava River. The station was established in 1950; the suspended deposit has been measured since 1958 and water temperature since 1969.

Figure 12. The river Kolubara becomes at mouth of the rivers Jablanica and Obnica, near Valjevo city

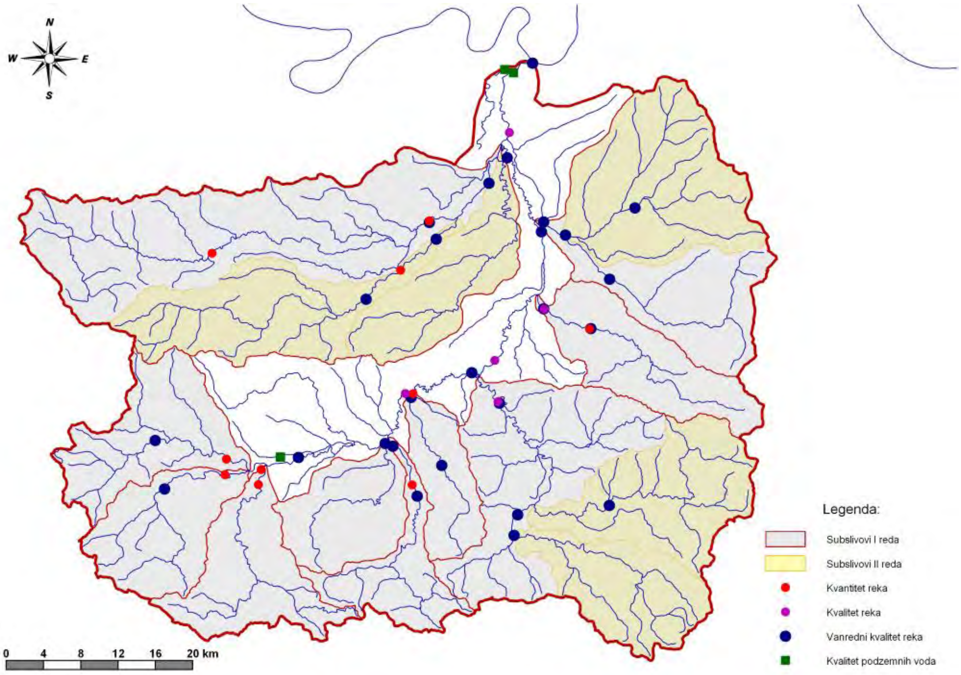

Figure 13. Distribution of hydrological measurement stations in the Kolubara catchment

The Kolubara River, with all its tributaries, belongs to the group of rivers with rain-snow water regime. An important feature of the water regime is abrupt and high fluctuations of the water level and discharge.

Water Quantity Resources as a feature of a specific catchment area, is best shown by its mean discharge. Based on observations and measurements at selected hydrological stations, mean annual discharge values (Qsr, m^3/s) have been calculated, and a histogram for selected time intervals has been produced.[1] (Figure 13.)

[1] *Source*: (1) *Pilot Plan of Kolubara Catchment Management*, Swedish Environmental Protection Agency & MINISTRY OF AGRICULTURE, FORESTRY AND WATER MANAGEMENT, Republic Water Directorate, 2010; (2) *Hidrological Yearbook – surface water*, Hydrometeorological Service of the Republic of Serbia, 1992-2011.

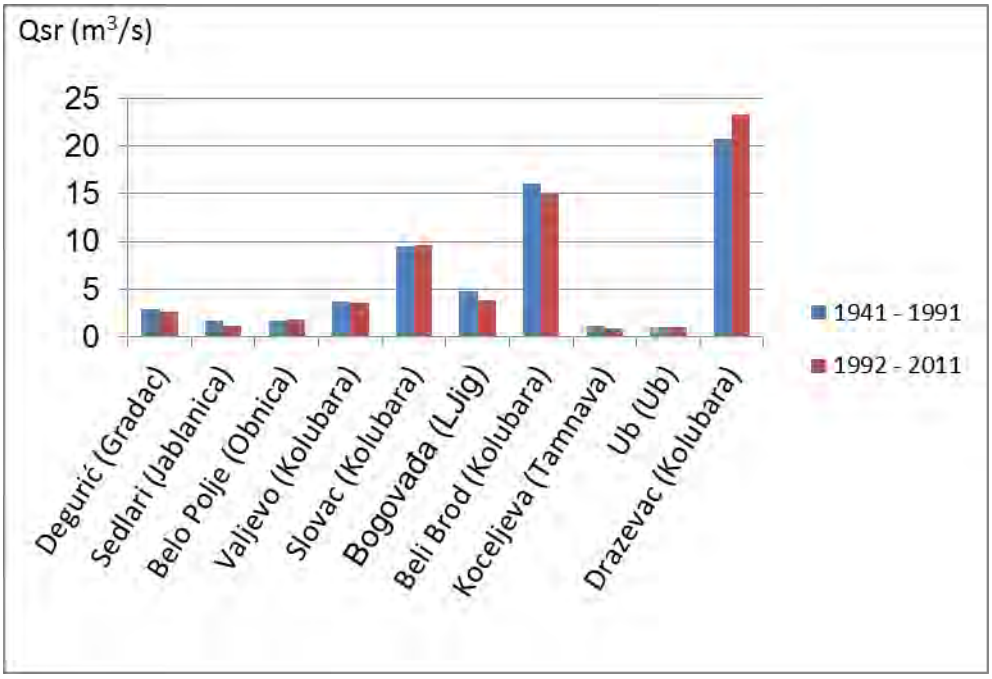

Figure 14. Mean multi-annual discharge of the Kolubara Catchment Rivers

A general conclusion based on the above histogram is that mean multi-annual discharge in the period 1992-2011 is lower than that in the period 1941-1991. Discharge at the water measurement station Drazevac is an exception. A possible cause could be the position of the station, as the water levels at this profile are influenced by the downstream flow of the Sava River.

Picture 1. The river Kolubara, railway bridge on the Belgrade-Bar, monitoring station Beli Brod

3. QUALITY OF SURFACE AND GROUND WATER IN THE AREA OF KOLUBARA CATCHMENT

3.1. SURFACE WATER

A quality analysis of surface waters of the Kolubara Catchment against the parameters: total nitrogen and total phosphorus is based on the results of physical-chemical analyses of water sampled performed by RHMS[1] according to the Temporary Monitoring Programme, in accordance with the guidelines of the Water Framework Directive. A total of 291 samplings /analyses were carried out in the two-year period 2009 – 2010 at 18 control profiles in the catchment, at the confluence of I and II order tributaries.

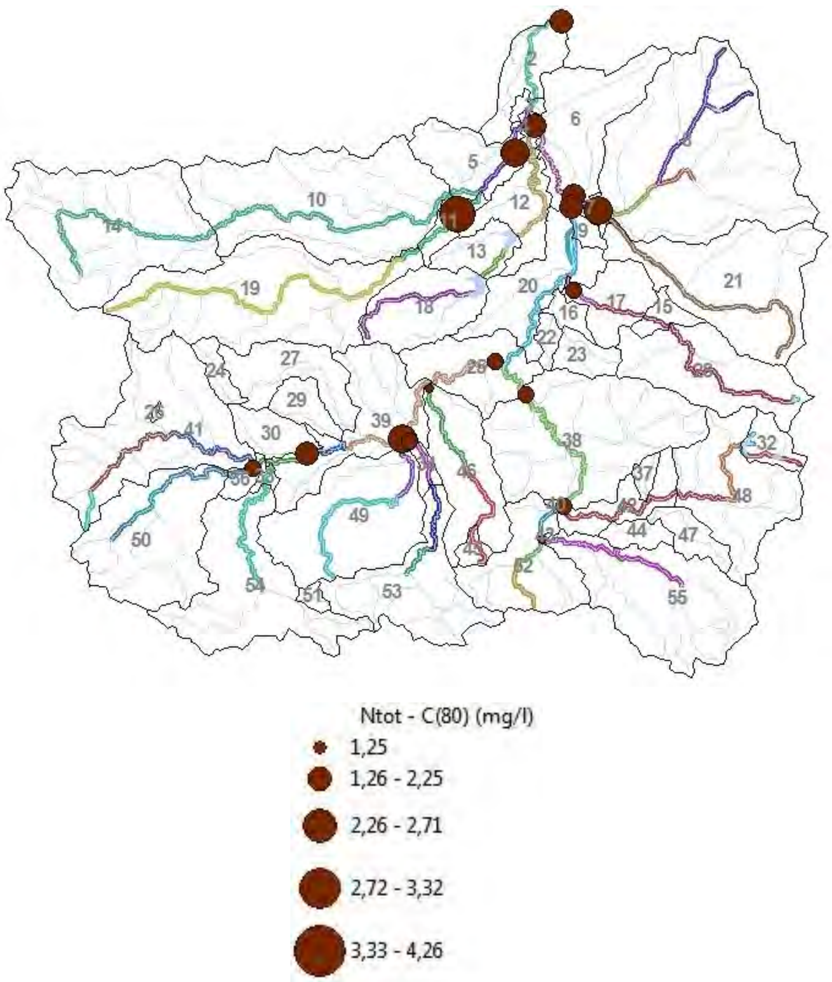

Figure 15. Temporary monitoring stations and concentrations of total Nitrogen Ntot-N

[1] Note: In the framework of the EU Twinning project "Capacity Building of the Republic Water Directorate", SR2006/IB/EN/01, implemented during 2007 and 2008. Guidelines for harmonization of the existing programs for monitoring of surface and ground water have been given, together with conceptual elements of the relevant European directives, as well as national legal regulations in force and international commitments.

On the basis of the obtained results, percentile values (C80) of total nitrogen concentrations (Ntot-N) for each control profile have been determined[1] (Figure 15.). Based on the results it has been identified that on 22% control profiles percentile values of Ntot-N concentrations were within limits prescribed for II quality class, while at 78% control profiles these values ranged within limits prescribed for III quality class (Chart 1.).

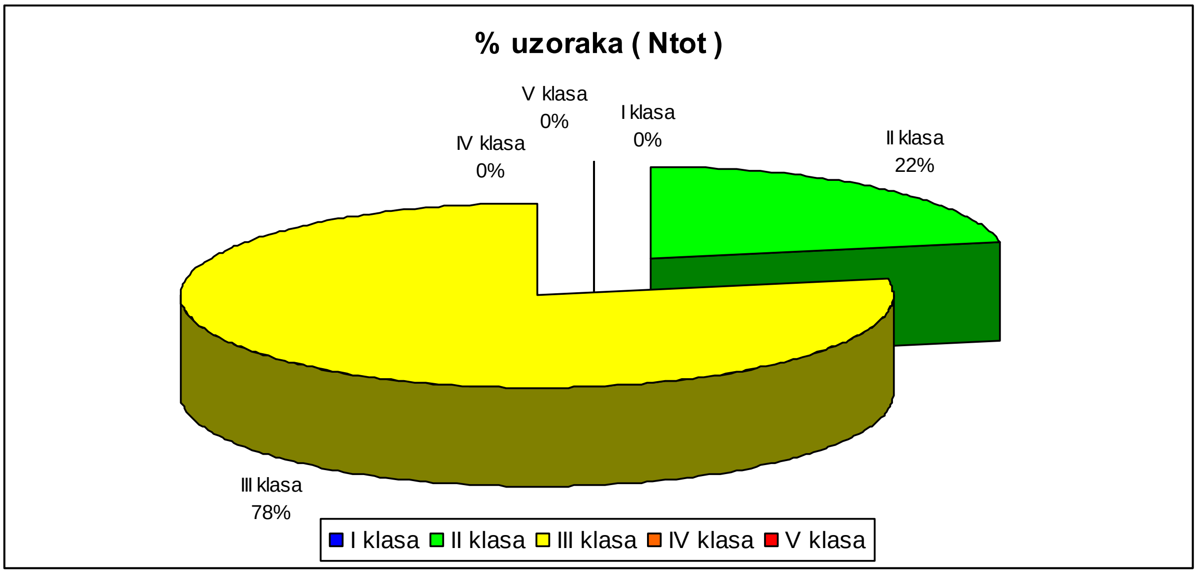

Chart 1. Percentile values of the total Nitrogen concentrations (Ntot-N) in the Kolubara Catchment

For the purpose of determining concentrations of total Phosphorus (Ptot-P), 282 samples were taken/analyzed at 18 control profiles in the Kolubara Catchment (at the confluence of I and II order tributaries). (Figure 16.)

[1] (1) *Regulation on Limit Values of Pollutants in Surface, Ground Water and in the Sediment and on the Deadlines for Obtaining them (Off. Gazzette of RS, No. 50/2012) and* (2) *Rulebook on the Parameters of Ecological and Chemical Status of Surface Water and Parameters of the Chemical and Quantitative Status of Ground Water (Off Gazette of RS, No. 74/2011)*

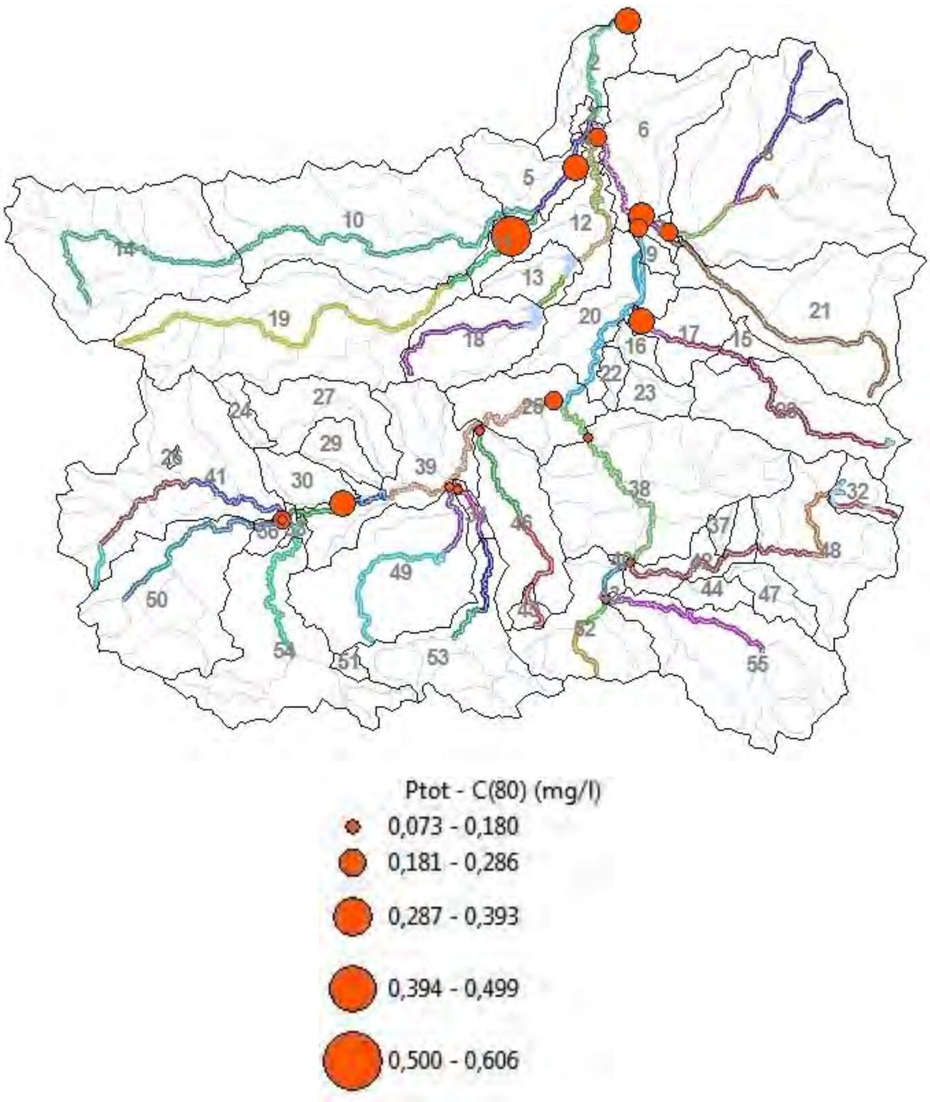

Figure 16. Temporary monitoring stations and concentrations of total Phosphorus (Ptot-P)

On the basis of the obtained results, percentile values (C80) of total Phosphorus concentrations - Ptot-P, were determined for each control profile.

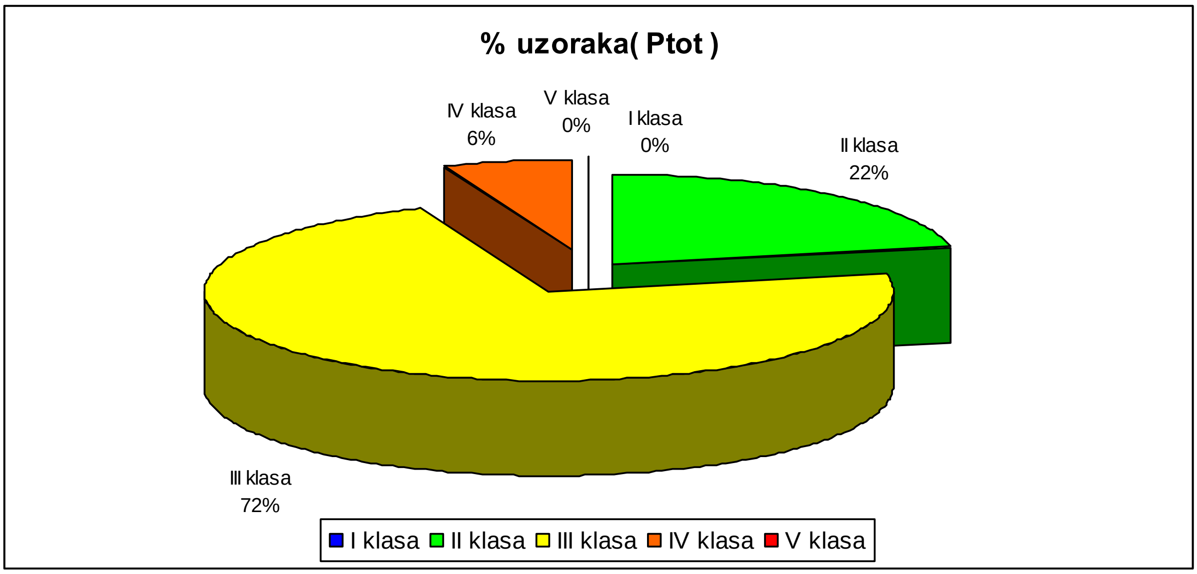

Chart 2. Percentile values of concentrations of total phosphorus (Ptot-P) in the Kolubara Catchment

The results obtained show that at 22% control profiles percentile values of Ptot-P concentrations were within limits prescribed for II quality class, at 72% control profiles within limits for III quality class, while at the remaining 6% profiles, the value corresponded to IV quality class. (Chart 2.)

3.2. Ground water

Ground water quality in the Kolubara Catchment was determined on the basis of the results of systematic observation program of the Republic Hydrometeorological Service of Serbia.[1] Sampling is performed once a year in three piezometers along river banks; they are usually located in an agricultural zone influenced by the water bodies, and thus ground water of the aquifers is vulnerable to pollution from leached surfaces, lateral inflow from water bodies and impacts of septic tanks and outflow from village yards. Average depth of inbuilt pipes is 6-12.5 m. (Figure 17.)

Nitrate as a parameter was used in the analysis of ground water quality. Nitrates are chemical indicators of use of nitrogen fertilizers and waste generated by the farms or of industrial origin. Generally speaking, the quality is within the legally prescribed limits, as all nitrate concentrations are < 50 mg/l.[2]

[1] Republic Hydrometeorological Service, Hydrological Yearbook – 3 Water Quality 2006-2010, Belgrade.

[2] Limit value in form of a pollutant concentration not to be exceeded amounts to 50.0 mg/l NO_3 with the view to protecting human health (*Regulation on Limit Values of Pollutants in Surface, Ground Water and in the Sediment and on the Deadlines for Obtaining them (Off. Gazzette of RS, No. 50/12*).

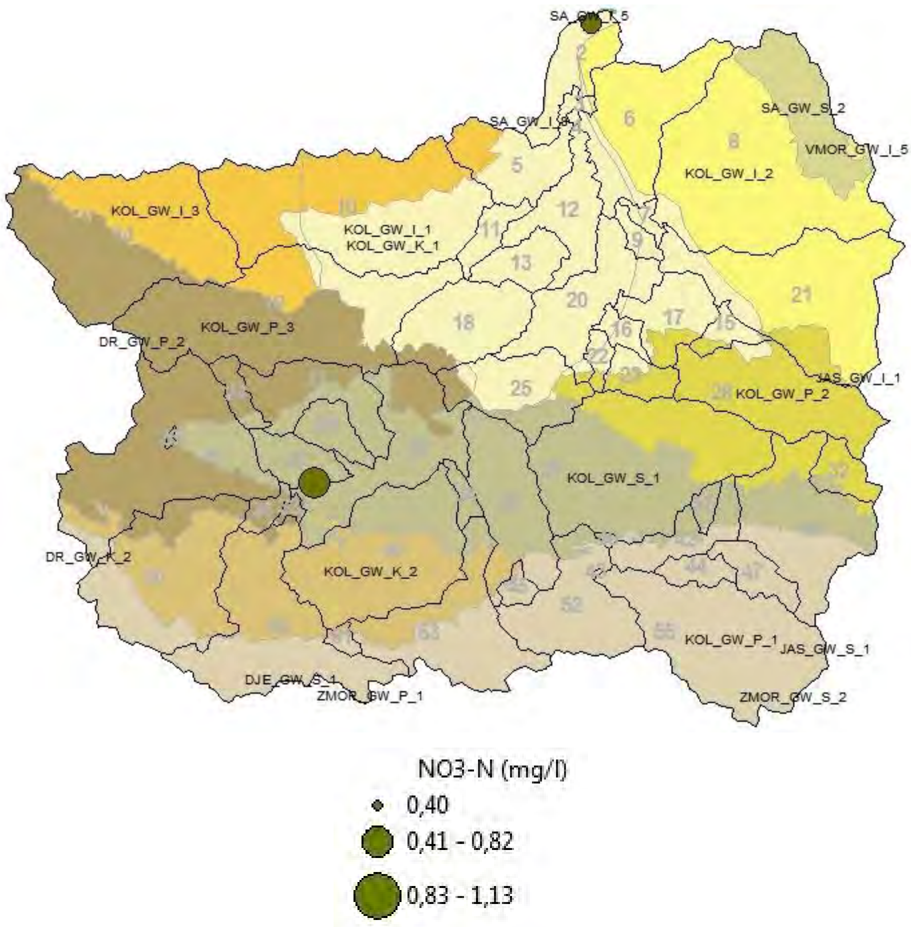

Figure 17. Surface water monitoring stations and nitrate concentrations (mg/l NO_3)

In the area of Kolubara District 88% of the population uses drinking water from public distribution pipelines; this tap water comes from surface and ground sources. The population living in the city area not connected to the city network, is supplied with drinking water through local water bodies from the sources of ground water. Rural population is supplied with drinking water from local pipelines and individual wells, exclusively from ground water. Central water pipelines and a part of local pipelines (usually bigger ones) are under control of the Public Health Institute of Valjevo, which performs micro-biological and physical-chemical analyses. In the period 2009-2010, on average 340 physical-chemical analyses were performed of local water pipelines; non-acceptable results were below 5%.[1] The reasons for deviation from the standard were higher values of electric conductivity, turbidity, ammonium, nitrates and pH.

[1] *Potable water regulation*, Official Gazette of the Republic of Serbia, No. 42/98, 44/99.

4. ASSESSMENT PRINCIPLES OF WATER POLLUTION FROM DIFFUSE SOURCES

Losses and loads of pollutants from diffuse sources are difficult to monitor, since they either lack distinct discharge points or have many small outlets. This means that the input to water cannot be quantified by actual measurements at an outlet, but it must be assessed by indirect methods. Several methods to do this can be found in literature and many of them are also in practical use in several countries. When choosing a suitable method or an assessment tool the aim of the assessment has to be considered as well as the availability of data on selected scale.

4.1. The local scale

On the local scale, initial estimates of pollution load from diffuse sources can be determined by monitoring of streams draining the considered area. If the catchment of the stream is small and dominated by a single source category the annual load can be estimated by analysing water samples taken monthly and multiply concentrations with water flow (see also section 6.5). Normally, more than one source of pollution occurs even in relatively small areas. In such cases the input can be estimated by multiplying the water runoff with leaching coefficients for specific land categories and adding the contribution from point sources (see also section 5.3.2.). Such leaching coefficients can be derived from experimental data or by modelling.

By summing up contributions from all sources the input on a local water body can be estimated. The sources may include losses from different land use categories, storm water and direct atmospheric deposition, but also direct discharges from point sources (wastewater treatment plants, industrial facilities).

Atmospheric deposition directly on water is generally considered as a separate diffuse source, while deposition over land is included in land-use leaching coefficient.

4.2. The catchment scale

In principle, the amount of pollutants entering water bodies in a large river catchment can be estimated in the same way as for the local scale, but the data requirement is more extensive. The pollution input to the nearest water body in the whole catchment is denoted gross load. After entering a water body, pollutants may be transformed by chemical, physical and biological processes, which remove them from the water. These transformations are collectively called retention. Pollutants can also be added by erosion of river banks and lake sediments, diffusion and re-suspension from sediments or by biological fixation processes. The total amount of a pollutant leaving a catchment is called net load.

For a catchment we can set up the following equation:

Net load = Gross load - Retention + Erosion in stream

The terms gross and net load can be applied for a whole catchment as well as for its sub-catchments (Figure 18.). By adding up the gross loads in all sub-catchments the total gross load of the catchment is obtained. The net load leaving a single sub-catchment will enter the nearest downstream sub-catchment where it will be exposed to further retention. This process will be repeated all the way down to the mouth of the major catchment. With many sub-catchments in a river basin, the load calculation can be very complicated.

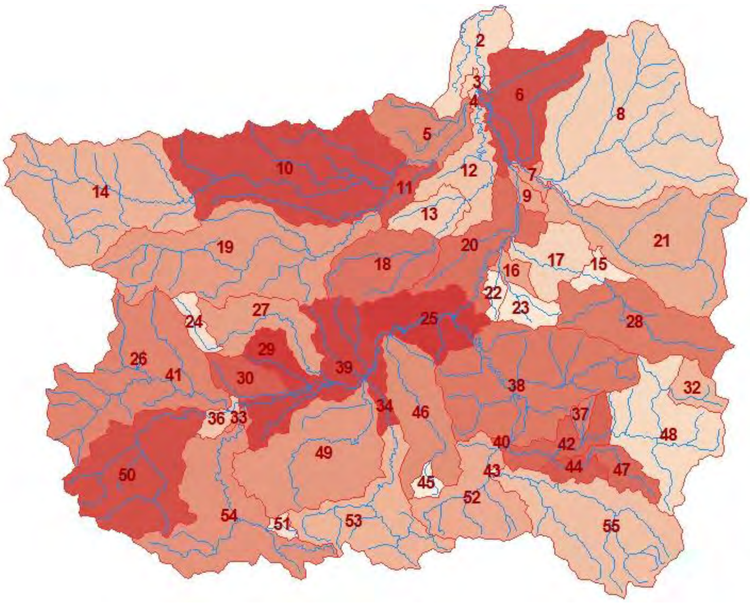

Figure 18. The Kolubara river catchment, with 54 identified sub-catchments. Sub-catchment 2 represents the outlet into River Sava

Retention mainly occurs in relatively large lakes with slow water turnover, but especially for nitrogen compounds it can also take place in groundwater. Nutrient losses in soil water and groundwater below the root zone are denoted <u>soil retention</u> as opposed to <u>lake retention</u> that takes place in the water and sediments of the lake.

4.3. Delineation of sub-catchments

A catchment may sub-divided in several sub-catchments in order to make a more detailed description of sources and pollutants in the catchment. After characterizing land use and discharges from point sources it is possible to calculate the load from each sub-catchment as well as their contribution of the total load from the whole catchment. By taking into account the position of point sources and monitoring stations when delineating the sub-catchments the analysis of retention and source apportionment can be improved.

The best result can be achieved if the delineation of sub-catchments is made according to the following principles:
- stations for water quality and flow should be located at the outlet of sub-catchments
- larger lakes should be situated at the outlet of sub-catchments
- location of the large point sources; point sources should be located at the upstream end of the sub-catchments

The delineation of sub-catchment might be done manually or by using a GIS software, based on Digital Elevation Model (DEM) and stream network. The available data from Catchment Characterization and Modeling (CCM) from Joint Research Centre (JRC) might be used if better local data is lacking.

There are several nutrient models, like e.g. the Swedish FyrisNP model, can calculate loads from each sub-catchments and how they add to the load of all downstream sub-catchment in the river network, provided that proper indata is available . The calculation principle is relatively simple, but the complexity increases with the number of sub-catchment. An example is given in (Figure 19.)

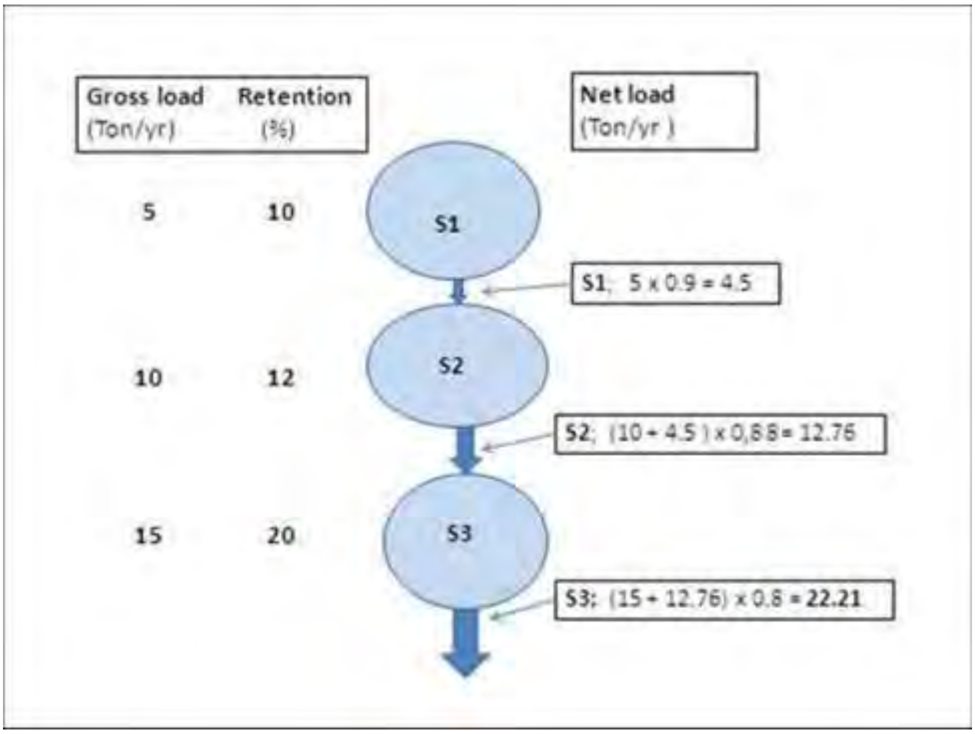

Figure 19. Calculation of the load from a catchment with three interconnected sub-catchments, S1, S2 and S3 according to the FyrisNP model. The net load from S1 is calculated by multiplying the gross load multiplied with (100 – retention)/100=0.9, i.e. the fraction of the gross load that is transferred to S2. The net load from S2 is calculated by applying the retention coefficient to the sum of the gross load in S2 plus the amount transferred from S1. Finally the net load from S3 is calculated with the same principle. The total retention over the whole catchment is (22.21/(5+10+15)) x 100 = 25 %.

5. QUANTIFICATION OF DIFFUSE SOURCES

5.1. QUANTIFICATION OF ATMOSPHERIC DEPOSITION TO INLAND SURFACE WATERS

Direct atmospheric deposition of pollutants on inland surface waters may represent an important input and should be quantified, especially for areas with many large lakes. In areas with no lakes and only minor rivers, very small inputs can be expected and this contribution may be neglected. Atmospheric deposition to land eventually enters surface waters via percolation through soil and via groundwater, but this supply is generally handled as an integrated part of the input from the land environment.

Atmospheric deposition of nitrogen, phosphorus, heavy metals and organic pollutants can be obtained by monitoring wet and dry deposition over open land. Deposition from local point sources can be estimated by monitoring emissions to air and apply local-scale dispersion models. In order to assess the total deposition over a catchment area appropriate wet and dry deposition rates should be multiplied by the area of inland surface waters (e.g. rivers, lakes, reservoirs) in the catchment.

EMEP (www.emep.int) can provide regional and national nitrogen deposition rates for specific years in 50x50 km grids, based on national monitoring results (emission and deposition) combined with a common modeling approach for Europe and the North Atlantic. Quantification of phosphorus deposition is not part of the EMEP programme.

EMEP can provide deposition maps and data for the following pollutants;

- nitrogen, NHy and NOx (Figure 20.)
- metals (Cd, Hg, Pb)
- particulate matter
- some persistent organic pollutants (POPs)

At present the following POPs have been modeled by EMEP:
PCDD/Fs, B[a]P, HCB. Development is in progress for several others substances.

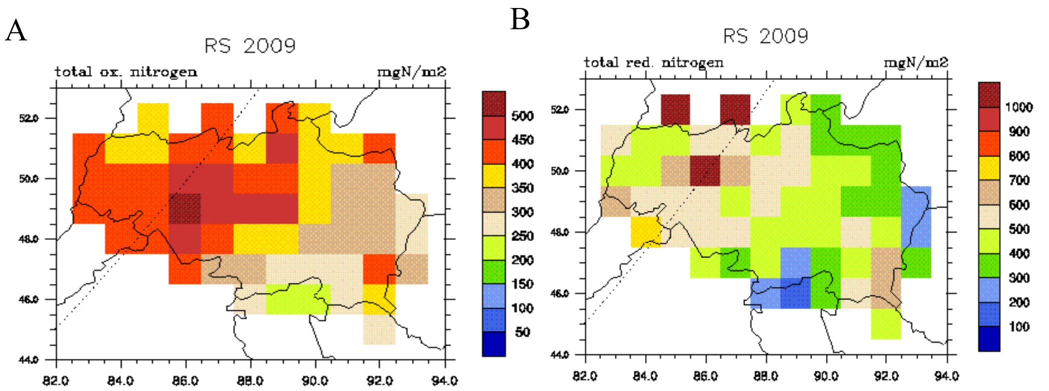

Figure 20. Deposition of oxidized (A) and reduced (B) nitrogen over Serbia 2009 as calculated by 50x50km grids over Serbia (mgN/m^2 yr): Source EMEP

5.2. Quantification of Natural Background Loads

Natural background loads to water bodies refer to losses that occur from land areas that are unaffected by human activities (except for anthropogenic atmospheric deposition). These include losses from unmanaged land and the part of the losses from managed land that would occur irrespective of anthropogenic activities (e.g. agriculture).

In many cases nutrient losses from unmanaged land can be used as an approximation for natural background losses. Unmanaged land areas include:

- unmanaged forest and woodlands;
- unmanaged heathland;
- shrub land;
- unmanaged bogs, wet meadows and wetlands;
- abandoned agricultural land.

Natural background losses can be estimated using different approaches or a combination of approaches. The most common approaches are:

A. Monitoring of small unmanaged catchment areas lacking point sources;
B. Monitoring of concentrations of pollutants in soil water or groundwater unaffected by human activity;
C. Use of calibrated nutrient pollution models.
D. Sediment-water relationships providing historic data from sediment cores.

The use of results from defining reference conditions under the Water Framework Directive will assist in this regard. In (Table 7.) estimated natural background nutrient losses as reported to HELCOM are shown. The countries have used different methods to estimate the background losses.

Table 7. Examples of annual natural background losses and flow-weighted concentrations of nutrients as reported by HELCOM countries: Source: Fifth Pollution Load Compilation. Baltic Sea Environment Proceedings No 128. 2011.

Countries	Total nitrogen (kg/ha)	Total nitrogen (mg/l)	Total phosphorus (kg/ha)	Total phosphorus (mg/l)
Denmark	2.6	1.5	0.09	0.05
Finland	0.5-2.0		0.02 – 0.06	
Estonia	3.0-3.2	1.1	0.11	0.04
Germany		1.0		0.25
Lithuania	0.2-1.6	0.42-0.72	0.02-0.07	0.01-0.04
Poland	0.1-9.0	0.3-1.2	0.01-0.28	0.04
Sweden	0.5-4.8	0.2-1.4	0.01-0.18	0.01-0.06

5.3. QUANTIFICATION OF POLLUTION LOAD FROM AGRICULTURAL LAND

5.3.1. INTRODUCTION

Many factors influence losses of nitrogen and phosphorus, as well as other pollutants, from agricultural land to inland surface waters. A multitude of processes and pathways is involved, as illustrated in (Figure 2. Chapter 1.3.). Arable land is especially complicated, since cultivation and management varies considerably between regions and also from year to year. Pastures on the other hand represent a more stable land-use characterized by long-term or permanent grass-cover.

Quantification of nutrient loss from agricultural land can be made using the same principles as described in Chapter 5.2. Monitoring can be performed at different geographical scales, but models are often used either to quantify losses or to calculate leaching coefficients. A large number of models have been developed to quantify nutrient losses from arable land (See also Chapter 8.).

It is important to recognize that losses of nutrients and metals from agricultural land is composed of both an anthropogenic and a natural background component (see also Chapter 5.2.). Organic pollutants like pesticides are anthropogenic in origin.

5.3.2. LEACHING COEFFICIENTS

Leaching coefficients can be expressed in two different ways:

a) Specific loss rates, given as amount per surface area (e.g. kg/ha)

b) Land use coefficients, given as concentration (e.g. mg/l) in runoff water from a field or a small catchment dominated by arable land. To estimate the actual losses per unit of time from a defined area, concentrations should be multiplied with the amount of runoff water during the selected time period.

Leaching coefficients for agricultural land vary with the climatic situation as well as with soil characteristics, but also crop type, land management and the slope of the fields near streams are important factors.

Picture 2. Agricultural area in the Kolubara catchment with the different slope

All these characteristics vary within an agricultural landscape, and in order to estimate the total input of pollutants to water a whole set of leaching coefficients are required. This is a challenging task, and generally some simplifications have to be introduced, e.g. by concentrating on the most important determining factors according to (Table 8.)

There are several ways of assessing the required leaching coefficients. The most common ones, namely controlled experiments/plots and the small catchment approach, are described below.

Table 8. Main factors affecting the loss of pollutants from agricultural soils

Factor /Pollutant	Nitro-gen	Phos-pho-rus	Cadmi um	Lead	Mercu ry	Pestici des*
Tempera-ture						x
Runoff	x	x	x	x	x	x
Suspended solids in runoff	x	x	x	x	x	x
Soil texture	x	x	x	x	x	x
Soil chemistry						
-acidity			x			
-organic matter				x		x
Crop cover**	x	x				x
Soil manage-ment ***	x				x	x

** Pesticides are only spread on certain crops and are thereby dependent on crop cover. Environmental effects of organic pollutants depend to large extent on the physico-chemical properties of the substance, which determine degradation rates, affinity for air, water or soil and transport of the substance to surface and ground water.*
*** A permanent grass cover efficiently reduces erosion and surface losses. Effects of other crops largely depend on the management of the specific crop.*
**** Soil management includes e.g. fertilization, plowing and irrigation, and the effects of these differ considerably depending on soil texture.*

Controlled experiments

The first approach is to derive leaching coefficients from experimental field plots with a single crop and controlled management. Concentrations in soil water or in the drainage system are measured. In order to cover all combinations of crops, fertilization regimes, soil types and climatic conditions, a large number of experiments are needed. Generally only the most common combinations can be studied.

Soil water can be sampled by lysimeters installed in the soil. These can be classified as tension lysimeters or zero-tension lysimeters. Tension lysimeters extract soil water samples by applying a suction at a specified soil depth, normally just below the rooting zone. The samples can then be brought to the laboratory and analyzed for its chemical compounds (Figure 21.). Zero-tension lysimeters only collects freely draining water (soil water potential near zero), e.g. in groundwater or water in soil drainage systems.

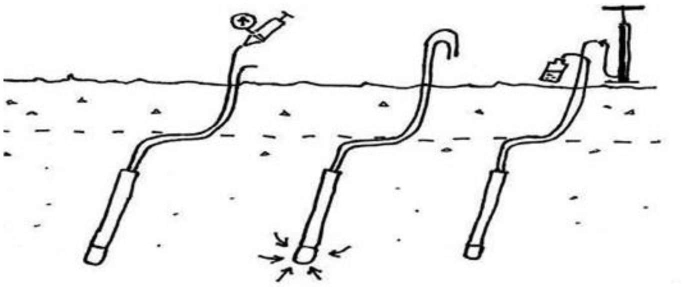

Figure 21. Installation of suction cup lysimeters. Suction is achieved by a pump. (Source: Lital & Tattari 2012)

An experimental set-up should contain at least three replicate plots to monitor the impact of selected treatments like fertilization rates or different crops. These plots should be established on land with similar soil texture. Untreated plots should be used for comparison in all experiments.

5.3.3. WATER QUALITY ASSESSMENT IN SMALL WATERSHEDS

Background

In this approach, long-term monitoring of small catchments is applied. The selected catchments should be dominated by agricultural land and have no larger settlements in them. The data collected will give an estimate of the integrated losses from a whole agricultural landscape. Generally, there are also other pollution sources within a catchment, e.g. discharge from households, roads or forest management. Estimates should be made in order to determine the influence of these additional sources, the influence of which might be compensated for. Small sources can be neglected.

Monitoring of the water quality parameters N, P, pesticides, metals, suspended matter, TOC, and DOC can be used as a tool to determine the load of for example nutrients causing eutrophication on the water bodies from arable land. In Sweden there is a national monitoring programme for agricultural land, which is divided in several sub-programmes. One of these sub-programmes include studies in small watersheds with 21 stations representing different climate and geological characteristics in Sweden. The exact location of the watershed is not registered so that farmers are encouraged to give information on crops and how much manure and fertilizers they apply, as well as possible measures they have taken to reduce nutrient leakage. This information provides possibilities to determine whether farmer practices and measures give response in nutrient leakage concentrations.

Figure 22. Outlet from watershed F26 in Sweden, May 2010. Photo: Lovisa Stjernman Forsberg.

Recommendation for monitoring setup

The selection of the small monitoring watersheds should be done by a GIS analysis based on shape files of:

- Digital Elevation Model (DEM),
- Land use,
- soil map,
- climate map,
- farming practice representation (best possible crop map using table data and community shape file and fields/pasture land use map),
- point source locations,
- urban wastewater sewage coordinates

The following selection criteria should be used:

- Watershed areas should represent the variation in climate, soils and overall farming practice (types of crops as vegetables, corn or potatoes, or energy crops, intensive or extensive farming, pasture or grown fields etc).
- The land use in the watershed should be dominated by the investigated land use; at least 50% for arable land, or >70% forest.
- The watersheds should be reasonable small (about 10 km^2) to be able to do a future inventory of the applied farming practices with reasonable efforts.
- The watersheds should have no or small contributions from point sources such as industries or wastewater.
- There should be suitable monitoring sites in the stream to monitor the water level and/or flow.

Monitoring and sampling:

- The flow should be monitored near the mouth of the watershed, preferably using flow measurements at the time for sampling of water quality. The salt-dilution method can be used which is very useful for measuring flow in small streams and only requires a conductivity meter.
- Monitor the water and air temperature at least during sampling for water quality and flow.
- The sampling for water quality should be done at different flow regimes (high, about the same as the yearly mean, and low). Often high flow results in high release of nutrients due to flushing of nutrient pools in the soils.
- The sampling should be done at least at 5 occasions during the initial sampling campaign.
- The samples should be analysed for
    - priority 1. Total N (or a summary of inorganic substances and organic substances), total P (or summary of substances),
    - priority 2. metals, pesticides, Total Organic Carbon, Dissolved Organic Carbon,
- Additional parameters as deposition of N, temperature in air, sun hours, rainfall and snow are as well important for interpreting the transport of nutrients and other pollution. Most of these parameters are available in

national as well as in international databases and might not need to be monitored.

It is recommended to continue monthly sampling, at least at some stations, for an intended period (at least 1 year). The interpretation of the results could benefit a lot if flow-proportional monitoring is possible (i.e. if sampling could be done automatically at high flow occasions or during intensive long rain periods.)

Picture 3. Measuring water flow using *Ott Nautilus* instrument on small experimental watershed Milanovac (Beomuzevic site)

During the Project, four small experimental watersheds were defined and water quality and water quantity were measured twice. Water flow was determined by using the instrument HACH HQ 14d and using the salt-dilution method. The salt-dilution method confirmed that it could be used if there are no conditions for using the instrument. The measured parameters are given in (Table 9.).

Table 9. The measured parameters in small experimental catchments

Station	Unit of measurement	Beomuzevic	Bukovi	Berkovac	Kozelj
River		Milanovac	Kozlica	Berkovacka reka	Kozeljica
Longitude(WGS84 UTM)		7399797	7413859	7431921	7449146
Latitude(WGS84 UTM)		4906080	4888726	4896027	4896012
Date		19/05/2012	19/05/2012	19/05/2012	19/05/2012
Vmax (on surface)	m/s	0.379	0.84	0.688	0.402
h max	m	0.09	0.17	0.24	0.33
B	m	1	3.5	2.5	2.7
Vsr	m/s	0.313	0.549	0.422	0.33
F	m2	0.055	0.353	0.439	0.666
Q	m3/s	0.017	0.194	0.185	0.22
Q (the salt-dilution method)	m3/s	0.013	0.166	0.177	0.21
Temperature (water)	°C	11.9	11.5	14.2	14.6
Temperature (air)	°C	19.6	20.6	22.6	19.8
Total ammonium	mg/lN	0.06	0.17	0.22	0.31
Nitrite	mg/lN	0.009	0.005	0.008	0.008
Nitrate	mg/lN	1.1	0.4	0.8	0.4
Total organic nitrogen	mg/lN	3.1	0.22	1.57	1.28
Total nitrogen	mg/lN	4.3	0.8	2.6	2
Orthophosphates	mg/l P	0.063	0.041	0.035	0.027
Total phosphorus	mg/l P	0.081	0.076	0.054	0.063
Total organic carbon (TOC)	mg/l C	4.8	3.1	3.7	4.2
Date		19/11/2012	19/11/2012	19/11/2012	19/11/2012
Vmax (on surface)	m/s	0.039	0.069	0.19	dry riverbed
h max	m	0.05	0.11	0.08	dry riverbed
B	m	0.58	0.92	0.71	dry riverbed
Vsr	m/s	0.034	0.064	0.225	dry riverbed
F	m2	0.02	0.065	0.034	dry riverbed
Q	m3/s	0.001	0.004	0.008	dry riverbed
Q (the salt-dilution method)	m3/s	0.00038	0.00326	0.00679	dry riverbed
Temperature (water)	°C	7.4	7.4	9.2	dry riverbed
Temperature (air)	°C	7.6	8.3	8.6	dry riverbed
Total ammonium	mg/lN	0.08	0.06	0.04	dry riverbed
Nitrite	mg/lN	0.004	0.004	0.008	dry riverbed
Nitrate	mg/lN	0.8	0.3	0.4	dry riverbed
Total organic nitrogen	mg/lN	0.1	0.1	0.1	dry riverbed
Total nitrogen	mg/lN	0.96	0.42	0.52	dry riverbed
Orthophosphates	mg/l P		0.026		dry riverbed
Total phosphorus	mg/l P	0.031	0.057	0.023	dry riverbed
Total organic carbon (TOC)	mg/l C	3.5	2.5	2.7	dry riverbed

5.3.4. CALCULATION OF LOSSES FROM AGRICULTURAL SOILS

Calculations can be made manually or with some numerical modeling tool. The principle is to multiply the land area with a leaching coefficient (*Leach Conc*) for the study area. Depending on how the leaching coefficient is expressed the loss of a pollutant is calculated as:

1) Area (km^2) x Areaspecific L*coeff* (kg//km^2 yr) = Annual loss (kg/yr)

2) Area (km^2) x Leach*Conc* (mg/l) x runoff (l/s km^2) x 0.365 x 86.4 = Annual loss (kg/yr)

Applying area-specific coefficients is technically easier than to use concentrations, since they can be applied without information about runoff. However, this type of coefficient does not take into account temporal variations in runoff, and in years with extreme weather conditions they will not produce reliable results. Typically, there is a correlation between concentration and runoff, and thus leaching coefficients should not be applied in areas with hydrological conditions that are very different from the area where they were derived.

Soil characteristic, crops and soil management may have a profound influence on the leaching coefficients for nutrients. It is difficult to cover all combinations of these factors occurring over a large area. If there is a choice, soil texture should be considered in the first place and then crop type. For heavy metals, concentrations in soil may be an important factor. Lead is e.g. strongly bound to organic matter in soil and leaching can be low even if the soil pool is relatively large. Leaching of lead can anyway occur if concentrations reach very high level.

A detailed soil map is thus an important tool for selecting proper leaching coefficients. In areas described by scattered (not systematic) soil sampling the results has to be interpolated to describe the spatial variation of soil properties over the study area. For organic pollutants such as pesticides, crop distribution is important since the pesticide substances applied on the fields are specific for different crops. Effects of organic pollutants depend to large extent on the physico-chemical properties of the substance, which determine degradation rates, affinity for air, water or soil and transport of the substance to surface and ground water.

5.3.5. MANUAL FOR SOIL INTERPOLATION

Introduction

If soil texture and crop type is available in an area of arable land it is possible to estimate the leaching concentrations of nutrients, and with these nutrient losses. To be able to allocate, already available, soil-specific leaching concentrations within a catchment it is required to have as accurate knowledge as possible regarding the geographic distribution of soil texture and crop type within the catchment.

Interpolation methods are frequently used to describe spatial distributions of soil properties over various spatial scales, provided that the data are abundant and spatially dependent. If not so, i.e. data samples are few and the degree of spatial dependency is poor or unknown, as in the case of Kolubara, interpolation methods can be improved by introducing complementary information like topography, land cover, geological information etc. into the interpolation scheme. A multivariate interpolation methodology using different sources is beyond the scope of this manual and will most likely not improve the result in correspondents with the effort or cost needed to accomplish such a task.

Materials and methodology

Available soil data for the Kolubara catchment consists of a soil map at an approximated scale 1:50000 with unknown origin with soil types according to *World Reference Base* (WRB) and data from 88 spatially distributed soil profiles. Provided that the soil map is accurate, this resolution, is more than necessary, considering this specific task.

Soil classification should be based on the *Food and Agriculture organization of the United Nations (FAO)* soil texture classes according to (Table 10.). This information is not present in the Kolubara soil map but can be determined from texture data from the investigated soil profiles. Soil classification should be based on the texture of fine soil (grain size distribution < 2 mm) determined on topsoil samples. The soil classes form different weight combinations of sand, silt and clay fractions.

The proposed method for creating soil texture maps is to use the existing soil map to determine spatial distribution of the soil types and then use data from the soil profiles to determine the texture of the defined spatial soil units.

Table 10. FAO soil texture based on the USDA particle-size classification

Common names of soils (General texture)	Sand %	Silt %	Clay %	Textural class
Sandy soils (Coarse texture)	86-100	0-14	0-10	Sand
	70-86	0-30	0-15	Loamy sand
Loamy soils (Moderately coarse texture)	50-70	0-50	0-20	Sandy loam
Loamy soils (Medium texture)	23-52	28-50	7-27	Loam
	20-50	74-88	0-27	Silty loam
	0-20	88-100	0-12	Silt
Loamy soils (Moderately fine texture)	20-45	15-52	27-40	Clay loam
	45-80	0-28	20-35	Sandy clay loam
	0-20	40-73	27-40	Silty clay loam
Clayey soils (Fine texture)	45-65	0-20	35-55	Sandy clay
	0-20	40-60	40-60	Silty clay
	0-45	0-40	40-100	Clay

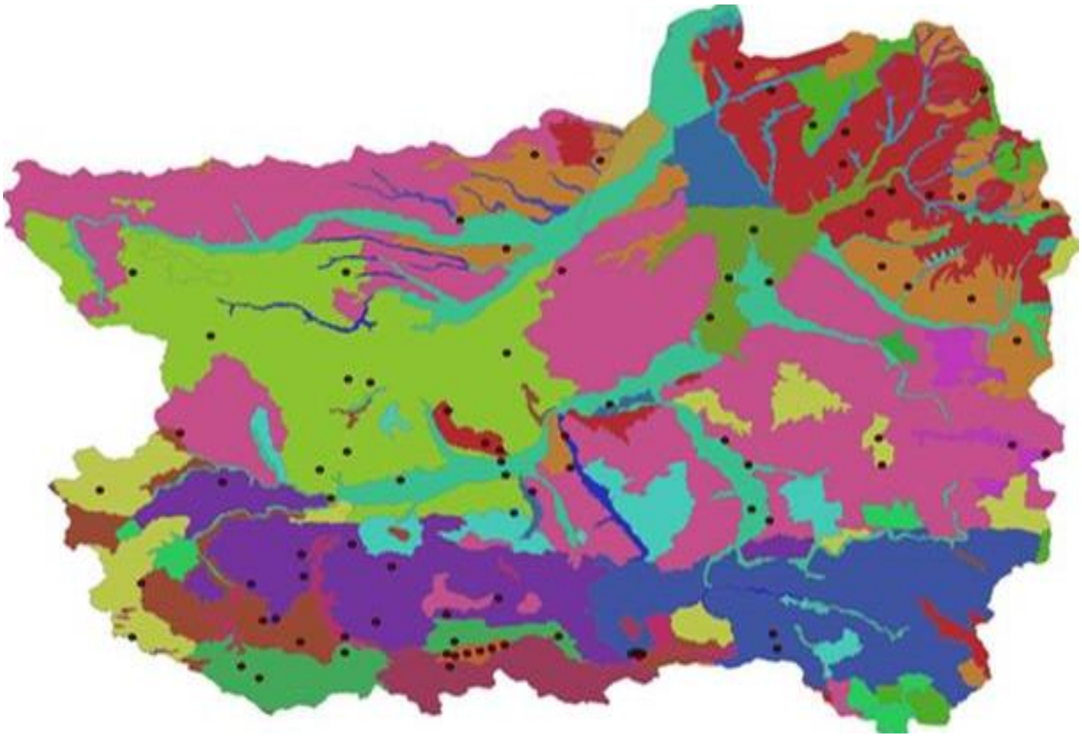

Figure 23. Soil map of Kolubara with sampling points indicated

Visual inspection of the soil map with soil profiles superimposed reveals that several soil profiles may occur within one WRB soil type. This problem can be solved by averaging the topsoil distributions of sand, silt and clay to respectively WRB soil type.

Walk trough

To accomplish the above proposed solution in an ESRI ArcGis environment is to:

1. Compile a new soil profile table using only the topsoil content of sand, silt and clay from each soil profile. The result should be a table with at least 4 columns, unique sample id, sand content, silt content and clay content.
2. Link the new topsoil table with the spatial features representing the soil profile samples and save the result to a new feature layer.
3. Spatially join the WRB soil type polygons with the new feature class using the summary functions and mark all statistics.
4. Analyse the resulting feature layer for large standard deviations or variances and investigate extreme values
5. Use the resulting to estimate the content of sand, silt and clay in each WRB soil type class.

Recommendation

The proposed solution is rough but straight forward and easy to logically understand. Due to the nature of soil forming processes and resulting coherence of soil texture properties, it is difficult to interpolate soil texture using general continuous interpolation method. Therefore it is suitable to use the soil class distribution available in the soil map. One completely different approach is to interpolate the topsoil content of sand, silt and clay in three separate layers and to combine the result to a new topsoil layer using the texture classification according to (Table 10.).

One additional approach is to investigate if the data available from *European soil database*[1] is sufficient to solve the task. Relevant leaching coefficients for agricultural land may be difficult to find. In Serbia no site-specific coefficient are yet available, and for the present information from other countries has to be used.

5.3.6. Manual to the input data generator for Fyris NP - leaching concentrations[2]

Leaching concentrations from land use with combinations of crops and soil types has been calculated for nitrogen based on concentrations produced in the EUROHARP project derived for Kaposvar catchment in Hungary using the model SOILNDB (Swedish University of Agricultural Sciences). The conditions in Kaposvar is similar but not the same as the conditions in Kolubara basin, which means that the type concentrations are very uncertain. Monitoring in small headwater watersheds in Kolubara would improve the certainty of concentrations and preliminary results have been used to reduce the leaching concentrations proportionally to adjust for local climate, soil, and agricultural practices.

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[1] http://eusoils.jrc.ec.europa.eu/ESDB_Archive/ESDB/index.htm

[2] Leaching concentration is also called type concentration.

The similarity of climate between Kaposvar and Valjevo can be seen in (Figure24.) and (Figure 25.) [1]

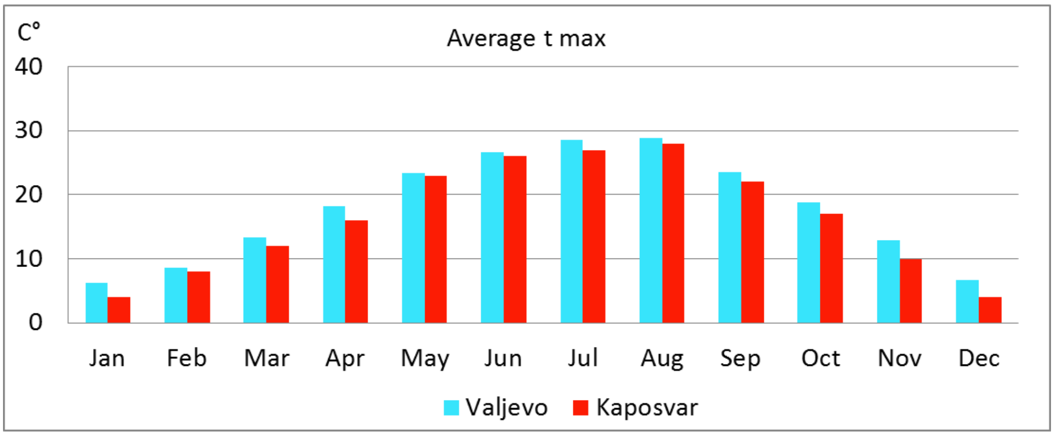

Figure 24. Average maximum temperature per months in Valjevo and Kaposvar

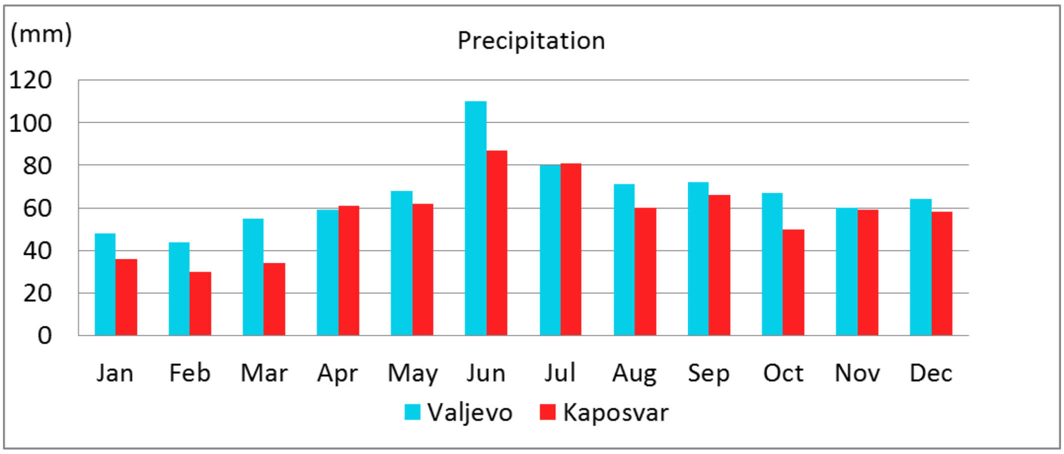

Figure 25. Average precipitation per months in Valjevo and Kaposvar

For phosphorous, no calculations or monitoring results of leaching concentrations from arable land are available in the nearby region to our knowledge, other than the sparse monitoring in small catchments performed within this project. However, ICECREAMDB model calculations illustrated in (Figure 27.) have been done in 22 regions in Sweden (Brandt et al 2008[2]) and produced leaching concentrations with a multiple regression relationship on crop, soil types, slope of arable land within 50 m to the river and the mean of leachable P concentration in the soil of the arable land within the catchment. The regression relationship and coefficients for the regression equation in the Southernmost region in Sweden was used for calculations of leaching concentrations in Kolubara. Preliminary results from monitoring performed in small Kolubara headwater catchments,

[1] Source: (1) http://www.myweather2.com/City-Town/Hungary/Kaposvar/climate-profile.aspx
(2) METEOROLOGICAL YEARBOOK 1 (1991-2010), CLIMATOLOGICAL DATA

[2] Nutrients load on the Swedish marine environment 2006
http://www.naturvardsverket.se/Documents/publikationer/978-91-620-5995-8.pdf

have been used to reduce the leaching concentrations proportionally to adjust for local climate, soil, and agricultural practices

Figure 26. Map of location of Kolubara and Kaposvar, Hungary. Distance between the Kolubara and Kaposvar is 271 km^2. Source: Google earth

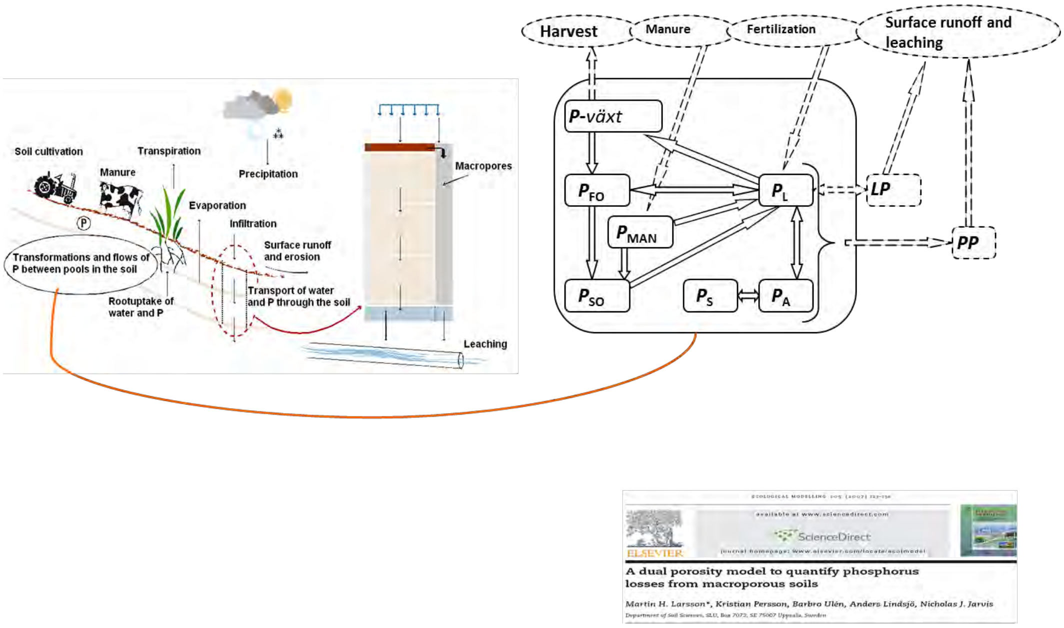

Figure 27. Illustration of the ICECREAMDB dynamic model used to develop leaching concentrations of phosphorous

Leaching concentrations of nitrogen were calculated in Kaposvar only for a combination of 6 crop types dominating the area and a mean of all crop types on the FAO classification soil type "Loam" (Table 11.) and for pasture on Loam (Table 12.).

Table 11. Leaching concentration for different crops (mg N/l) calculated for Kaposvar, Hungary

Crop	Loam
Maize	12.9
Winter wheat	16.5
Winter rape	16.8
Sunflower	15.0
Winter rye	15.7
Winter barley	13.5
Mean	14.8

Table 12. Leaching concentration of pasture (mg N/l) calculated for Kaposvar, Hungary

Crop	Loam
Pasture	4.3

To be able to calculate the mean agricultural leaching concentration for a catchment as needed in FyrisNP the nitrogen type concentrations have been extrapolated to other soil types using leaching concentrations calculated for an area in southern Sweden (production area 1a, (Table 13.)). Leaching concentration is sometimes named type concentrations.

Table 13. Leaching (type) concentrations of nitrogen (mg/l) calculated for southern Sweden; Production area 1a (Southernmost Sweden)

	sand	loamy sand	sandy loam	loam	silt loam	sandy clay loam	clay loam	silty clay loam	silty clay	clay	mean
area (%)	0	0	72	25	0	3	0	0	0	0	
spring barley	20	15.6	12.4	11	10.1	9.1	7.1	6.1	4.7	2.7	12
winter wheat	16.5	13	11.4	10.4	9.6	6.5	5.3	4.5	3	2.4	11
Ley	11.6	9.6	6.2	4.8	3.8	4.1	2.7	2.2	1.8	1.6	5.8
Sugar beets	17.7	11.9	9.6	8.5	8	4.8	3.7	2.9	1.7	1.3	9.2
winter rape	22.2	19.3	16.1	13.8	12.2	10.6	7.8	6.6	4.7	3.9	15.3
green fallow	14.6	13.1	9.6	7.9	6.4	7	4.9	4.2	3.3	2.7	9.1
Oats	19.6	15.8	13	11.8	10.9	9.7	7.7	6.7	5.1	3.1	12.6
spring wheat	19.1	15.6	13.3	12.2	11.5	10.2	8.2	7.1	5.2	4.3	12.9
winter rye	15.7	13.9	12.7	11.9	11.4	9.3	7.9	6.7	4.5	3.5	12.4
spring rape	-	-	-	-	-	-	-	-	-	-	-
potatoes	29.2	26.3	23.5	20.4	18.3	18.4	13.6	11.7	8.7	7.1	22.6
mean	17.4	13.9	11.3	10	9.1	7.5	5.8	4.9	3.5	2.6	10.9

The leaching concentrations used in the template access database resulted in a complete set of soil types to the combination of the 6 crop types and mean (Table 14.).

Table 14. Calculated nitrogen leaching concentrations for the input data generator (mg/l)

	sand	loamy sand	sandy loam	loam	silt loam	sandy clay loam	clay loam	silty clay loam	silty clay	clay	Mean
Maize	20.64643	16.36339	13.72768	12.9	11.31161	9.115179	7.138393	6.040179	4.283036	3.075	13.28839
Winter wheat	26.17788	20.625	18.08654	16.5	15.23077	10.3125	8.408654	7.139423	4.759615	3.807692	17.45192
Winter rape	27.02609	23.49565	19.6	16.8	14.85217	12.90435	9.495652	8.034783	5.721739	4.747826	18.62609
Sun-flower	25.17857	19.95536	16.74107	15	13.79464	11.11607	8.705357	7.366071	5.223214	3.75	16.20536
Winter rye	20.71345	18.33866	16.75546	15.7	15.04034	12.26975	10.42269	8.839496	5.936975	4.617647	16.35966
Winter barley	24.54545	19.14545	15.21818	13.5	12.39545	11.16818	8.713636	7.486364	5.768182	3.313636	14.72727
Mean	25.752	20.572	16.724	14.8	13.468	11.1	8.584	7.252	5.18	3.848	16.132

The leaching concentration of phosphorous described by multiple regression on soil, crop, slope and P leachable soil concentration is illustrated by an example in (Figure 28.) and examples of soil and crop to corresponding a, b and c coefficients are presented in (Table 15.)

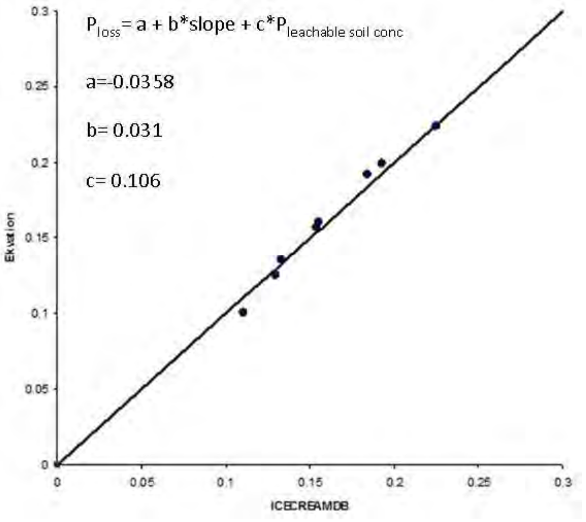

Figure 28. Example of multiple regression equation results of ICECREAMDB model on phosphorous leaching concentrations (loss) in Southernmost Sweden e

Table 15. Some examples of coefficients for the regression equation describing the leaching concentrations of phosphorous calculated using ICECREAMDB model for Southernmost Sweden. 161 combinations of soil, crop and corresponding a, b and c are included in the type conc generator for phosphorous.

a	b	c	Soil type	Crop
-0.01708	0.005279	0.041969	SiltyClay	Potatoes
-0.01552	0.000504	0.006919	LoamySand	spring wheat
-0.0148	0.000955	0.011387	SandyLoam	Sugarbeets
-0.01424	0.004029	0.028539	Clay	Oats
-0.01406	0.000483	0.006211	LoamySand	Oats
-0.01378	0.000516	0.006246	Sand	Potatoes
-0.01346	0.000479	0.005964	LoamySand	Spring barley
-0.0132	0.000499	0.005885	Sand	spring wheat
-0.01283	0.000495	0.005853	LoamySand	Sugarbeets
-0.01254	0.003662	0.03199	SiltLoam	Extensive Ley
-0.01254	0.003662	0.03199	SiltLoam	Winter barley
-0.01254	0.003662	0.03199	SiltLoam	Maize
-0.01254	0.003662	0.03199	SiltLoam	spring rape
-0.01254	0.003662	0.03199	SiltLoam	Sunflower

Instructions

Preparations

1. Produce a table of area of soils on agricultural land use (km^2) per catchment area with the following format:

catchment soil		
Catchment Id	soil type name	arable area per soil type km2
1. Obnica	loam	60
1. Obnica	loamy sand	60
1. Obnica	sandy loam	7
2. Jablanica	loam	50
2. Jablanica	loamy sand	50

Only soils types included in the (Table 15.) are allowed. If there are other soil types it has to be replaced by the soil type "Mean". Catchment id do not have any specific format demands other than it should be the same in both catchment soils table and catchment crop table.

2. Produce a table of percentage of the agricultural land use producing each crop type per catchment with the following format:

catchment crop			
Catchment Id	crop name	completed crop	percentage of arable
1. Obnica	wheat	winter wheat	30
1. Obnica	sunflower	Sunflower	20
1. Obnica	fruit	Mean	50
2. Jablanica	wheat	winter wheat	30
2. Jablanica	sunflower	Sunflower	20
2. Jablanica	fruit	Mean	50
3. Gradac	wheat	winter wheat	30
3. Gradac	sunflower	Sunflower	20

Only crop types included in (Table 15.) are allowed in the catchment crop table. If other crop types are produced in the catchment, for example ”fruit”, it needs to be replaced in the column ”completed crop” with the crop type ”mean” (see example catchment crop above).

3. Produce a table of catchment mean leachable phosphorous concentration in the arable soil and catchment mean slope within 50 m (on each side) from river:

Catchment_slope_P		
Catchment Id	P	slope
1. Obnica	3.10040313549391	0.83
1. Obnica	3.14514045620615	0.73
1. Obnica	3.14514045620615	0.55
2. Jablanica	4.49073775670936	1.13
2. Jablanica	6.10537625812864	2.06
2. Jablanica	3.95688346016685	0.24
3. Gradac	3.18804691621678	7.02

Working with the access templates

4. Open the access database ”input generator N arable type conc.accdb”.
5. Open the catchment crop table.
6. Copy only the data not header lines in the excel table catchment crop file you have prepared.
7. Paste the data into the catchment crop table in the database. Check that no extra lines are included and that all your data has been included.
8. Save the access data base
9. Open the catchment soils table in the access database.
10. Copy only the data not the header lines in the excel table catchment soils file you have prepared.
11. Paste the data into the catchment soils table in the database. Check that no extra lines are included and that all your data has been included.
12. Open the queries view in the database.
13. Double click the Q1_ query. That run the query and open the results.
14. Double click the Q2_ query. That run the query and open the results.
15. Copy the catchment id and mean type concentrations from Q2_query results and paste into the Fyris NP input file.

Phosphorous type conc generator

1. Open the access database ”input generator P arable type conc.accdb”.
2. Open the catchment crop table.
3. Copy only the data not header lines in the excel table catchment crop file you have prepared.
4. Paste the data into the catchment crop table in the database. Check that no extra lines are included and that all your data has been included.
5. Save the access database
6. Open the catchment soils table in the access database.
7. Copy only the data not the header lines in the excel table catchment soils file you have prepared.
8. Paste the data into the catchment soils table in the database. Check that no extra lines are included and that all your data has been included.
9. Open the catchment_slope_P table in the access database.
10. Copy only the data not the header lines in the excel table catchment slope P file you have prepared.
11. Paste the data into the catchment slope P table in the database. Check that no extra lines are included and that all your data has been included.
12. Save the access database
13. Open the queries view in the database.
14. Double click each of the Q1_ query to Q5_query in chronologic order. That will run the query and open the results.
15. Copy the catchment id and mean type concentrations from Q5_query results and paste into the Fyris NP input file.

5.4. QUANTIFICATION OF LOSSES FROM NON-AGRICULTURAL MANAGED LAND

Losses from non-agricultural managed land include:

- managed forest;
- managed heathland;
- other land-use categories not included as agricultural land or unmanaged land.

In principle a forest or a heathland is considered managed land as soon as it is regulated by human activity. If at least one of the following activities are present in the area it could be classified as managed.

- planting, harvesting, or burning;
- application of fertilizer and/or manure;
- major soil activities (ploughing, new tiles or ditches etc.);
- animal grazing.

The quantification procedures for phosphorus and nitrogen losses from non-agricultural managed land are in principle the same as for agricultural land, including appropriate monitoring and/or modeling approaches.

There are no leaching coefficients available for this kind of land use in Serbia, but (Table 16.), contains some provisional figures. In Sweden, a nitrogen coefficient of about 1 mg/l is used for clear-cuts which is added to the background leaching of 0.5 mg/l. For phosphorus the losses from clear-cuts are calculated using the factor 1.6 times a background loss of ca 0.01 mg/l. Forests in Serbia are mainly deciduous and grow on less acid soils, which probably would result in higher nutrient losses, especially for phosphorus.

Nutrient leaching from other land cover like managed wetlands and heathlands is difficult to assess. The management is normally grazing.

Table 16. Proposed leaching coefficients for Serbia (mg/l)

Land us category	Nitrogen	Phosphorus
Forest land	0.75	0.08
Forestry (clear-cuts)	1- 5	0.05 – 0.2
Wetlands; heathlands	0.5- 2	0.05 - 0.2

5.5. QUANTIFICATION OF LOAD FROM HOUSEHOLDS IN URBAN AND RURAL AREAS

Households not connected to public sewerage systems are considered as diffuse sources and include both scattered dwellings in rural areas and households in urban areas without connection to networks. The main pollutants entering water bodies from these sources are nutrients, mainly phosphorus, but also nitrogen, pathogens, organic matter (Biological Oxygen Demand, BOD), household-related chemicals and pharmaceuticals. Technical solutions for treatment of wastewater from households not connected to sewerage are highly variable and both the efficiency of the treatment facility and the distance to surface waters will influence the quantity of pollutants reaching the surface waters.

Households in urban areas connected to collection systems are considered point sources and the pollutants are normally added directly into water bodies. In networks without treatment plants no retention can be accounted for. Wastewater treatment plants with only biological treatment (secondary treatment) can remove about 90 % of the incoming organic matter but only 30 % of the nitrogen and up to 80% of the phosphorus. Higher levels of phosphorus removal require supplementary chemical treatment.

The quantification of losses of BOD, nitrogen and phosphorus to water bodies should be based on average specific loss coefficients, taking into account the level of water consumption, treatment methods, pathways of discharge, and distance from the water bodies.

The assessment of loads from unconnected households could be made on the basis of local, regional or national statistics. Ideally, registers, databases or maps should be established providing information on:

- the number of households not connected to sewerage systems
- the number of people living in the households, taking into account the "part of the year inhabitants" (e.g. offices, shops, hotels, tourist accommodations and secondary houses)
- the wastewater treatment technology
- location of the households in relation to watercourses (if available) and soil conditions (which influences the fraction of the load that actually reaches the surface waters).

The annual amount of nutrients, BOD and chemicals ending up in the sewer as a result of excretion, dish-washing, food preparations and other activities in an average household is the starting point for the calculations. In (Table 17.) are given standard values used in Sweden referring to the 2010 situation, for households with water-flushed toilets.

Table 17. Standard values for annual amount of BOD, nitrogen and phosphorus added to wastewater per person in Sweden. (Source: Ek, M. et al. 2011)

Type of detergent	BOD_7 (kg/p/yr)	N-tot (kg/p/yr)	P-tot (kg/p/yr)
Sweden; P - containing	27	5.4	0.77
Sweden; P - free	27	5.4	0.62

Table 18. Load coefficient used for calculation of loads from populations. (Source: Danube Water Management Plan)

Category	BOD_5 g/capita/day	Total N g/capita/day	Total P g/capita/day
Population connected to sewer networks (no treatment)	60	8.8	1.8
Population not connected to the sewer systems	0	3.1	0.4

These amounts would be typical for an average grown-up person staying permanently at home. In reality, most persons periodically stay out of home for work, school or vacation. Thus, the values should be reduced accordingly. An average figure for a community population is to spend 60-65% of their time in their home.

The actual load from a household depends on what kind of wastewater treatment is available, use of P-free detergents, etc. For a whole population, standard values taking into account as many site-specific factors as possible should be used. In Serbia, load coefficients are based on literature data, adjusted to be in accordance with measurement data for selected watercourses (Table 18.). The typical Serbian situation is no wastewater treatment in urban areas. For rural areas open septic tanks are commonly used, but also many dry systems which tend to reduce the load.

The load of nitrogen and phosphorus households not connected to sewerage systems may be validated by monitoring in streams receiving nitrogen and phosphorus from many households, provided that all other main nutrient sources are known. The share coming from scattered dwellings can then be derived as a difference.

A more explicit approach would be to test existing treatment facilities by *in situ* sampling. This is more resource-demanding. It should be noted that the functioning of individual treatment facilities may vary depending on its age, construction and management.

5.6. QUANTIFICATION OF TRANSPORT OF POLLUTANTS WITH STORM WATER

Storm water is derived as precipitation runoff from hard surfaces like e.g. streets, roads, buildings and parking lots. This runoff will carry a range of pollutants to rivers and lakes, and it can also erode watercourses (streams and rivers) as well as cause flooding if the storm water collection system is overwhelmed.

Storm water contains nutrients, metals and organic pollutants. Concentrations are especially high after periods of extended droughts and during runoff at the start of a rain. Pollutants in storm water generally originate from atmospheric deposition, car fuel exhaust, leaching from surfaces as well as from mechanical erosion of roads, tires and brakes. Water and air pollution due to salting and sanding of roads is a large issue in areas where temperature below the freezing point is common. The pollution level is dependent on traffic intensity, temperature, road moisture, use of metal dub tires, sand and salt application.

The transport to a receiving water body can be estimated with reference to land use, precipitation, surface runoff coefficients for various land uses and the proportion of the storm water entering the recipient. In order to estimate the load, runoff should be multiplied by concentration estimates for different land uses. The load calculations should relate only to pollutants in surface runoff, and should not include the load from basic runoff such as drainage water and groundwater.

The assessment of surface areas in urban and rural environments is made by specific inventories or by generally available digital land cover maps like the European CORINE (2006). Many countries have also developed more detailed digital maps. Runoff can be estimated from precipitation data or by models. One such model is StormTac (www.stormtac.com), which calculate water flow from precipitation data and land use specific runoff coefficients and areas. Pollution load rate (kg/year) is quantified from calculated flow and from standard concentrations.

The StormTac model contains standard concentrations of storm water and base flow for 33 priority substances, estimated empirically from a large set of flow proportional field sampling data in Sweden. These are tabled as standard, minimum and maximum values and can be downloaded from the website. Concentrations are mainly derived from monitoring programs in urban areas and those related to other land use categories should be used with more care. Applications in other countries than Sweden should consider geographic difference in long-range transported air pollution on water as well as differences in use of chemical substances which could affect the presence of pollutants in recipient waters.

Storm water in urban areas are often led to sewerage networks and are thus included in the measured load from an agglomeration. In newly built areas, local systems for storm water treatment are more common. This implies that storm water should be considered a separate source in built-up areas if loads in wastewater are calculated using standard values based on population. In cases where the loads are measured in sewerage systems, the storm water is already included.

6. METHODOLOGY FOR ASSESSING RIVERINE LOAD

Riverine load is the transport of pollutants at a certain geographical point in a river. The transport of different substances integrates the loads from all upstream sources in the catchment as well as the transformation processes in the stream itself. Concentrations of different substances in the river can be used as input data to numerical models, and both concentrations and loads can be used for calibration of models and validation of the results.

Loads in small river catchments may be used to estimate leaching coefficients (see section 5.3.2.). Load data for larger rivers, containing several land use categories, may be used as a starting point for making a source apportionment (see chapter 7.) in order to develop regional or national programs of measures. The recommendations in (sections 6.1.-6.5.) are applied by reporting to the Helsinki Commission (HELCOM).

6.1. Sampling strategy

The sampling strategy should be designed on the basis of historical records. It should have the aim to cover the whole flow cycle but concentrate on periods of expected high river flow. Experience has shown that there is a positive correlation between periods of high river flow and high load, especially for suspended solids, heavy metals and nutrients.

Sampling sites should be selected from a catchment perspective. The number of sites should be determined after taking into account catchment size, location of larger point sources and land use distribution. In larger catchments the location of sites should be based on a sub-catchment delineation (see section 4.3.). Stations should be placed in several tributary rivers near the outlet to the main stream. At least one station should be placed relatively close to the mouth of the whole catchment. In a case where there are several nearby sub-catchments with similar land-use and point sources, it might be enough to monitor only one of them and extrapolate the results to the other ones.

Both runoff and concentrations can show large variations over time, especially in small streams and in agricultural landscapes. Therefore, water sampling routines allowing maximum handling of these variations should be selected. Traditionally, grab sampling with fixed time interval is used, but in rivers with large fluctuations in water flow, sampling with variable time intervals may be more appropriate. Sampling frequency should then be higher during periods of high flood periods (see section 6.3). Automatic sample collectors using flow-proportional sampling will give the best result.

6.2. Site selection

The sampling sites should be placed in an area where the water is well mixed (such as at or immediately downstream of a weir) and hence of uniform quality, otherwise it would be necessary to establish the relationship between the concentration at the sampling point and at a representative number of sampling points over the whole river cross section (established by weighting the concentrations at each sampling point by the volume of water per unit time at that point).

6.3. Flow measurement

For rivers with hydrological stations the location of these stations as well as the measurement equipment, the frequency of water level and flow measurement and the methods for calculation of annual run-off should follow the WMO Guide to Hydrological Practices (WMO-No. 168, 1975).

For rivers without permanent hydrological stations the flow measurement, equipment and methods for measurement and calculations of annual run-off should also follow the WMO Guide to Hydrological Practices.

6.4 Sampling frequency

In order to estimate the annual load in a major river, there should be a minimum of 12 datasets, collected within a 12-month period. The datasets need not be collected at regular monthly intervals but can be collected at a frequency reflecting the expected river flow pattern.

For those rivers with very high load the sampling frequency may be increased beyond the minimum 12 datasets. However, it should not be necessary to take samples more than once per week.

For rivers where the concentrations are at or below the limit of detection (LOD) for the specified determinants, the requirement for 12 datasets may be too stringent. In such cases sufficient samples should be taken to obtain a “best estimate” of the pollution load.

Thus, for some rivers it may be necessary to monitor certain determinants at the "standard" frequency of 12 datasets per year where concentrations are significantly above the detection limit, but to monitor other determinants at a reduced frequency.

6.5 Estimation of annual load

There are different methods to estimate the transport of a specific substance in a river. All methods are based on multiplication of concentrations with water flow. The ideal situation is that water flow and concentrations are measured daily, but this is rarely the case. Generally, concentrations are measured monthly or bi-weekly, which means that concentrations have to be interpolated between sampling occasions. This can be made as linear interpolation between sampling point or by an algorithm describing the relationship between water flow and concentration.

When both hydrological and hydro-chemical measurements or estimates are performed at the same station, one of the calculation methods below is recommended. If hydrological and hydro-chemical observations are not performed at the same station the flow should be calculated to the hydro-chemical station prior to the load calculation.

The methods described below are recommended by HELCOM (Helsinki Commission, www.helcom.fi).

A) Daily flow and daily concentration regression:

$$L = \tfrac{m}{n} \sum_{i=1}^{n} Q_i * C_{ri}$$

$$C_{ri} = \frac{a}{Q_i} + b + c * Q_i$$

Qi = daily flow (measured or modeled);
Cri = the regression value of concentration for the stream flow;
M = conversion factor of units;
a,b,c = coefficients typical of each quality parameter, observation station and time series;
n = number of measurements

B) Daily flow and daily concentration (interpolated)

This method utilizes interpolated concentration values at days were pollutants have not been measured.

The pollutants concentrations are measured at the days denoted by $t_i, i = 1,2,\ldots,n$. Concentrations are denoted $C_i, i = 1,2,\ldots,n$. Let t_0 and t_{n+1} be the start, respectively, the end of the year. The assumption is made that $C_0 = C_1$ and $C_{n+1} = C_n$.

Then the load L is estimated by:

$$\hat{L} = \sum_{i=0}^{n-1} \sum_{t_i < t \le t_{i+1}} Q_t \frac{C_i \cdot (t_{i+1} - t) + C_{i+1}(t - t_i)}{t_{i+1} - t_i}$$

$\sum$ =denotes summation, i.e.

$\sum_{i=0}^{n-1}$ =denotes summation of values for the index in the interval 0 to *n-1*,

an $\sum_{t_i < t \le t_{i+1}}$ =denotes summation of values for *t* in the interval t_i to t_{i+1}, but t_i is not included in the interval

The assumption that that $C_0 = C_1$ results in $C_{\text{interpolated}} = C_1, \text{for } t_0 < t \le t_1$, and the assumption $C_{n+1} = C_n$ results in $c_{\text{interpolated}} =_n, \text{for } t_n < t \le t_{n+1}$.

Concentrations are given in mg/l, run-off as l/s. To obtain a daily load multiply the estimate from the equation by 0.0864.

C) Mean monthly concentration and monthly flow

Mean monthly concentration and monthly flow:

$$L = \sum_{i=1}^{12} W_{ki} * C_{ki}$$

Wki = volume of monthly run-off;
Cki = mean monthly concentration

D) Minor rivers with few data

For minor load bearing rivers, for which 12 data sets per year is not available, the best available estimates of flow and flow-weighted concentration should be used to estimate contaminant loads. In the absence of estimates of flow and flow-weighted concentration, estimates of contaminant loads based on per capita or per hectare calculations may be used.

6.6. Flow normalisation of load data

Variation in water flow is generally the main cause of temporal variation in pollution load from diffuse sources. This suggests that it is difficult to compare loads unless differences in riverine water flow are compensated for. Water flow is largely dependent on precipitation and temperature, but also other climatic factors may have an influence.

Flow-normalization of data provides a better opportunity to make a more correct assessment of trends in the total load from a river catchment. A relatively simple way of flow-normalizing measured annual riverine load (L) during a time-period (e.g. 10 years) is to calculate a linear regression between the log-values of loads and water discharges for these 10 years. This gives the slope (b) and the intercept (a). The log average flow for the period (*q average*) is then inserted in the regression equation, which is then divided with the same equation using the log value for a particular year (*q year n*) giving the following equation for year 1:

$$L(normalized\_year\ 1) = L(year\ 1) * \frac{a + b * q(average)}{a + b * q(year\ 1)}$$

By applying this equation for all 10 years, and then back- transforming the resulting load values, a set flow-normalized load values is obtained

There are more sophisticated flow-normalisation methods; an overview is given by Silgram & Shoumans (2004) in the EUROHARP project. There are also a number of statistical tools including flow normalization available. A user-friendly tool is the MULTITREND, which is based on the EXCEL format and performs both flow-normalisation and trend analysis simultaneously. This tool and a manual can be down-loaded from the Linköping University website.

7. POLLUTION SOURCE APPORTIONMENT AND MITIGATION MEASURES

7.1. SOURCE APPORTIONMENT

In order to develop measures for abating water pollution it is important to know the loads from all pollution sources that contribute to the pollution of a particular water body. Thus, the impact from both point sources and diffuse sources has to be considered. Furthermore, basic data about the catchment and the different sources has to be collected.

In a small catchment with few pollution sources it is possible to calculate the load from each source using the methodology described in chapters 5-10 above. For large catchments with many sources it is necessary to divide the catchment into sub-catchments as a basis for organizing information on land-use, hydrological conditions, point sources and leaching coefficients. To perform a source apportionment, it is further necessary to model the loads since monitoring of all sources is expensive and also difficult, especially for diffuse sources. It is possible to calculate both gross loads and net loads in EXCEL, but it is more convenient to use an existing modeling tool (see chapter 8.). If possible, the loads from diffuse sources should be divided in an anthropogenic and a background part.

In order to conclude whether the load from a specific source in a catchment is increasing or decreasing over time, the assessment must be repeated several times, normally over a period of 5-10 years (see Figure 29.) for an example). If more than three comparable assessments of the same object have been made, it is possible to make a statistical trend analysis. This gives a better basis for assessing the changes.

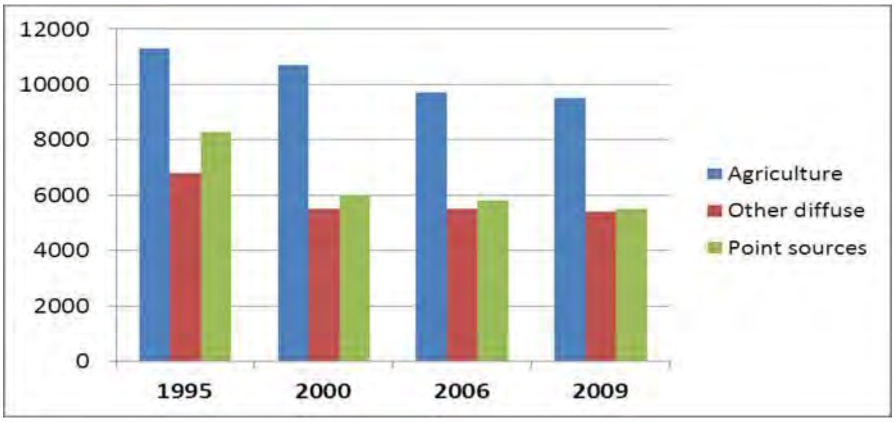

Figure 29. Anthropogenic nitrogen load from different sources from Sweden to the Kattegat Sea calculated at four occasions with the same methodology, using long term water from calculation load from diffuse sources. It appears that the load from agriculture has been decreasing during the whole time period, while point sources mainly reduced their discharges during the period 1995-2000. (Source: Ejhed et al. 2011).

In the Kolubara project the FyrisNP model has been used to calculate loads of nitrogen and phosphorus. All indata are stored in an EXCEL-file and the model calculates retention and delivers gross and net load for all sources and sub-catchments as well as for the whole catchments.

7.2. Effects of mitigation measures

By making repeated estimates of the pollution load from one or several sources, the effects of applied mitigation measures can be evaluated. For point sources such an assessment is rather straightforward, especially if emission data is available for individual plants or establishments.

Diffuse sources are more challenging in this respect, since several factors tend to make such an assessment uncertain. First of all, it may be difficult to include specific measures in the model description of the pollution load. If a measure, like e.g. a new soil treatment technique, is introduced in agriculture, the physical and chemical effect of this treatment can be taken into account by modifying the leaching coefficient. Furthermore, the extent to which this new technique has been introduced in a specific area should also be described, and possibly also on which soils and crops it is applied. This requires experimental data for a combination of all the identified confounding factors, which might not be available for recently introduced measures.

Another problem is that the load from diffuse sources often varies from year to year, depending on runoff. High losses from arable land are generally related to high runoff and are caused by surface runoff and soil erosion. By flow-normalizing the load data (se section 6.6) the variation can be reduced, and thus the possibility to draw conclusions based on a statistical analysis is improved.

There are inherent difficulties in the assessment of effects of mitigation measures and these are not easily handled. It might be impossible to include the effects of a specific measure in an assessment model or other calculation tools. In such cases an alternative is to try to understand the observed load changes by analyzing the monitoring data itself. Anyway, modeling tools are very useful in helping to identify which are the major sources to be mitigated.

8. MODELING TOOLS

8.1 BACKGROUND

When modeling diffuse loads there is a fundamental need to first organize input data in a geographic referenced database with respect to the water catchments. Geographic Information System tools, like ArcGIS, can be used to delineate catchments and to build up flow networks. All input data for modeling should be geographically connected to the catchments through the database and **GIS** tool. Once input data have been organized with a catchment a modeling tool can be applied.

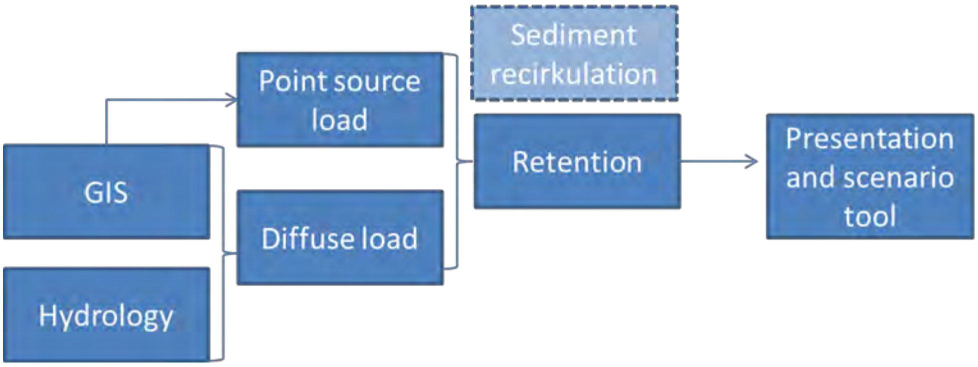

Figure 30. Illustration of basic tool boxes in load assessments and pressure analysis.

Common for all modeling tools is that the load calculation process is performed in the same order, which starts with **hydrology** by determining the runoff from the catchment (Figure 30.). The runoff can be determined by either; a) flow monitoring, b) calculated runoff calibrated against monitoring data or by c) modeling of the runoff from climate and catchment conditions. The method to determine the runoff has an impact on the model output since it determines the temporal and geographical scale of the load calculation.

Having determined the runoff, the **diffuse load** is calculated from the catchment statistics on land cover in combination with data on soils and climate, leaching coefficient of the land cover combined with GIS area, runoff data and atmospheric deposition. **Point source load** is normally a list of loads from individual facilities (annual average or temporally distributed) geographically connected to the catchment.

There are many ways to categorize modeling tools used for assessing nutrient loads in a catchment. A common feature of most models is that runoff from the modeled area has to be described by measurement data or by calibrating the model against measured time series. If no measurements are available the runoff can be modeled by using climate data and catchment characteristics.

8.2. Classification of catchment models

Catchment models should be able to model both the hydrology of the area, i.e. water flow dynamics over time, and pollution transport. A model intended for calculation of load and retention of pollutants and simulate the effects of measures should be deterministic, distributed or semi-distributed and non-stationary. A *deterministic* model has the charactistics that it always produces the same result for a given indata set, as opposed to a *stochastic* model. A model with *distributed parameters* solves the model equations for spatially defined points in the model domain and a *non-stationary* model allows the water flow to vary over time.

8.3. Conceptual or physically based models

A *conceptual* model provides a simplified description of a particular hydrological process, while a PHYSICALLY BASED MODEL is able to describe the relevant processes in a physically correct way. A physically based model is often used in conjunction with distributed catchment models because such models should be able to describe the variation in the input data and parameters in the model domain.

The division between conceptual and physically based model with respect to hydrology is useful for a practical classification of catchment models. E.g. a more process-based description of the hydrological processes that is connected to parameters that numerically describes soil, vegetation and soil characteristics provides better possibilities to describe in greater detail water flow and flows of nitrogen and phosphorus. A conceptual model uses far fewer parameters and equations describing the path of water from precipitation, via transport through the basin and finally to the recipient. A physically based model also provides more opportunities for process descriptions of a load reduction measure which makes them more suitable for evaluating the effects of measures.

The physical models are suitable for use at a local scale, from a few km^2 to 5000-6000 km^2. However, they require more detailed input data than the conceptual models, which are often based on the principle of using specified leaching coefficient multiplied by the run-off to give the load on the recipient.

The big difference between conceptual and physically based models of river catchment scale is the amount of input data in order to perform a simulation. Many of the parameter values needed for a physically based model is sometimes not available for a new region, and therefore one must apply parameter values based on experience or such found in the literature. When working with a conceptual model, it is easier to find an input (read: leaching coefficients) at catchment scale, but the results are more difficult to interpret because of a simplified description of both transport processes and effects of measures.

8.4. Hydrological and nutrient load models

To select the most suitable modeling tools for a certain application, focus should be on;

- the purpose of the modeling and expected targets,
- the spatial and temporal resolution,
- the model data requirement and data availability,
- the models tests for similar conditions,
- the modularity of models to benefit from developments,
- the user interface to the model and the user competence.

A choice between a freeware model and a commercial product contains aspects on support, availability, developments and costs of the model application.

The EUROHARP EU FP6 project evaluated and tested models with the purpose to compare different model approaches used for international reporting obligations in Europe in order to harmonize reporting procedures on diffuse sources of nutrients (EUROHARP 1-2003). Nine models were tested in seventeen different countries. Only four models included hydrological modeling (ANIMO,TRK, SWAT, EveNFlow) and only four models included enough processes to be classified as very suitable for scenario assessments (MONERIS, NL-CAT, TRK, SWAT). Thus only SWAT and TRK out of the nine EUROHARP models were very suitable for the purpose to model eutrophication issues.

It is important to note that ecological modeling develops rapidly and that any description of model design and capacity may change over time. The models presentations below are based on available information around 2009-2010.

8.5. Hydrological models - examples

SCS Curve number - The SCS curve number method is a simple, widely used and efficient method for determining the approximate amount of runoff from a rainfall, even in a small area. The SCS curve number method is often included in more distributed hydrological models to evaluate surface runoff (e.g. SWAT). Although the method is designed for a single storm event, it can be scaled to find average annual runoff values. The data requirements for this method are very low; rainfall amount and curve number. The curve number is based on the area's hydrologic soil group, land use, treatment and hydrologic condition. Model developer: United States Department of Agriculture.

HBV - The HBV model is a rainfall-runoff model, which includes conceptual numerical descriptions of hydrological processes at the catchment scale. The model has been applied for scales ranging from lysimeter plots to the entire Baltic Sea drainage basin. HBV can be used as a semi-distributed model by dividing the catchment into sub-basins. Each sub-basin is then divided into zones according to altitude, lake area and vegetation. The model is normally run on daily values of rainfall and air temperature, and daily or monthly estimates of potential evaporation. The model is used for flood forecasting in the Nordic countries, and many other purposes, such as spillway design floods simulation, water resources evaluation, nutrient load estimates. Model owner: SMHI, http://www.smhi.se/sgn0106/if/hydrologi/hbv.htm

8.6. NUTRIENTS LOAD MODELS

WARMF - Watershed Analysis Risk Management Framework: Combines basin modeling and modeling of water quality, retention and dynamics in lakes, including internal load. Also habitat suitability for different organisms, such as fish species, can be calculated. WARMF also makes a comparison of the load, its impact and the gap to achieve specified state standards, which might be interesting from the perspective of the Water Framework Directive. The software is freely available and can be downloaded from the U.S. EPA website.

SWAT - Soil Water Assessment Tool (linked to Basins): Computes load and response simulations for diffuse and point sources. Especially suitable for analyzing the effects of agricultural measures. The calculation of retention has weaknesses and this, together with high demands on input data, suggests that this model should be used in combination with Aquatox or WASP. The software is freely available and can be downloaded from the U.S. EPA website.

HSPF - Hydrological Simulation Program - Fortran (linked to Basins): The same type of model as SWAT, calculates load, retention, internal load and action effects. The software is freely available and can be downloaded from the U.S. EPAs website.

WATSHMAN - Watershed Management System: calculates load based on hydrological modeling and leakage coefficients. To be used in combination with a water model, which calculates the internal load. Model Owner: IVL, Sweden.

AVGWLF-PREDICT - Arview Generalized Watershed Loading Function - Pollutant Reduction Impact Comparison Tool: AVGWLF calculates the total load within a sub-basin. The model is designed for relatively large areas, which gives a low spatial resolution. Retention and internal loading is calculated in an oversimplified way. If AVGWLF is used together with PREDICT, which is an advanced simulation software, it is possible to analyze effects of measures. The software is freely available and can be downloaded from the Pennsylvania State University.

FYRISQ-FYRISNP: It is a conceptual model which can compute loads and effects of different measures, especially in agriculture. Leakage coefficients can be produced from ICECREAM / SOILNDB. The model calculates the retention but not internal loading as erosion in the river channel. Model Owner: SLU, Sweden.

HYPE Hydrological Predictions for the Environment: - Based on a central national database at SMHI. Load and retention can be calculated, but not internal load. Solution Scenarios can be run for selected sub-basins. Model Owner: SMHI, Sweden

MIKE BASIN: Computes load and retention. Developed and marketed by DHI. Purchasing and operating costs considerably more than the above models. Model Owner: DHI, Danish Hydrological Institute, Denmark.

With one exception, HSPF, the models do not calculate internal loadings. Internal loads can be calculated by an external lake model, e.g. LEEDS, Biola or any of the U.S. models, and the result can be added to the load at a point in a river basin. This can be done in all the models that do not calculate internal loads. An overview of the discussed nutrient load models are given in Table 19.

Although the specific details of model applications will differ depending on the particular model being applied, there are standard procedures which should be adopted in all model applications. For example, model version number and data inputs should be recorded and retained, and key (i.e. sensitive) parameters used in model applications should be documented and appropriately referenced (e.g. expert judgement, scientific literature, measurements, etc.). Further details of the requirements of Good Modelling Practice are available for model users at http://www.info.wau.nl/research%20projects/gmp.htm

Table 19. Overview of model characteristics (Source: Ekstrand et al. 2009)

Model		**Calculates**		**High geo-graphical resolution**	**Measures in agriculture**	**Measures at point sources**
		loads	**retention**			
AWGWLF-PREDICT	Conceptual	**x**				**x**
FyrisNP	Conceptual	**x**	**x**		**x**	**(x)**
HSPF	Physical	**x**	**x**	**x**	**x**	**x**
HYPE	Semi-physical	**x**	**x**			**x**
MIKE BASIN	Conceptual	**x**	**(x)**			**x**
ArcSWAT	Physical	**x**	**(x)**		**x**	**x**
WARMF	Physical	**x**	**(x)**			
WATSHMAN	Conceptual	**x**	**x**			**x**

8.7. Priority substances - WFD

The EU water framework directive (WFD) (2000/60/EG) and the daughter directive (2008/105/EC) on environmental quality standards in the field of water policy include classification of chemical status and pressure analysis of priority substances and priority hazardous substances. The list of priority substances in the WFD included originally totally 33 metals and organic pollutant substances, and 8 other substances were added by the daughter directive. The list is updated every fourth year and 15 new substances have been suggested to be included, e.g. several pharmaceuticals and Perfluorinated substances PFOS. The new list has been reviewed and the final list is to be adopted in the near future. Within the WFD, the status and targets for priority substances for water bodies are set by risk levels (EQS). These risk levels are based on observed effects in eco-toxicological risk assessments. The eco-toxicological risk assessments are carried out by establishing the concentration-effect relation for individual chemical components and individual test species (single-species toxicity tests, measuring effects to individuals).

Monitoring to determine the occurrence and sources of all priority substances is usually costly and demand big efforts, and it is also not necessarily the best and only way to determine their environmental presence and pressure. The monitoring performed to investigate presence and trends of priority substances should be done in the surveillance monitoring program. The monitoring of new substances should be introduced within the WFD surveillance monitoring in a screening program with an assessment of which substances to be included in surveillance monitoring national trend program. The screening program setup should be based on the geographic distribution of load on the environment from known or suspected pollution sources. It should also consider the results from chemical fate modeling combined with previously existing knowledge on environmental occurrence of the target compound. Fate models describe the fractionation of the substances between the media (air, water, sediment, biota), i.e. where the substances will be found in the environment (see below). The screening monitoring program will result in recommendations of continuous trend monitoring program. Operative monitoring should be performed to establish the status of those bodies identified as being at risk of failing to meet their environmental objectives, and to assess any changes in the status of such bodies resulting from the programmes of measures.

The pollution sources can initially be determined from a substance flow analysis describing major pathways and pools of the substance (Figure 31.). When using a load source apportionment as a basis of the WFD pressure analysis, type concentrations of the substance flow from the major sources need to be connected to the geographic distribution of the sources, analog to the source apportionment of nutrients. Organic pollutants are often related to the urban environment due to the use of products and materials containing the substance, and sewage systems can often be a node of pollution as a collector of urban storm water and wastewater. However, also long-range transported air pollution and substances used in rural areas, as pesticides, can be found in the runoff from different land cover and in deposition. Other important sources of priority substances in water may be industry, polluted soils, mining, forestry, roads, airports, firefighting exercise sites (Perfluorinated compounds as PFOS), household chemicals, pharmaceuticals and personal care products from onsite rural wastewater and waste deposit sites, as well as unintentionally produced pollution as PAH´s from combustion processes.

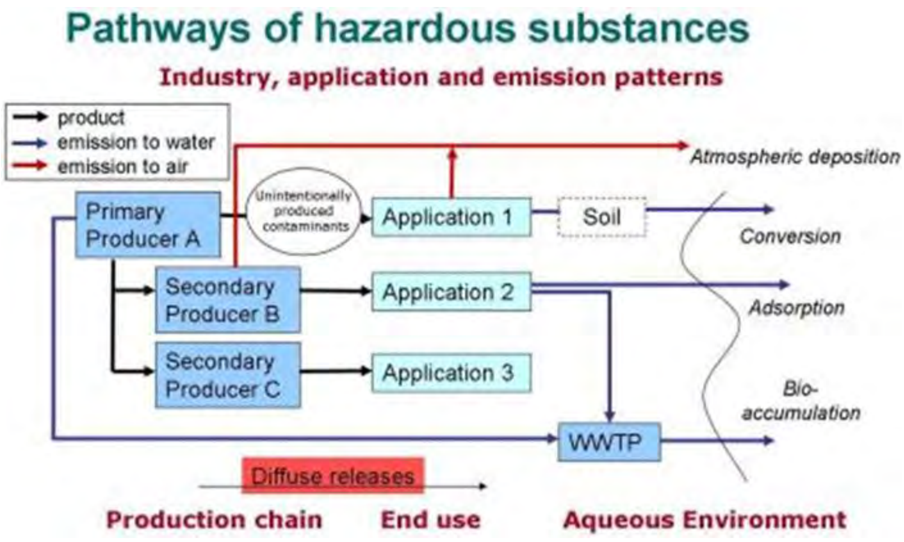

Figure 31. Illustration of pathways included in a substance flow analysis.

8.7.1. CHEMICAL FATE MODELS

Fate models describe the fractionation of the substances between the media (air, water, sediment, biota), i.e. where the substances will be found in the environment. The use of chemical fate models in combination with monitoring is a cost efficient solution. The priority substances have affinity to certain media such as sediment or biota and may not always be detected in the water phase. The affinity of the substance to the different media is determined by the physical and chemical characteristics of the substance, their chemical structure and active groups. To determine the presence of priority substances in the water environment, chemical fate models can be used, based on the chemical and physical properties of the substance, degradation rates and emission data.

Chemical fate models are used to determine the partitioning of a substance between different media such as e.g. air, water, sediment, soil and biota. Some models include additional compartments such as urban surfaces, plants/forests, or entire aquatic food-webs. In their most simple form, the results from such a model can be used to e.g. obtain information on the free water concentration and thereby the toxic pressure on the ecosystem or for information on the overall environmental fate of a substance for monitoring purposes. Chemical fate models are often based on concentration, or, fugacity. The models can give valuable information on the distribution of the substance between different phases ('compartments') in the environment. The models also provide information on residence time, accumulation and concentrations.

Fate models have further been used to describe the retention of the substance from source to the water environment for pressure analysis. A system is under development in Sweden by IVL in cooperation with the Swedish Water Authorities and SMHI. The retention is treated through steady-state, assuming equilibrium in the system, and model use mass balance equations of affinity of the substance for the different media. In Figure 32. the retention processes in lakes and rivers are presented. Equations for soil retention are described with fewer processes but with similar equations. The largest differences in description of the organic priority substances retention compared to nutrients retention are the processes of evaporation and degradation which depend on the substance physico-chemical properties. The model for nutrients is otherwise similar depending on the water residence time to large extent, but the particles and organic content in the particles are further more important for metal and organic pollutants than for nutrient retention.

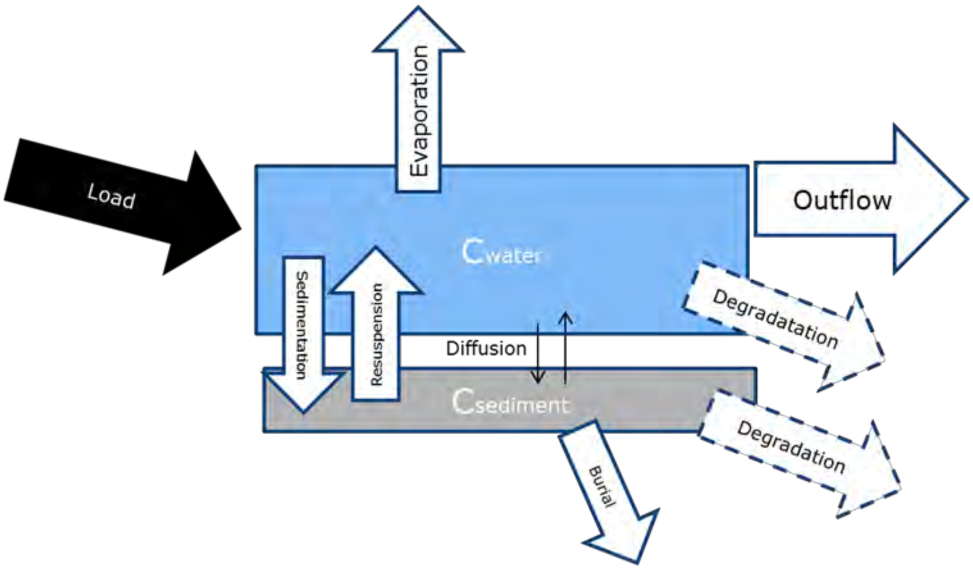

Figure 32. Illustration of the processes described in the IVL steady state fate model application of retention in lakes and rivers. Loads are point source, diffuse source and/or transport into a catchment or lake and outflow is transport out of the catchment to the next catchment or the sea.

Link to level III fugacity model EQC (Mackay et al, downloadable freeware) http://www.trentu.ca/academic/aminss/envmodel/models/VBL3.html

8.7.2. QSAR MODELS

For many substances, chronic toxicity, and for new substances, physico-chemical properties which are needed in the chemical fate model may not be available. A quantitative structure–activity relationship (QSAR) model is a relation between chemical structure and a property of the chemical compound. The features of a chemical structure are captured by so called chemical descriptors that can be related to toxicological effects of known substances. Quantum chemical models can be used to determine the physic-chemical properties of new substances.

8.8. Relation between monitoring and modeling

Modeling is a tool to assess and understand processes and pollution sources in a catchment, and it is a supplement to physical monitoring. If the model cannot represent the monitoring data, there is a need for deeper investigation of the catchment conditions. This may also indicate a need for checking the quality of the monitoring data. However, even if the model produces good dynamics and quantifies the load in good correspondence with monitoring data, there is still a need for expert judgment to critically review the results. Most models need some kind of calibration and the result of the calibration process gives important information. It should be considered if the calibration parameters fall within reasonable limits.

In the Kolubara project, the FyrisNP model was applied to 52 sub-catchments. This model has only two parameters used for calibrating the retention calculation; c0 that adjusts the temperature dependence and kvs that adjusts the hydraulic conductivity (flow/area) dependence. The c0 should be allowed to vary between 0 and 1, while the kvs should be 0 or higher, but values above kvs = 30 are uncommon. Calibration results outside those limits should be investigated further, critically assessing the input load data of the different sources or assessing the retention capacity of the lakes and rivers in the catchment.

The sensitivity of a model can be used as guidance to which information and data that need further attention and refinement. Sensitivity analysis is most easily performed by varying the data input (e.g. 10%) and compare the results of the gross and net load in the sub-catchment.

There is no perfect model to represent a catchment. The usefulness of a model is very much depending on the data need of the model in comparison with available input data. It can be useful to apply the same data set to several models, so called ensemble modeling, to get a better view on how the results vary and are represented.

9. INPUT DATA AND LOAD MODELLING USING FYRISNP MODEL – KOLUBARA RIVER BASIN

The dynamic FyrisNP model calculates source apportioned gross and net transport of nitrogen and phosphorus in rivers and lakes. The main scope of the model is to assess the effects of different nutrient reduction measures on the catchment scale. The time step for the model is in the majority of applications one month and the spatial resolution is on the sub-catchment level. Retention, i.e. losses of nutrients in rivers and lakes through sedimentation, up-take by plants and denitrification, is calculated as a function of water temperature, nutrients concentrations, water flow, lake surface area and stream surface area. The model is calibrated against time series of measured nitro-gen or phosphorus concentrations by adjusting two parameters (Hansson at all, 2008).

Data used for calibrating and running the model can be divided into time dependent data, e.g. time series on observed nitrogen and phosphorus concentration, water temperature, runoff and point source discharges, and time independent data, e.g. land-use information, lake area and stream length and width (Figure 33.) (Hansson at all, 2008).

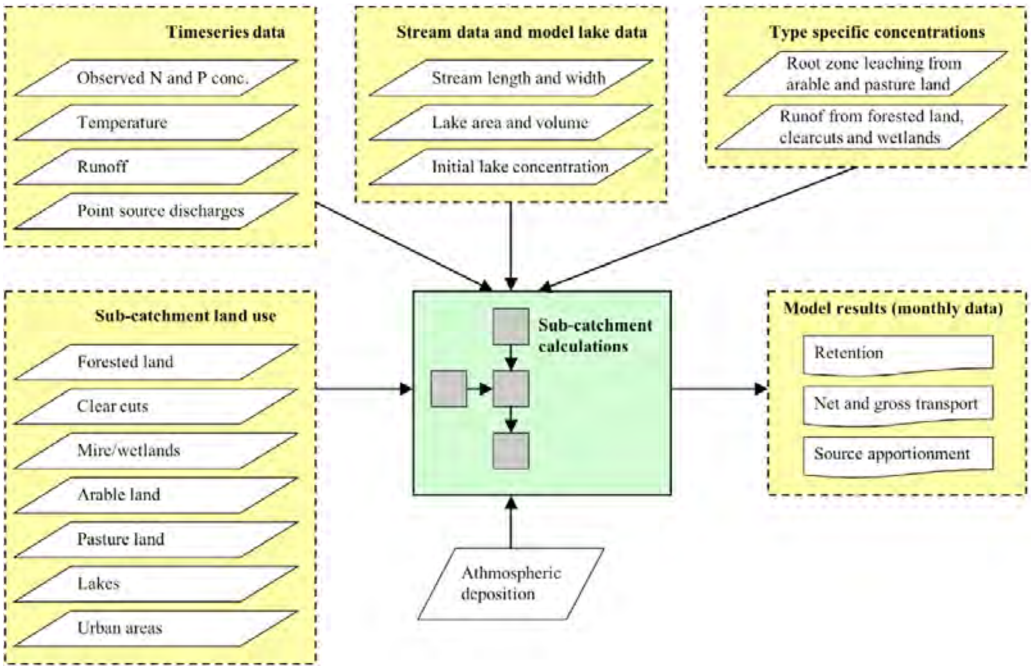

Figure 33. The general structure of inputs and outputs to the FyrisNP model (Hansson at all, 2008)

In order to perform simulations with the FyrisNP model, an Excel-file containing all input data is required. Any name may be chosen for the Excel file as long as it has the xls extension. The Excel data file contains between eight and ten different work-sheets depending on what features are used.

9.1. THE GENERAL DATA STRUCTURE TO THE FYRISNP FOR KOLUBARA RIVER BASIN

Input data for the FyrisNP model includes spatial and alphanumeric data grouped in eight main groups: a) delineation of sub-catchments, b) land use, c) EMEP/MSC-W modelled depositions of nitrogen, d) leaching concentrations of nitrogen and phosphorus in runoff from arable land and pasture and other types of land use, e) lakes, f) minor point sources – scattered rural households, g) minor point sources- manure depots and h) major point sources– urban and industrial sewage systems. Besides these, other data will be included in the model: results of surface water quality monitoring, specific runoff from sub-catchments, specific concentrations of nitrogen and phosphorus discharged from non-agricultural surfaces, etc. All this data can be divided into two large groups, time-dependent and time-independent data.

9.1.1. SUB-CATCHMENT DELINEATION

The following platforms were used for delineation /identification of sub-catchments in the Kolubara river basin:

1. Digital model of the terrain - raster 100x100 m (ArcGis);
2. Vector layer with hydrographic network in the Kolubara catchment (ArcGis);
3. Vector layer with spatial distribution of point source pollutants: municipal and industrial pollutant emissions (ArcGIS);
4. Vector layer with a spatial distribution of hydrological water level and flow measurement stations in the Kolubara catchment (ArcGis);
5. Vector layer with a spatial distribution of stations in the Kolubara catchment where water quality monitoring was performed in the observed period (ArcGis).

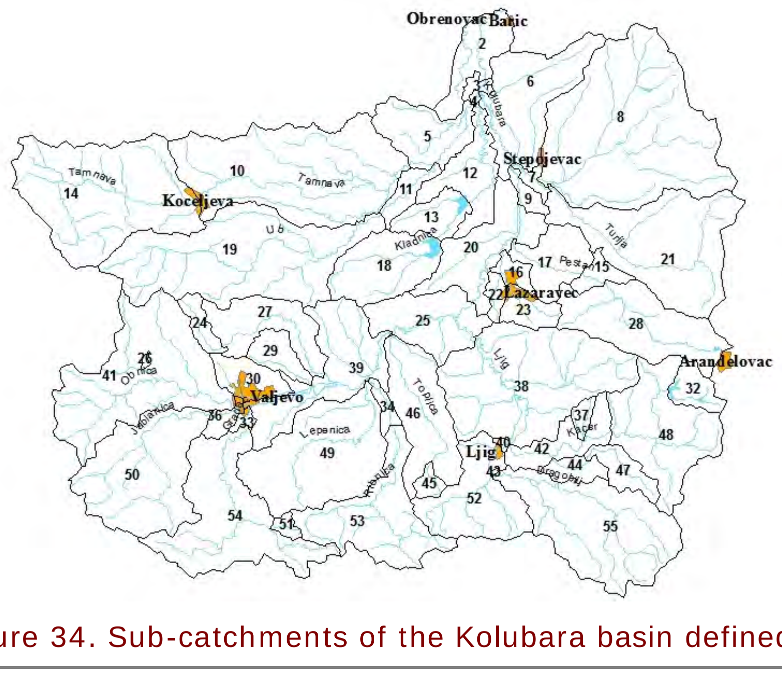

Figure 34. Sub-catchments of the Kolubara basin defined by delineation

Sub-catchment delineation was based on spatial information about emissions of pollutants from point sources, hydrological stations and water quality monitoring stations. Endpoints of the sub-catchments were then determined. By using ArcGis tools, a new vector layer with 52 sub-catchments was formed. For each sub-catchment: Area (km^2), Outflow index, Stream length (m), Stream area (km^2), Altitude average (m), Lake area (km^2) were determined (Table 20.).

Table 20. The variables included in the Catchment worksheet

Variable name	Unit	Description
Catchment_ID	-	Sub-catchment ID-number
Station_ID	-	The ID-number of the nearest downstream
Downstream_ID	-	Downstream sub-catchment
Area	km^2	Total area of sub-catchment
Lake area	km^2	Lake area
Stream Length	m	Stream Length
Stream area	km^2	Stream area
Mountain	km^2	Mountain area (above tree line)
Forest	km^2	Forested area
Clearcuts	km^2	Clear cuts (not older than 5 years in S Sweden and 10 years in N Sweden)
Mire	km^2	Mire/Wetland
Arable	km^2	Arable land
Pasture	km^2	Pasture
Open	km^2	Other open land
Settlements	km^2	Settlements
Urban	km^2	Urban areas
c_Arable	mg/l	Type specific concentration from arable land
c_Pasture	mg/l	Type specific concentration from pasture
Altitude*	m	Altitude above sea level
Lake Model	-	1 = Yes, 0 = No
Dep Lake	$kg/month/km^2$	Nitrogen deposition on lakes(zero forP)
Dep Clearcut	$kg/ month /km^2$	Nitrogen deposition on clearcuts(zero forP)
Model Lake Name*	-	
Model Lake Area	km^2	Model Lake Area
Model Lake Depth	m	Model Lake Depth
Model Lake Volume	$km^3 *10^6$	Model Lake Volume
Initial Lake Concentration	mg/l	Initial concentration for model lakes

Figure 35. Landscape of the village Beomuzevic, Valjevo municipality

9.1.2. LAND COVER/USE

The land cover/land use and the areas of each class (CORINE land cover classes) at the 52 sub-catchments were obtained by over-lapping of CORINE LAND COVER 2006 layer and a vector layer of Kolubara sub-catchments. The CORINE LAND COVER database was used due to a lack of relevant national satellite images and their interpretation. By using satellite images more precise data is acquired about the land uses and distribution of agricultural crops.

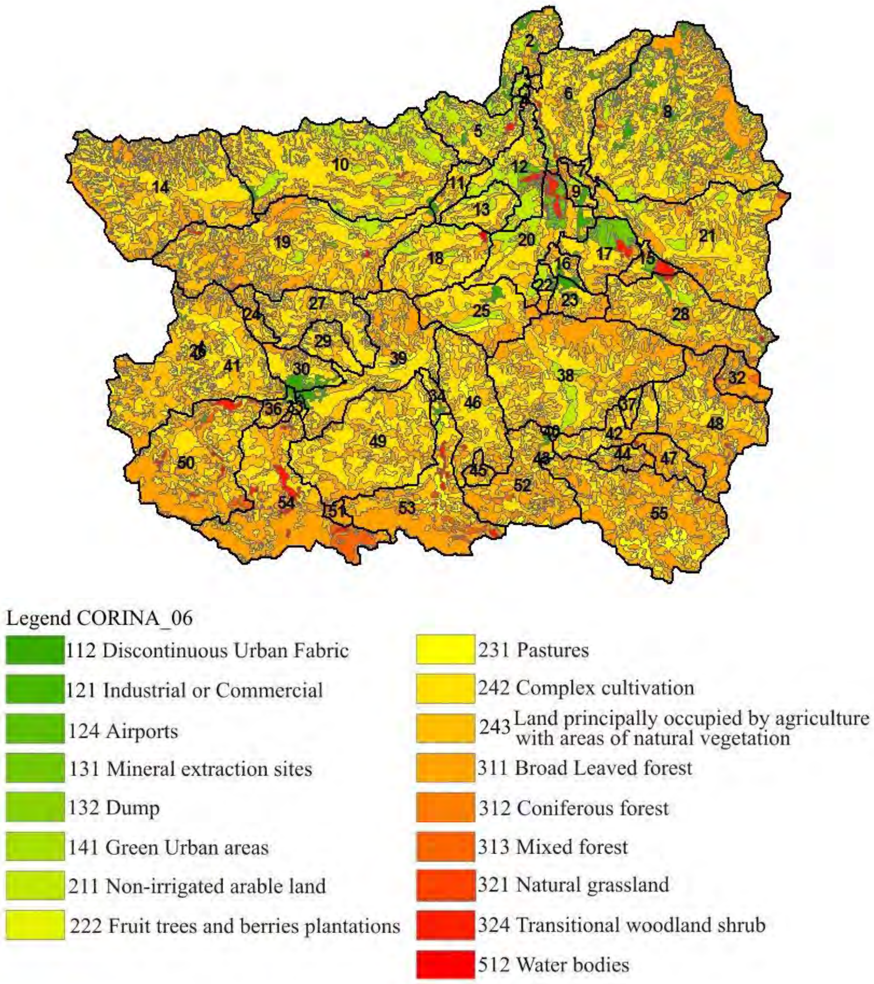

Figure 36. Land cover and land use of the Kolubara catchment

9.1.3. EMEP/MSC-W MODELLED DEPOSITIONS OF NITROGEN

Data on nitrogen deposition at sub-catchment level was performed achieved from the European Monitoring and Evaluation Programme (EMEP), available on at the website (www.emep.int) form of gridded (50x50 km) maps (Figure 37.)

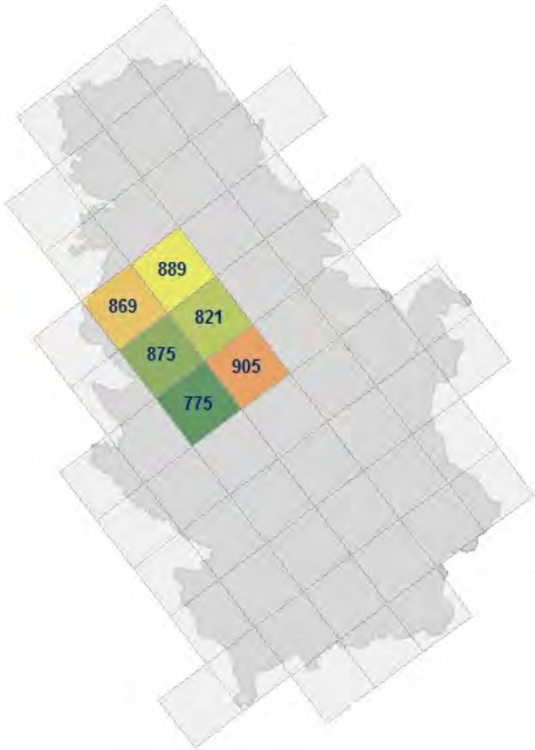

Figure 37. EMEP grid 50x50 km and average nitrogen deposition in mgN/m^2 (2006-2010)

Annual nitrogen depositions in the territory of Serbia shown through the EMEP grid (50x50km) were overlapped with a layer of Kolubara sub-catchments and thus the values of nitrogen deposition for all 52 sub-catchments were obtained. (Figure 38.)

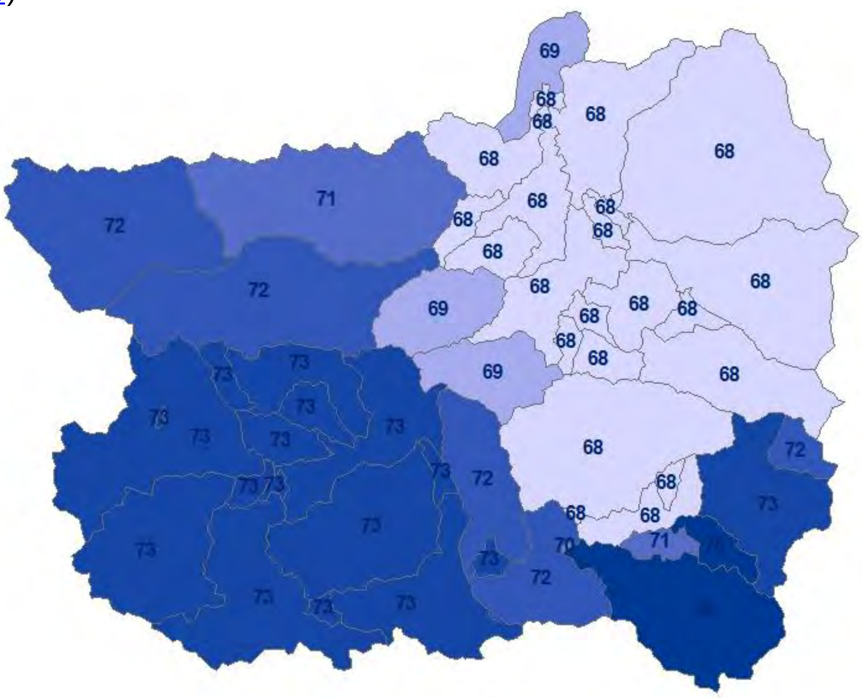

Figure 38. Nitrogen deposition at the level of Kolubara sub-catchments in kg/km^2/month (2006-2010)

9.1.4. LEACHING CONCENTRATION OF NITROGEN AND PHOSPHORUS IN RUNOFF FROM ARABLE LAND AND PASTURE AND OTHER TYPES OF LAND-USE

The soil texture map was made on the basis of a soil map for the Kolubara basin and data about average mechanical composition of the soil for a group of lands for the entire territory of Serbia, in accordance with the *World Reference Base* (*WRB)*.[1] By overlapping the layers of the sub-catchments, CORINA and Texture map, the surface of agricultural land according to the soil type in km^2 (arable land per soil type) for each sub-catchment was defined. This is the first entry table for the SOILNDB model (Swedish University of Agricultural Sciences).

The second entry table for the model was obtained by overlapping the sub-catchment layers, CORINE and the percentage of agricultural crops by municipalities,[2] and thus the percentage of agricultural crops was broken down by sub-catchments. The third entry table for the model was obtained on the basis of nitrogen concentrations defined by test measurements at the Kaposvar catchment in Hungary, from the EUROHARP project. The table contains data about the leaching concentration of nitrogen (mgN/l) in runoff from arable land depending on the type of agricultural crop and texture of the soil. Output from the SOILNDB model is the average value of the leaching concentration of nitrogen (mgN/l) broken down by the sub-catchment and is an input for the FyrisNP model (Figure 39.). The same procedure was applied for phosphorus.

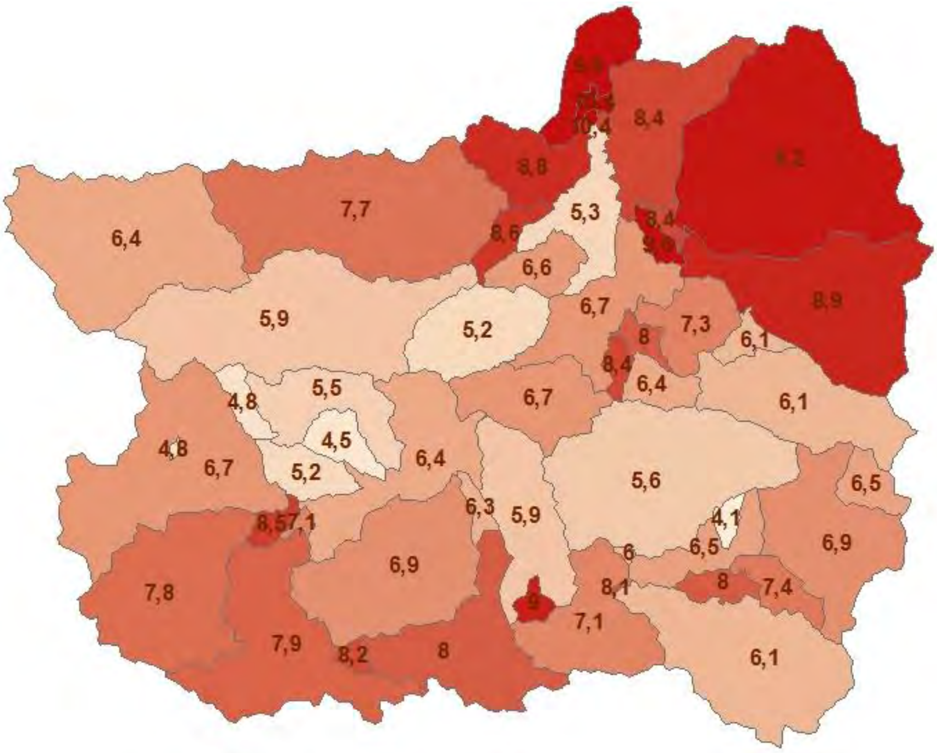

Figure 39. Average value of the leaching concentration of nitrogen (mg/l) broken down by sub-catchment

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[1] The basic pedological map of Serbia is 1:50000 with the accompanying database
[2] 2007-2011 Statistical yearbook data for 2006-2010

There is no information or results of scientific studies of the type specific concentrations for other land-use in the Kolubara river catchment, as used in the FyrisNP model (Forest, Mountain, Clear-cuts, Mires, Open, Urban). The proportions of land use types within the Kolubara river catchment are: 72% Arable and Pasture, 25%- Forest, 2.7% - Urban, 1.2%- Other and 0.1%-Water bodies. We estimated the types specific concentration for forest, urban and other land-use classes (except arable land and pastures) (Table 21.) on the basis of literature.[1,2] The type specific concentrations were compared to the monitoring data in small catchments setup during this project. The monitoring data in the area dominated by forest was measured to 0.8 mg/l of total nitrogen and 0.076 mg/l total phosphorous showing that values for nitrogen and phosphorous are reasonable.

Table 21. Type specific concentration of total nitrogen (mg/l) and total phosphorus (mg/l) for listed land types

Parameter	Mountain	Forest	Clear cuts	Mires	Open	Urban
N (mg/l)*	0.00	0.75	0.00	0.00	0.90	1.50
P (mg/l)*	0.000	0.08	0.000	0.000	0.056	0.087

* We did not take into account the seasonal variability of these parameters because we did not have the results of measurements.

[1] National calculation of gross load from storm water in Sweden, Mikael Olshammar, IVL
[2] Modelling the importance of baseflow in the runoff and transport of pollution in stormwater ditches and stormwater pipes, Maria Arwidsson, School of Earth, Atmospheric and environmental sciences, 2011

9.1.5. LAKES

Accumulations have a big influence on the downstream transport of nutrients. Input data for the model is based on the accumulation water volume observation data. The monthly change of volume was obtained on the basis of observed daily volumes. This change is included in the model taking into consideration the degree of influence of the water mass flow (Figure 40.).

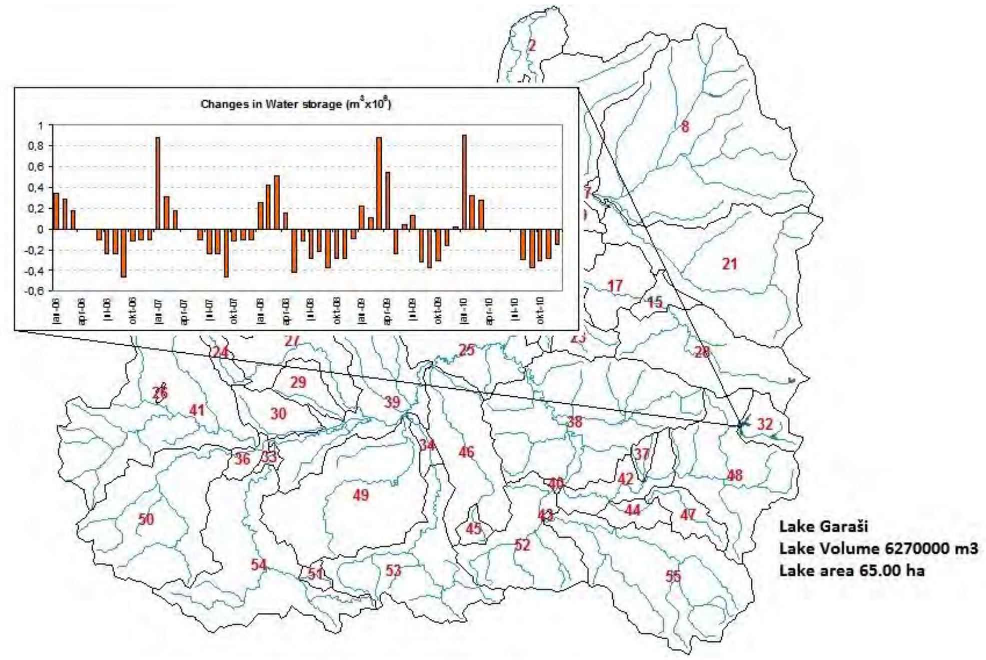

Figure 40. Garasi accumulation – volume change (m^3x10^6)

9.1.6. MINOR POINT SOURCES - SCATTERED HOUSEHOLDS WITH AUTONOMOUS SEWAGE TREATMENT SYSTEM

The impact of rural households on water bodies' pollution was calculated on the basis of statistical data about the size of local population and coverage of sewerage systems in these settlements[1]. The number of households in a settlement not connected to the sewerage system was estimated by first calculating the number of habitants per km^2 in the settlement. By using a GIS tool, the area of the settlement, as well as the share covered by the sewerage network, the number of persons not connected to the network could be determined, assuming that the population is equally distributed across the surface of a settlement. The obtained number of inhabitants not included in the sewerage system for each sub-catchment was then multiplied by the *loading coefficient* and thus total N and P load derived from these pollutants was determined in kg/month. (Figure 41.) The *loading coefficient* required for calculation of the pressure made by the population not-included in the sewerage system (totN=3,1g/per capita and day, totP=0,4g/per capita and day) was taken over from a relevant reference document.[2]

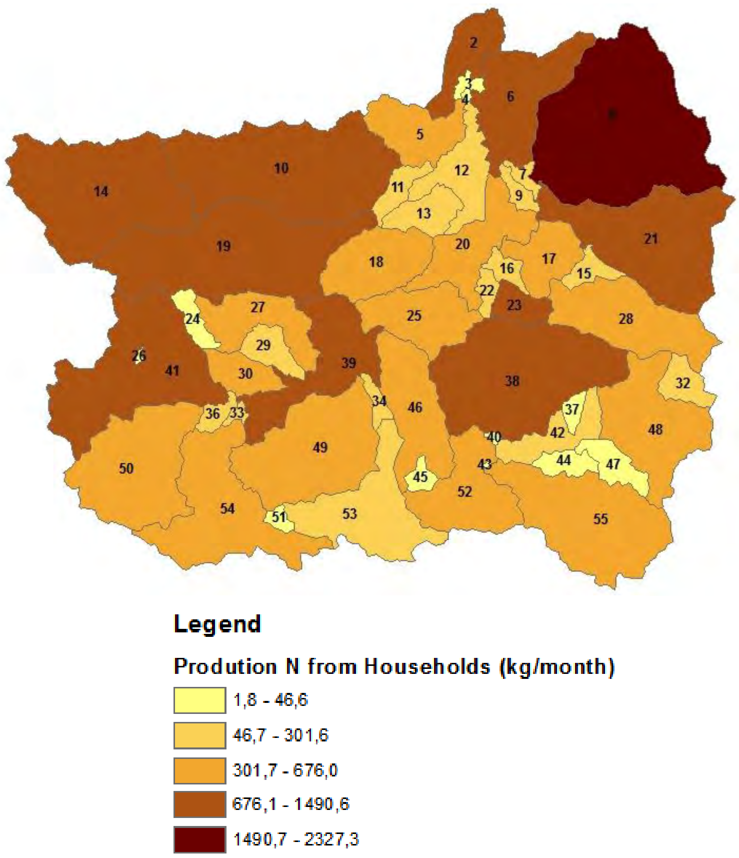

Figure 41. Total nitrogen load originating from rural households at the sub-catchment level

[1] Analysis of pressures and assessment of impacts on water resources, Water Management Institute „Jaroslav Černi", Belgrade, 2011.

[2] Water management plan for the Danube catchment, part 1: Analysis of the characteristics of the Danube catchment in Serbia - Draft, Water Management Institute Jaroslav Černi, Belgrade, December 2011.

9.1.7. Minor point sources - manure pits

The calculation of the amounts of nitrogen and phosphorus leached from manure pits was made in several steps. Firstly, digital platforms (map of the Kolubara catchment with defined sub-catchments and maps of municipalities within the catchment) as well as statistical data about the numbers of cattle in the municipalities expressed as Animal Units (AU). Then the production of manure per *AU* and average values of nitrogen and phosphorus in the manure, the total production of nitrogen and phosphorus originating from cattle was determined, broken down by municipalities.[1,2]

Figure 42. Typically stored manure in Serbia – Batalage village, Koceljeva municipality

[1] Republic Statistics Office, Statistics Yearbook for 2006,2007,2008.

[2] Adopted load coefficients:

a) 1 cow or horse = 1 ((*Animal Unit, AU*) , 1 pig = 0,12 (*Animal Unit, AU*) , 1 sheep or goat = 0,1 ((*Animal Unit, AU*), poultry = 0,00312 ((*Animal Unit, AU*), with *Animal Unit (AU*) per annum (Publication „Analysis of pressures and assessment of impacts on water resources – Water Management Institute Jaroslav Černi Belgrade 2011)

b) Production of manure in *AU* per annum is 10 tons (Reduction of Pollution Releases through Agricultural Policy Change and Demonstrations by Pilot Projects Table 2. Manure Standard – average value for cows)

c) Average values of nutrients in average-held manure are as follows: 0,5% N and 0,3% P_2O_5 (Source EU CARDS Regional program 2003, Sava Catchment Management Pilot Plan, Report for the Kolubara Catchment, 2007)

By overlapping vector layers and municipalities, the share of each municipality in %, and afterwards the production of nitrogen and phosphorus fertilizers were determined broken down by sub-catchments. By multiplying these values with the percentage of leakage from manure pits[1], total leakage loading was identified for the sub-catchments. (Figure 43.)

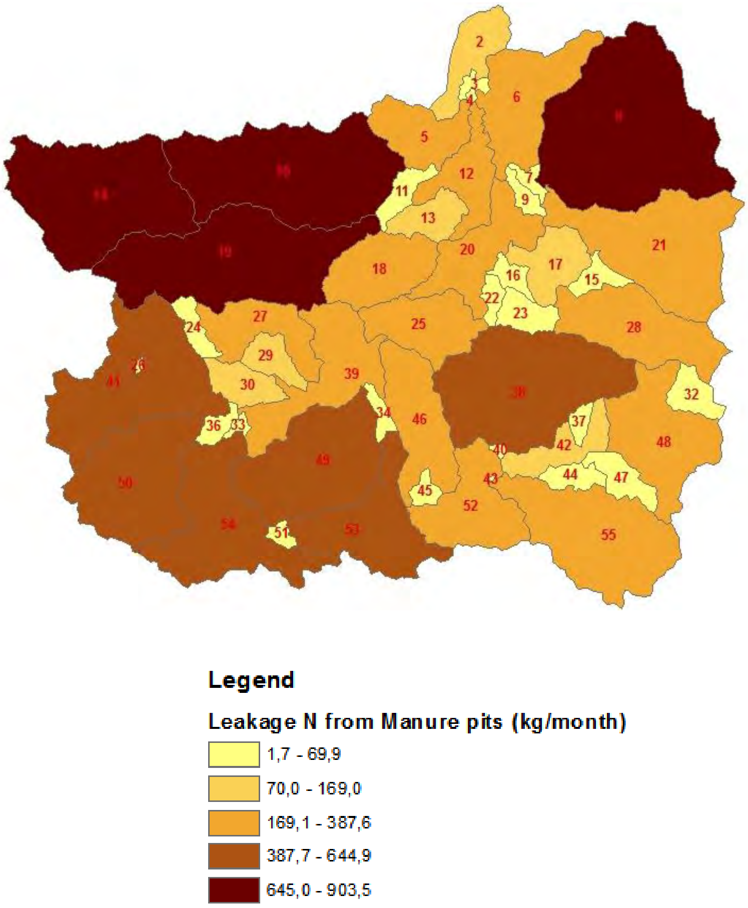

Figure 43. Nitrogen loading of sub-catchment from leakage from manure pits

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[1] Percentage of leakage from manure pits 2% (model *Srbijavode*)

9.1.8. MAJOR POINT SOURCES – URBAN AND INDUSTRIAL SEWAGE SYSTEM

Data about urban and industrial pollutants include coordinates of emissions, emission concentrations and volumes of discharged waste waters. This data is used to calculate the degree of nitrogen and phosphorus loading in relevant sub-catchments.

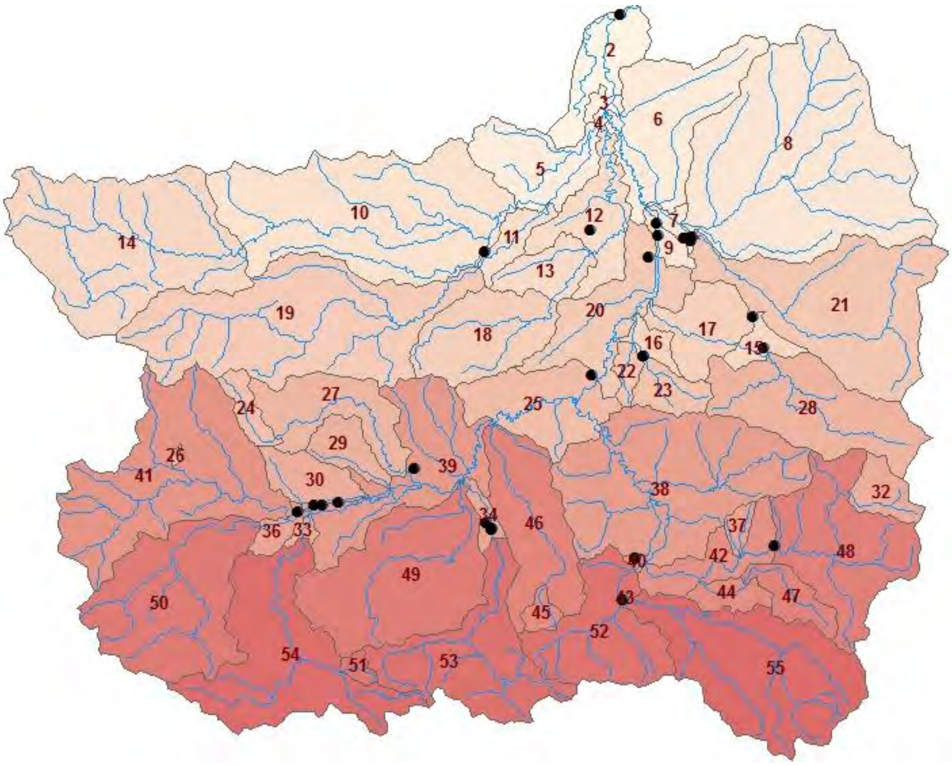


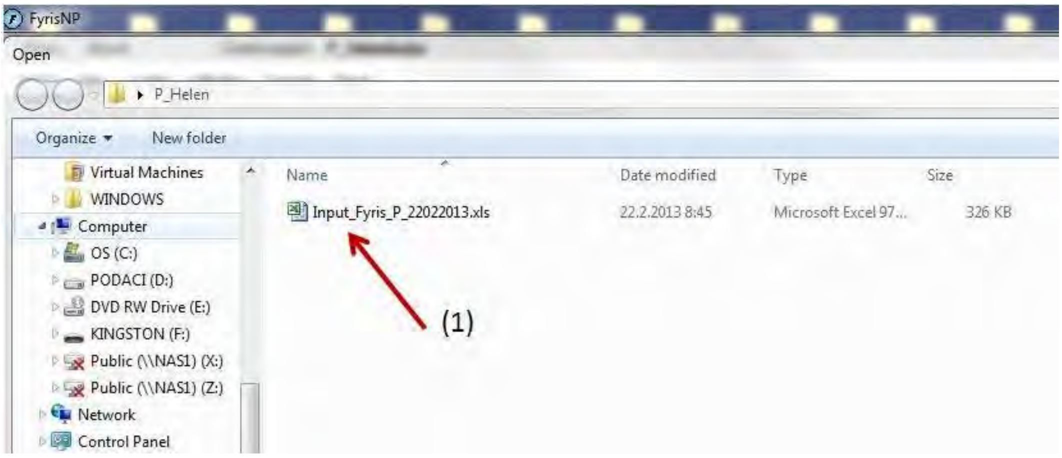
Figure 44. Major point sources – urban and industrial sewage system in Kolubara catchment

9.2. LOAD MODELLING USING FYRISNP – KOLUBARA RIVER BASIN

9.2.1 ADDING INPUT DATA TO THE PROJECT

During project implementation spatial and alpha-numerical data were prepared and processed in detail by using various general and special applications, such as: MSExcel, MSAccess, ArcGis AutoCad; also, the values of necessary input data were determined (See Chapter 9.1). Data was provided in the form of an *input file* in *xls* format with 8 worksheets: Catchment, COBS, Major point sources, Minor point sources, Temperature, Type specific concentration, Specific runoff, Storage.

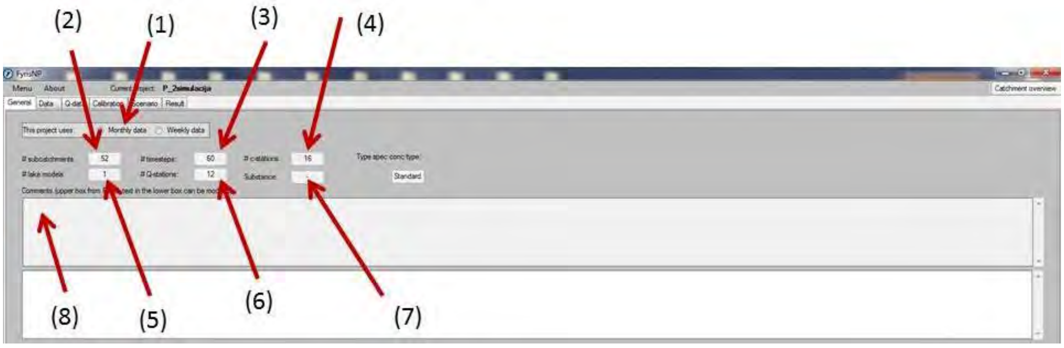
a) **Adding data to the project -** Load *the input file*



FyrisNP simulation is initiated by defining the working folder, working area and project, and/or by adding input data (1).

b) **Examine your data** - The *General* tab

The General tab window allows for defining the time frames of simulation (month, week) (1). It also enables the user to check the number of added sub-catchments (2), the length of added time series (3), number of stations where water quality was tested and concentrations of total Nitrogen and total Phosphorus were determined, on which basis the model would be calibrated (4), the number of lakes not included in the model (5), the number of hydrological stations where discharge was measured (6). The window allows for definition of the parameter for which the simulation is to be performed (7), and for adding the necessary comments written in a pre-determined field (8), which may be of importance in the interpretation of output results.

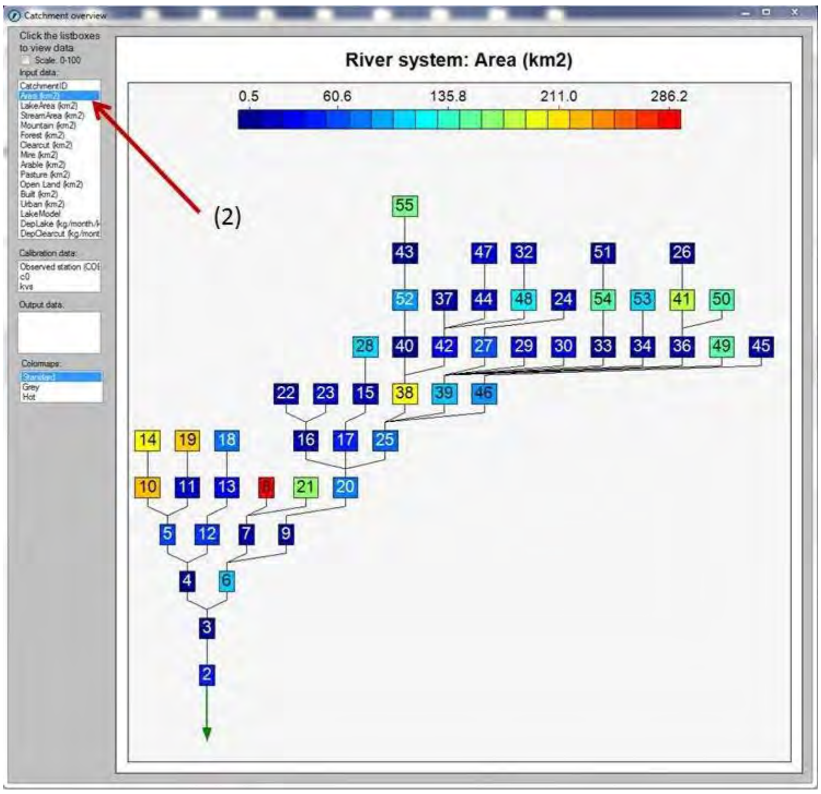


For the Kolubara catchment data from 52 sub-catchments have been added. The data includes time series of average monthly concentrations of total Nitrogen and Phosphorus for 5-year period (2006-2010), with a time interval of one month, or 60 intervals in total. The model includes one accumulation (Garasi), and hydrological data (discharge) was available for 12 stations.

c) **Catchment overview**

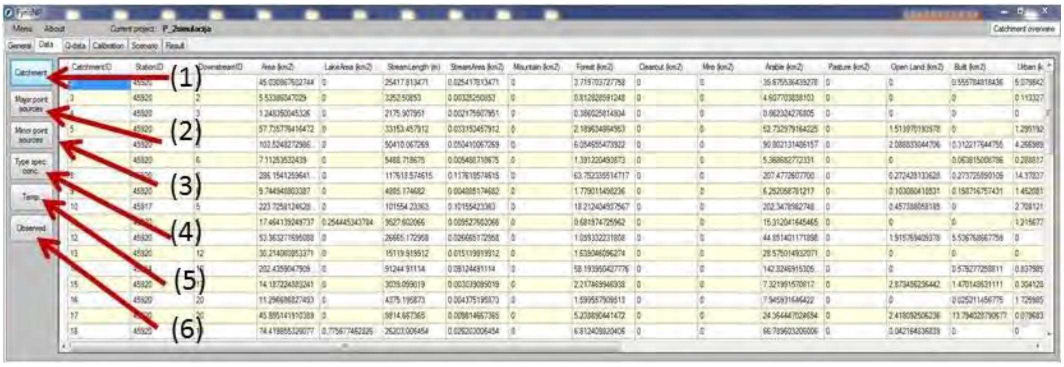
The Software provides visualization of input data (1).

The position of sub-catchments is shown in the tree structure, with precisely defined upstream/downstream arrangement of the sub-catchments and their interconnections.



d) **The *Data* tab**

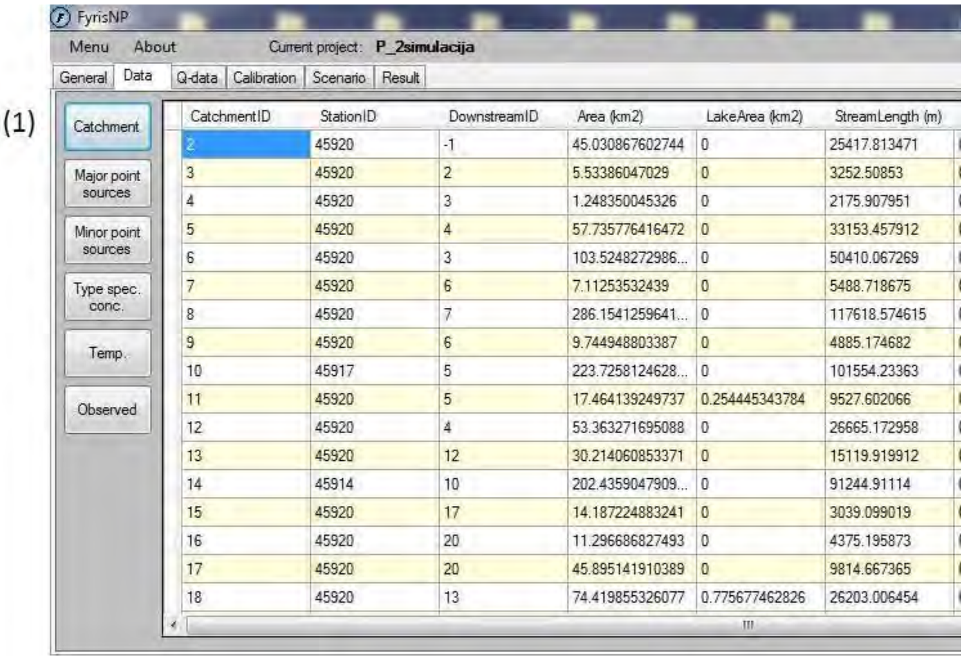
The Data window gives an overview of all input data necessary for the operation of the model in a tabular form as defined by the input file.



This window contains data about: sub-catchments (1), emission of major point sources (2), emission of minor point sources (3), specific concentrations of Nitrogen/Phosphorus in leaching water as a result of various land use (4), average monthly water temperature in the catchment (5), averaged values of measured monthly concentrations of total Nitrogen/Phosphorus (6).

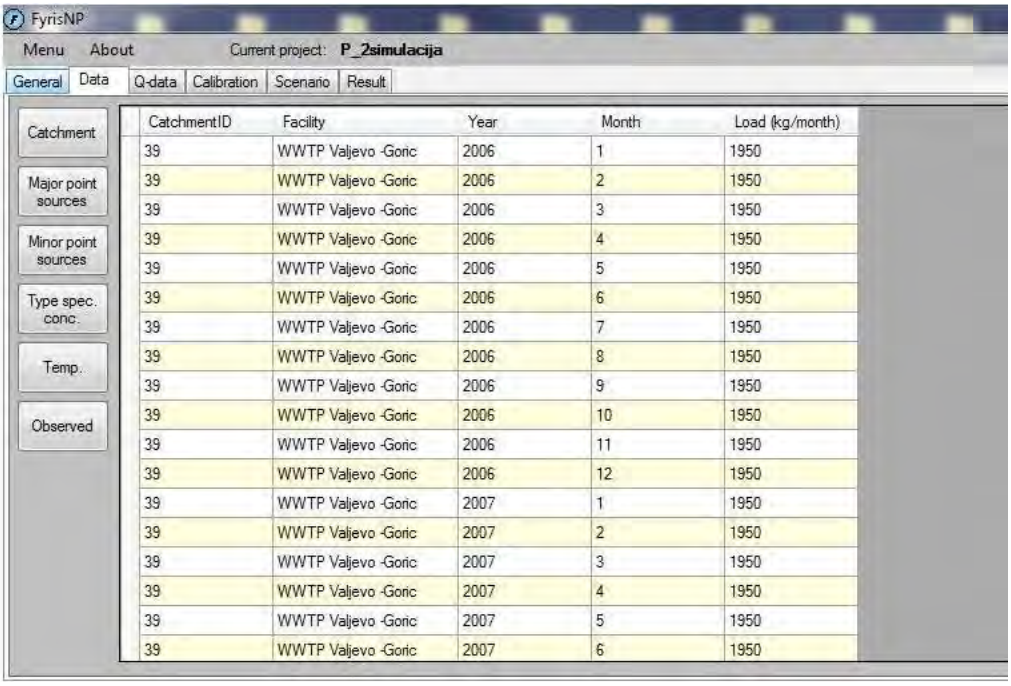
d.1) The *Data* tab - An example of Catchment-data:

The table in the *Catchment* window (1) contains characteristics on the 52 sub-catchments that are needed for the quantification of the nutrient transport. This includes information on hydrological network of sub-catchment and sub-catchment specific data on land-use, deposition, type-specific concentration in runoff from arable land and pasture and data on lake included in the model.



The table in the window *Major point sources* (2) contains data from large point sources such as wastewater treatment plants and industries. The example shows a wastewater treatment plant of Valjevo (WWTP Valjevo) including mass flow of total Nitrogen /Phosphorus, in kg/month, for the specific month and year.

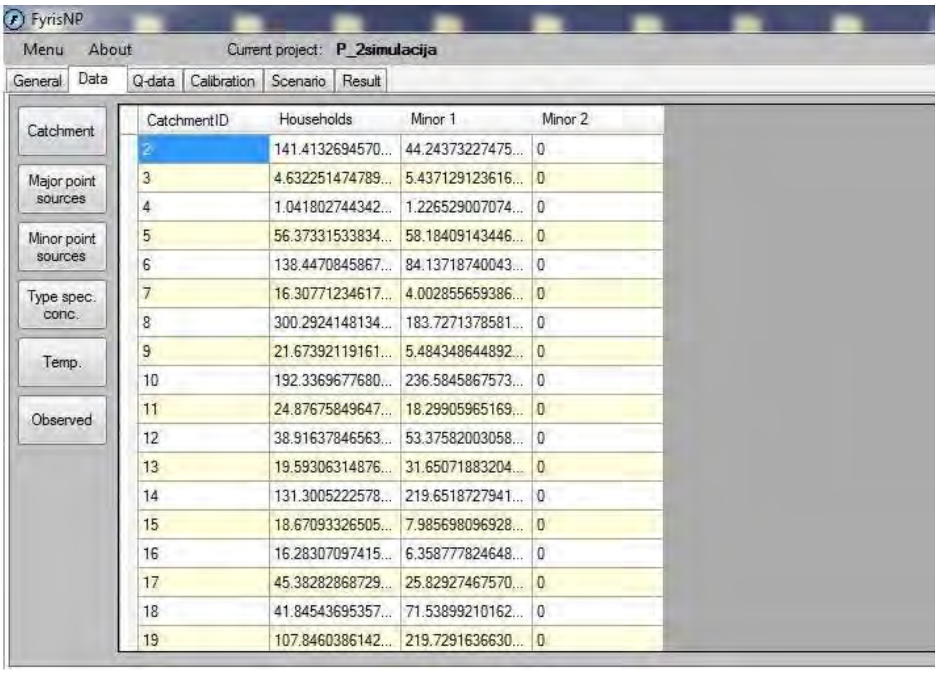
(2)



CatchmentID	Facility	Year	Month	Load (kg/month)
39	WWTP Valjevo -Goric	2006	1	1950
39	WWTP Valjevo -Goric	2006	2	1950
39	WWTP Valjevo -Goric	2006	3	1950
39	WWTP Valjevo -Goric	2006	4	1950
39	WWTP Valjevo -Goric	2006	5	1950
39	WWTP Valjevo -Goric	2006	6	1950
39	WWTP Valjevo -Goric	2006	7	1950
39	WWTP Valjevo -Goric	2006	8	1950
39	WWTP Valjevo -Goric	2006	9	1950
39	WWTP Valjevo -Goric	2006	10	1950
39	WWTP Valjevo -Goric	2006	11	1950
39	WWTP Valjevo -Goric	2006	12	1950
39	WWTP Valjevo -Goric	2007	1	1950
39	WWTP Valjevo -Goric	2007	2	1950
39	WWTP Valjevo -Goric	2007	3	1950
39	WWTP Valjevo -Goric	2007	4	1950
39	WWTP Valjevo -Goric	2007	5	1950
39	WWTP Valjevo -Goric	2007	6	1950

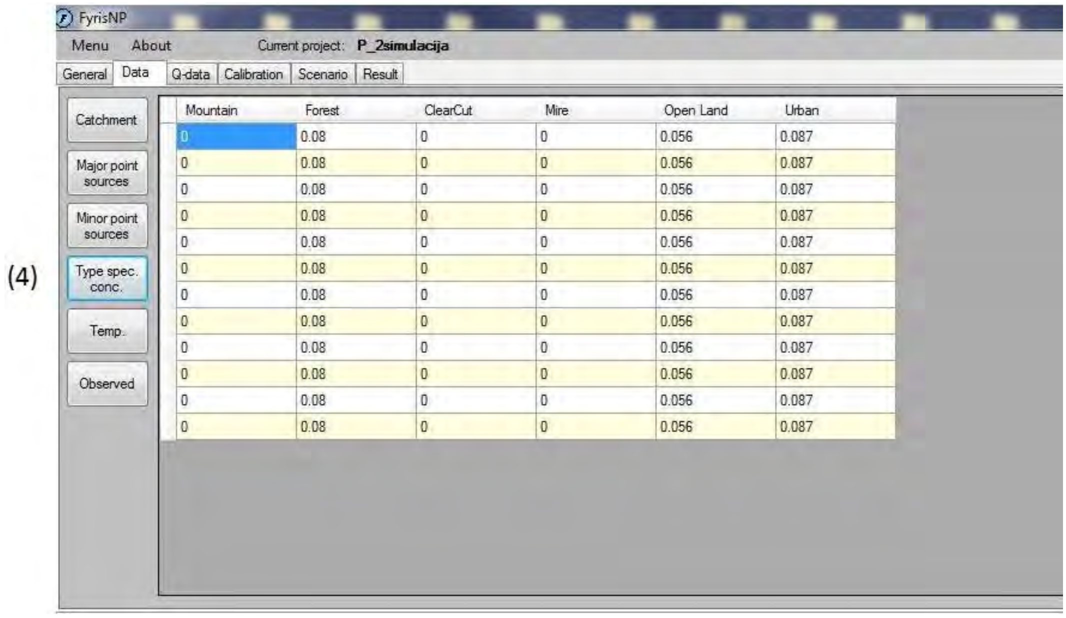
The table in the window *Minor point sources* (3) contains data from small point sources such as scattered households with autonomous sewage treatment system and estimated load from household animals (cows, pigs, poultry...). The estimated mass flow in kg/month, originating from households not included in the public sewage treatment system and manure pits have been shown at a sub-catchment level.

(3)



CatchmentID	Households	Minor 1	Minor 2
2	141.4132694570...	44.24373227475...	0
3	4.632251474789...	5.437129123616...	0
4	1.041802744342...	1.226529007074...	0
5	56.37331533834...	58.18409143446...	0
6	138.4470845867...	84.13718740043...	0
7	16.30771234617...	4.002855659386...	0
8	300.2924148134...	183.7271378581...	0
9	21.67392119161...	5.484348644892...	0
10	192.3369677680...	236.5845867573...	0
11	24.87675849647...	18.29905965169...	0
12	38.91637846563...	53.37582003058...	0
13	19.59306314876...	31.65071883204...	0
14	131.3005222578...	219.6518727941...	0
15	18.67093326505...	7.985698096928...	0
16	16.28307097415...	6.358777824648...	0
17	45.38282868729...	25.82927467570...	0
18	41.84543695357...	71.53899210162...	0
19	107.8460386142...	219.7291636630...	0

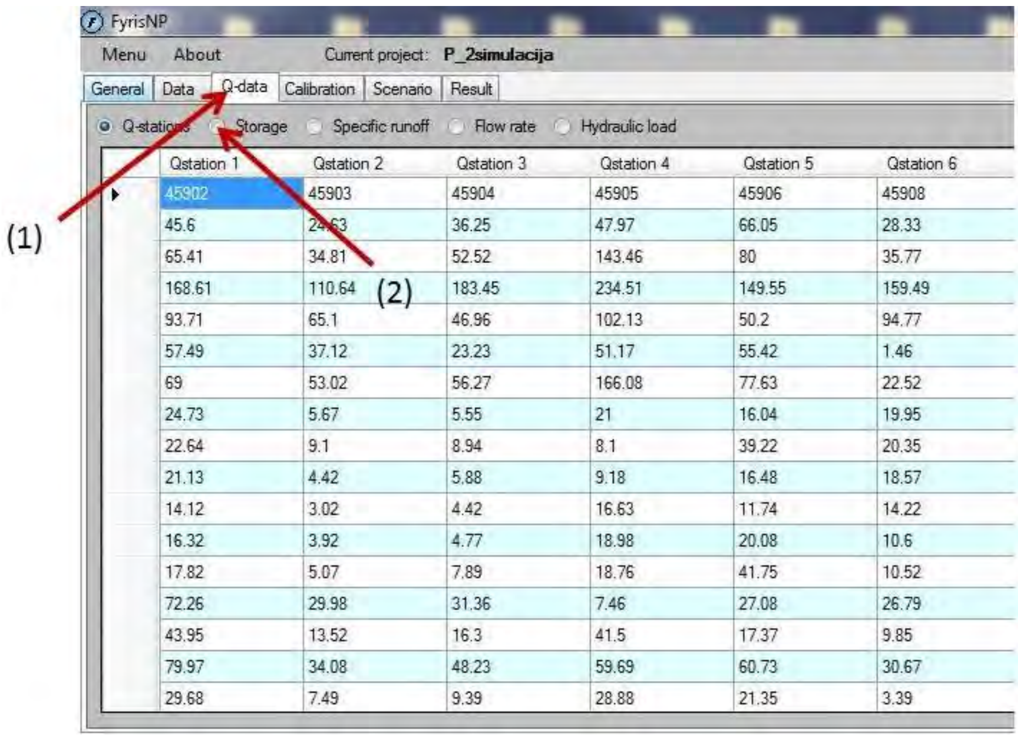
The table in the window *Type specific concentration* (4) contains assessed (accepted) data on type *specific concentrations* of total Nitrogen/Phosphorus as a result of various land use. Data have been given in mg/l per month for the relevant land use.



Mountain	Forest	ClearCut	Mire	Open Land	Urban
0	0.08	0	0	0.056	0.087
0	0.08	0	0	0.056	0.087
0	0.08	0	0	0.056	0.087
0	0.08	0	0	0.056	0.087
0	0.08	0	0	0.056	0.087
0	0.08	0	0	0.056	0.087
0	0.08	0	0	0.056	0.087
0	0.08	0	0	0.056	0.087
0	0.08	0	0	0.056	0.087
0	0.08	0	0	0.056	0.087
0	0.08	0	0	0.056	0.087
0	0.08	0	0	0.056	0.087

e) **The Q-data tab -** *Specific Runoff* (mm/month)

The window Q-data contains input data about the specific runoff expressed in mm/month (1), calculated on the basis of runoff measured at 12 hydrological stations, as well as data about the change of volume of the accumulation Garasi (2) in the period 2006-2010.



Qstation 1	Qstation 2	Qstation 3	Qstation 4	Qstation 5	Qstation 6
45902	45903	45904	45905	45906	45908
45.6	24.63	36.25	47.97	66.05	28.33
65.41	34.81	52.52	143.46	80	35.77
168.61	110.64	183.45	234.51	149.55	159.49
93.71	65.1	46.96	102.13	50.2	94.77
57.49	37.12	23.23	51.17	55.42	1.46
69	53.02	56.27	166.08	77.63	22.52
24.73	5.67	5.55	21	16.04	19.95
22.64	9.1	8.94	8.1	39.22	20.35
21.13	4.42	5.88	9.18	16.48	18.57
14.12	3.02	4.42	16.63	11.74	14.22
16.32	3.92	4.77	18.98	20.08	10.6
17.82	5.07	7.89	18.76	41.75	10.52
72.26	29.98	31.36	7.46	27.08	26.79
43.95	13.52	16.3	41.5	17.37	9.85
79.97	34.08	48.23	59.69	60.73	30.67
29.68	7.49	9.39	28.88	21.35	3.39

f) Model calibration

One of the most important steps in the modelling process is model calibration. It entails harmonization of the model results with the measurement values by setting (in the case of FyrisNP model) of two calibration coefficients: *Co* (determines how strongly the retention is reduced by temperatures) and *kvs* (the flow rate adjustment factor). Together, those calibration coefficients determine the retention within the catchment.

The model provides the user with three different methods for calibration and/or evaluation of sensitivity to individual parameter values.

1. **The automatic calibration** option uses the Simplex algorithm (Sorooshian, S., Gupta, V.K., 1995) to find the optimal parameter values within user specified parameter intervals. The optimal parameter values are considered to be the ones that provide the highest *E* value for the chosen calibration set up. The result is presented by means of parameter values, plus *E*and *r* values calculated in accordance with the selected statistical mode.

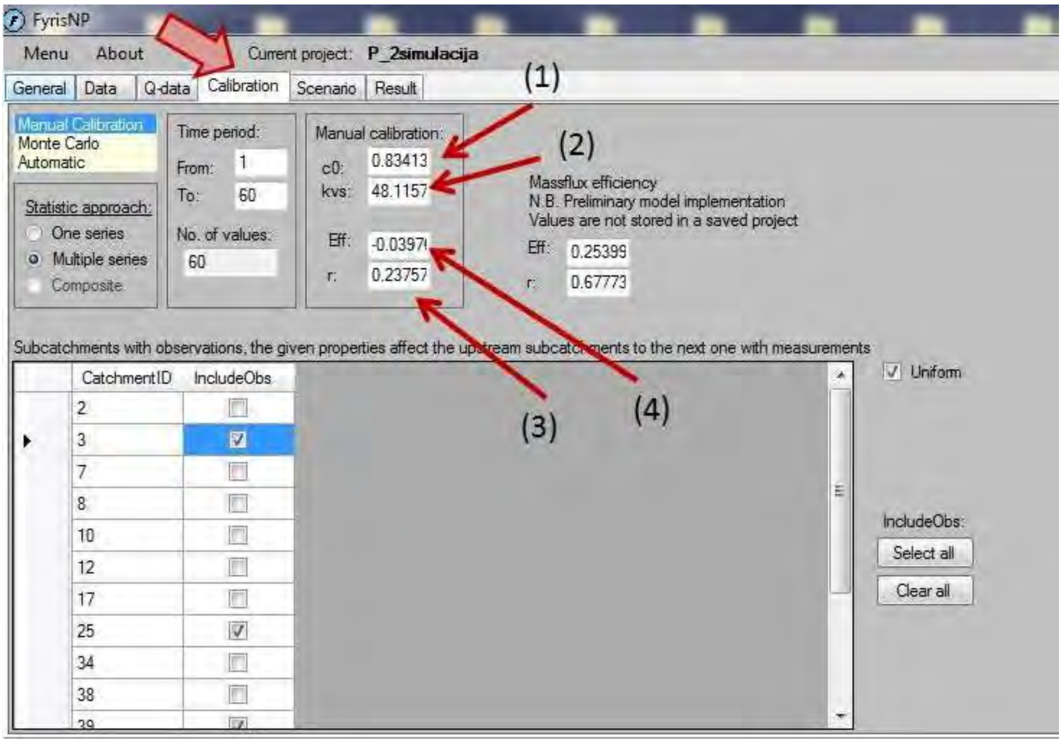
2. **In the Monte Carlo** simulation, the user specifies a uniform distribution of values for both parameters, and the number of individual simulations to carry out. As was the case for the manual calibration, the simulation covers the selected time period, and the selected in-stream concentrations are used to calculate model efficiency and correlation coefficient. The outcome may be analyzed graphically in the model by means of scatter plots.

3. **The manual calibration** allows the user to manually change both parameter values (*c0* and *kvs*), after which the model performs one simulation over the selected time period, using the selected measurement stations to calculate the model efficiency and the correlation coefficient. The user can inspect the simulation by looking at time-series graphs, or graphs of simulated versus observed concentrations for the selected sub-catchments.

In order to evaluate the fit of simulated to measured values, two statistical measures are used in the FyrisNP model: the model efficiency, *E* and the correlation coefficient, *r*. *E* = 1 implies that the measured and modelled series are identical, and *E* = 0 indicates that the simulation is no better than a straight line representing the average value of the observations.

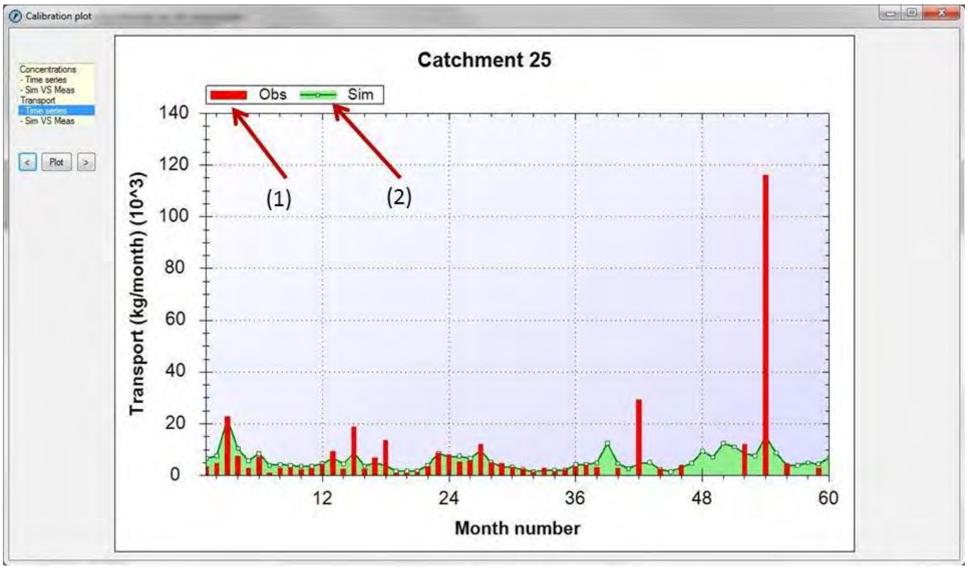
g) The *Calibration* tab

The Calibration window allows for setting calibration coefficients Co(1) and kvs(2) in order to obtain harmonized observation and simulation values of concentrations, i.e. mass flow of the total Nitrogen/Phosphorus. The degree of conformity is determined on the basis of the effectiveness coefficient Eff(3) and correlation coefficient- r (4) values.

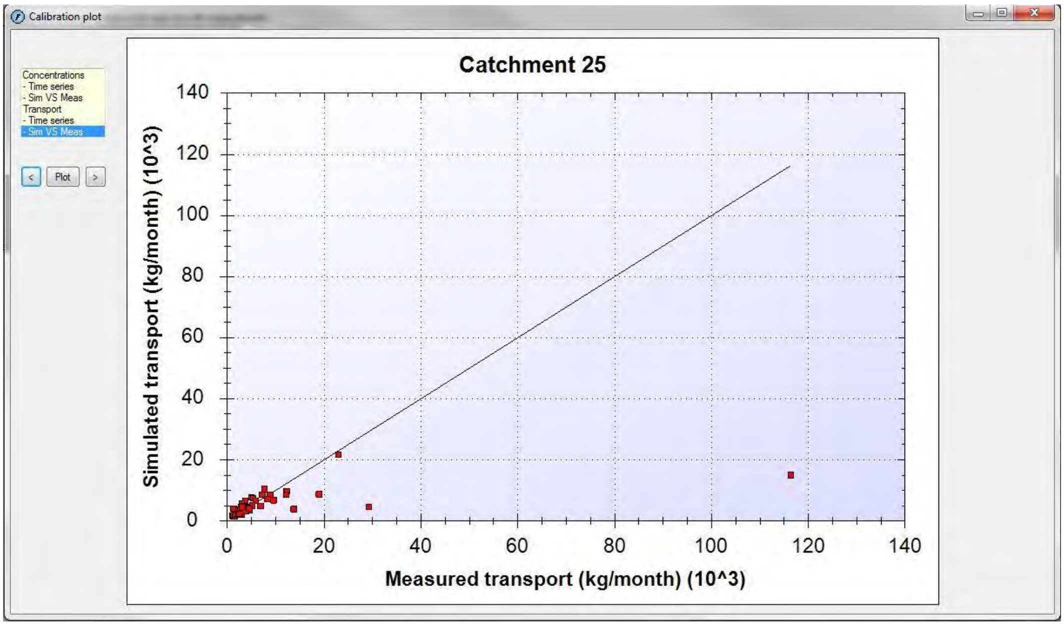


h) **Presentation of the calibration results -** ***Manual Calibration***

The window Calibration plot contains a chart with matching time series of observed concentrations or mass flows of total Nitrogen/Phosphorus and the values calculated by using FyrisNP, in the observed period for the chosen sub-catchment.



The level of conformity of the measured and simulated mass flow for the sub-catchment 25 has been visualized in the form of a correlation chart.

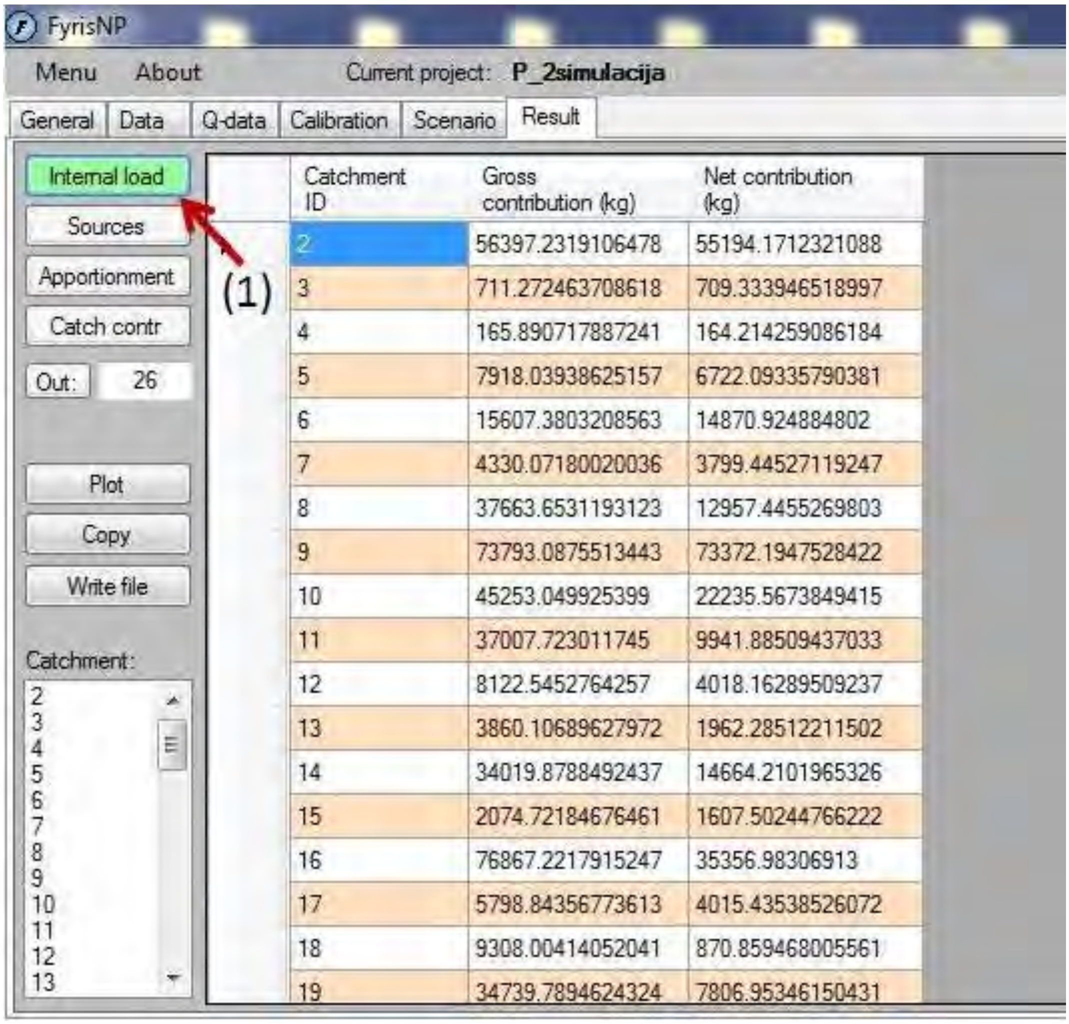


9.2.2 RESULT - LOAD ESTIMATION AND SOURCE APPORTIONMENT

The application window *Result* provides an overview of output data from the models obtained by making a Query: Internal load, Sources, Apportionment and Catchment control.

a) *Internal Load*

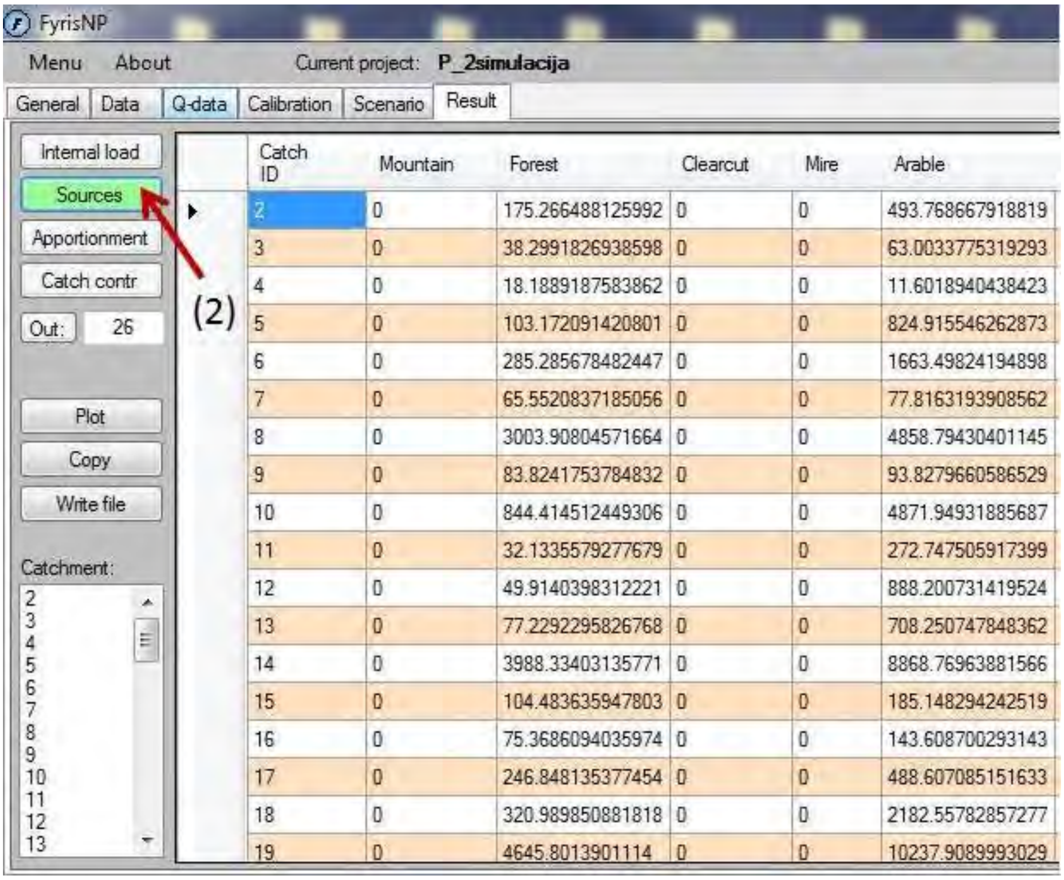
The summed up gross contribution, as well as the resulting downstream contribution after retention, from each sub-catchment. In the *Results* window, after making the query *Internal load* (1), gross and net mass flows of total Nitrogen/Phosphorus are shown broken down by sub-catchments. The Model allows for graphical presentation of the obtained data.



Catchment ID	Gross contribution (kg)	Net contribution (kg)
2	56397.2319106478	55194.1712321088
3	711.272463708618	709.333946518997
4	165.890717887241	164.214259086184
5	7918.03938625157	6722.09335790381
6	15607.3803208563	14870.924884802
7	4330.07180020036	3799.44527119247
8	37663.6531193123	12957.4455269803
9	73793.0875513443	73372.1947528422
10	45253.049925399	22235.5673849415
11	37007.723011745	9941.88509437033
12	8122.5452764257	4018.16289509237
13	3860.10689627972	1962.28512211502
14	34019.8788492437	14664.2101965326
15	2074.72184676461	1607.50244766222
16	76867.2217915247	35356.98306913
17	5798.84356773613	4015.43538526072
18	9308.00414052041	870.859468005561
19	34739.7894624324	7806.95346150431

b) *Sources*

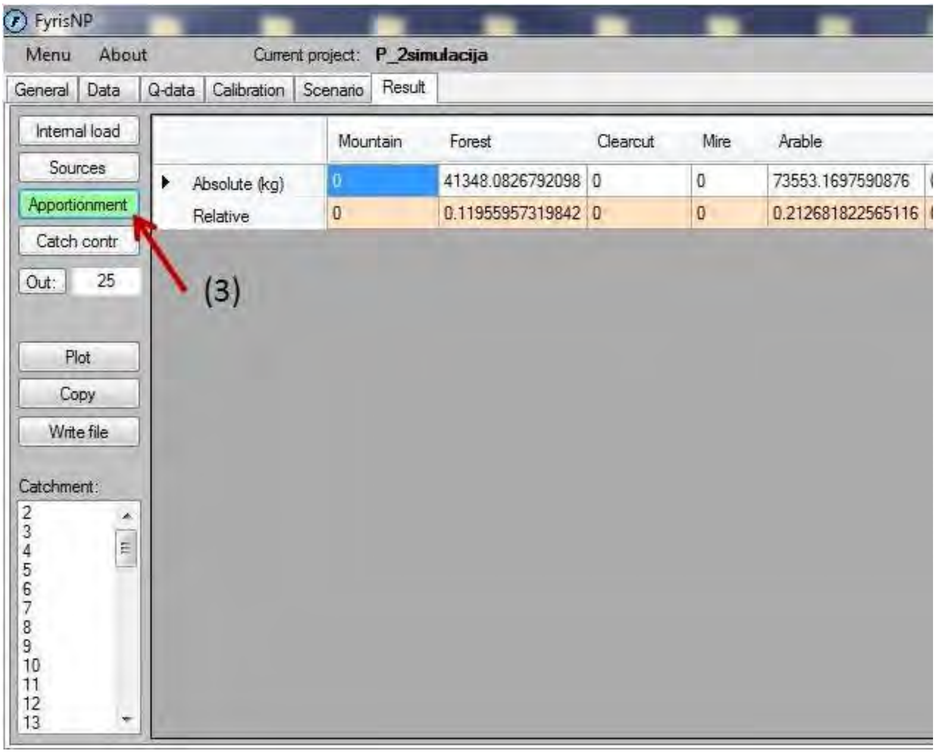
The summed up gross contribution, arranged by source type, is presented for each sub-catchment. In the window, after making the query *Sources* (2) gross contributions of total Phosphorus from individual pollution sources are shown, (Arable, Forest, Urban, Major point sources, Households) at the sub-catchment level. The Model allows for graphical presentation of the obtained data.



Catch ID	Mountain	Forest	Clearcut	Mire	Arable
2	0	175.266488125992	0	0	493.768667918819
3	0	38.2991826938598	0	0	63.0033775319293
4	0	18.1889187583862	0	0	11.6018940438423
5	0	103.172091420801	0	0	824.915546262873
6	0	285.285678482447	0	0	1663.49824194898
7	0	65.5520837185056	0	0	77.8163193908562
8	0	3003.90804571664	0	0	4858.79430401145
9	0	83.8241753784832	0	0	93.8279660586529
10	0	844.414512449306	0	0	4871.94931885687
11	0	32.1335579277679	0	0	272.747505917399
12	0	49.9140398312221	0	0	888.200731419524
13	0	77.2292295826768	0	0	708.250747848362
14	0	3988.33403135771	0	0	8868.76963881566
15	0	104.483635947803	0	0	185.148294242519
16	0	75.3686094035974	0	0	143.608700293143
17	0	246.848135377454	0	0	488.607085151633
18	0	320.989850881818	0	0	2182.55782857277
19	0	4645.8013901114	0	0	10237.9089993029

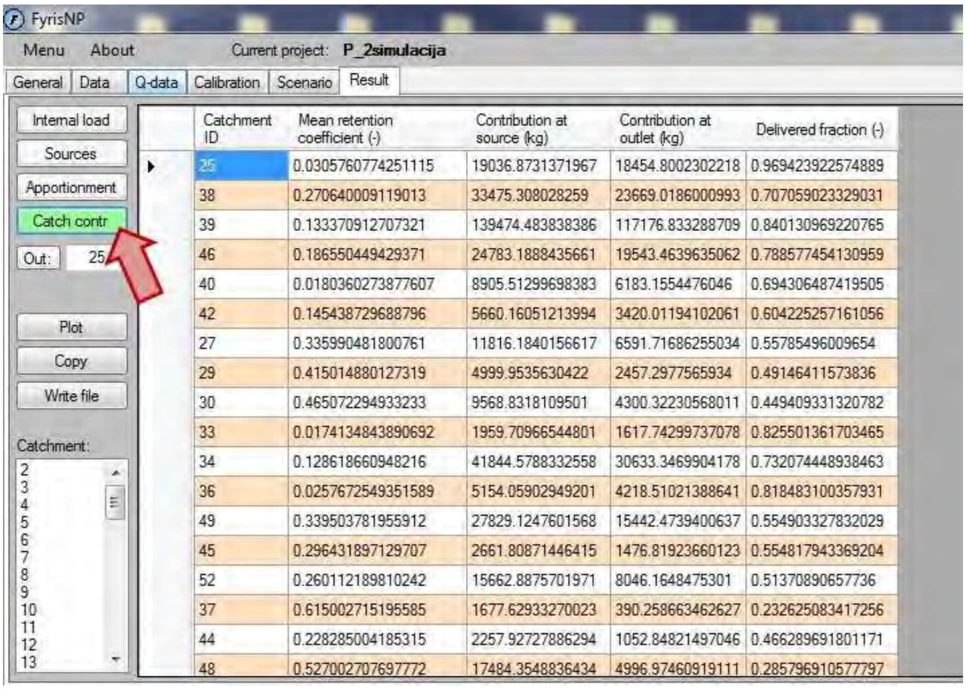
c) *Apportionment*

Computes the source apportionment for the selected outlet and its upstream area. In the *Results* window, after making the query *Apportionment* (3) absolute and relative values of mass flow of total Nitrogen/Phosphorus from individual pollution sources are shown (Arable, Forest, Urban, Major point sources, Households) at the outlet of the selected sub-catchment, including the impacts from all upstream sub-catchments. The Model allows for graphical presentation of the obtained data.



d) *Catchment control*

In the *Results*, window after making the query *Catchment control* (4) gross (contribution at source, kg) and net contributions (Contribution at outlet, kg) are shown for each upstream sub-catchment in relation to the outlet of the selected sub-catchment, including the selected sub-catchment, respective average values of the retention coefficient (mean retention coefficient) and the net load coefficient (delivered fraction). The Model allows for graphical presentation of the obtained data.



9.2.3 Results – Output load assessment and apportionment charts

The application window *Results* allows for activating the function *Plot, Copy, Write file* for export of output (calculated) data from the model and diagram presentation of load assessment and apportionment in the required format (txt, jpg, png, gif…).

a) **Output results for total Nitrogen**

The (Figure 45.) shows output results, obtained after making the query *Internal load,* i.e. gross and net mass flows of total Nitrogen, broken down by sub-catchments. The magnitude of retention of total Nitrogen in each sub-catchment can be observed from the difference between gross and net mass flow.

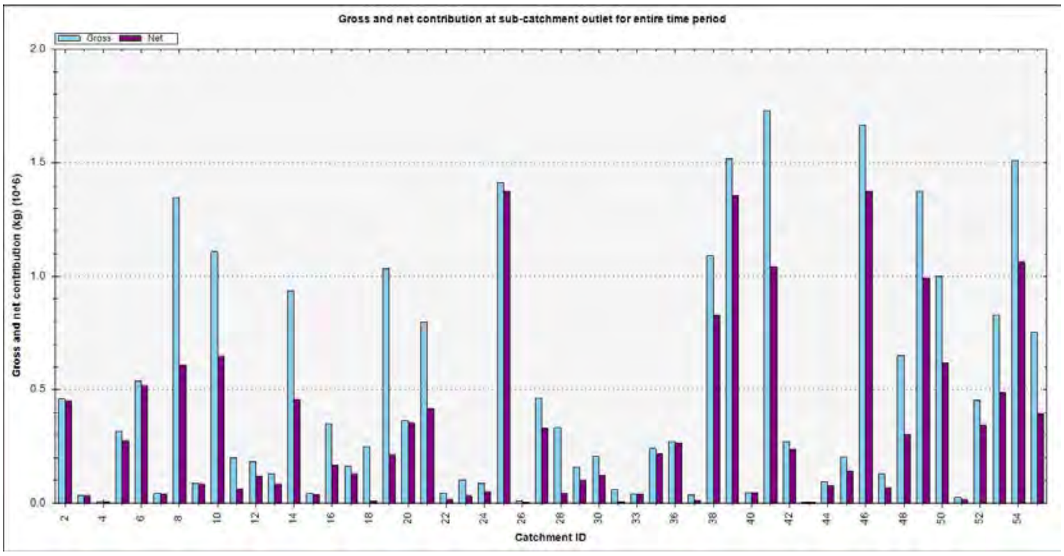


Figure 45. Gross and net mass flow at the outlet of sub-catchments

The (Figure 46.) shows output results, obtained after making the query *Sources*, i.e. gross contributions of total Nitrogen from individual pollution sources (Arable, Forest, Urban, Major point sources, Households), at the sub-catchment level. The yellow colour prevails at the chart: it represents agricultural land load. The sub-catchments with larger towns sewage treatment systems are shown in red (sub-catchment 2- Obrenovac, sub-catchment 16 - Lazarevac, sub-catchment 39 -Valjevo)

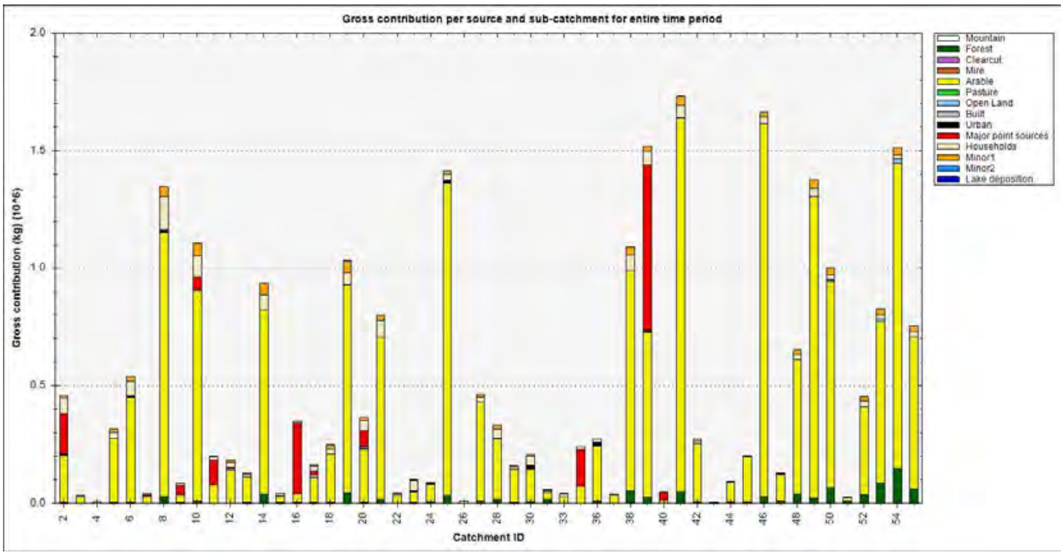


Figure 46. Gross contributions of total Nitrogen from individual pollution sources, broken down by sub-catchments

After making the query *Apportionment* for the selected sub-catchment the relative values of mass flow of total Nitrogen from individual sources are obtained (Arable, Forest, Urban, Major point sources, Households) at the outlet of the selected sub-catchment, including impacts from all upstream sub-catchments.

The (Figure 47.) shows impacts from all pollutants on the most downstream point in the Kolubara Catchment (at the confluence of the Kolubara and the Sava river). 80% of the pollution is from agricultural surfaces, as a diffuse source of pollution.

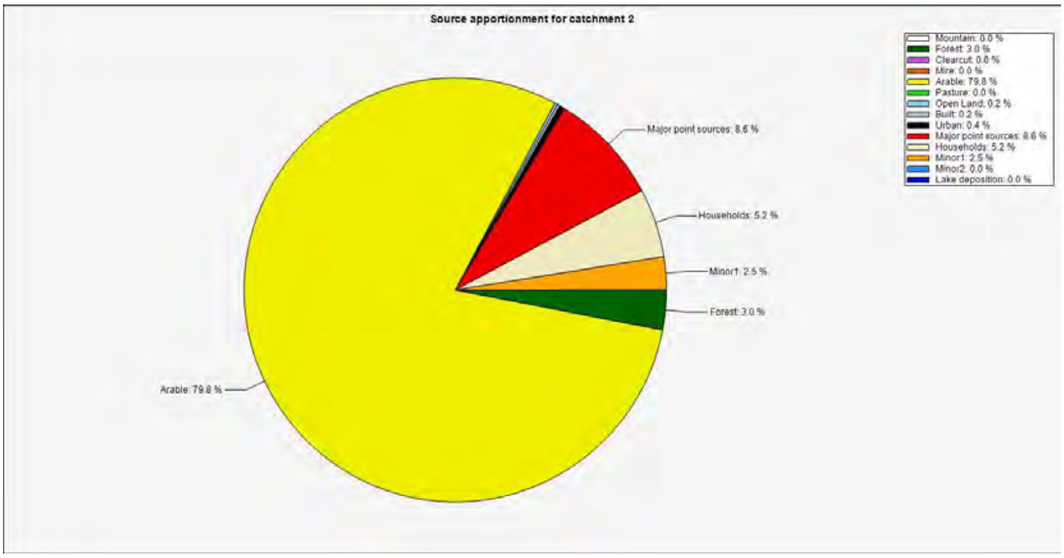


Figure 47. Relative values of mass flow of total Nitrogen from individual sources at the outlet of the Kolubara Catchment

The (Figure 48.) shows impacts from all pollutants on the most downstream point in the Catchment 16 (at the confluence of the Kolubara and the Ocaga river). 75% of the pollution originates from a large point source (the sewage system of the town of Lazarevac).

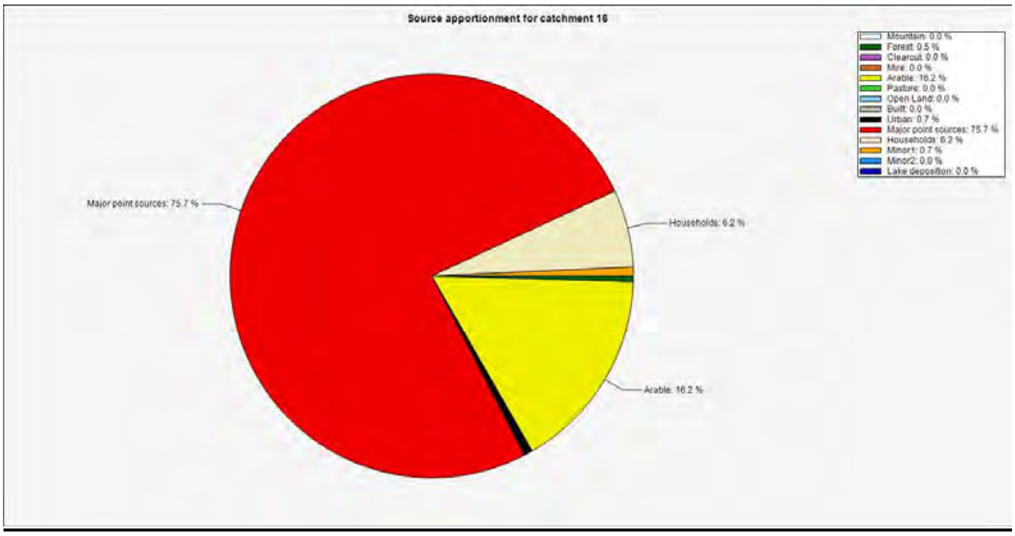


Figure 48. Relative values of the mass flow of total Nitrogen from individual sources at the outlet of the sub-catchment 16 – where the sewage system of Lazarevac is located.

The output results, obtained after making the query *Catchment control,* have been shown in a tree diagram, with specified inter-relations and upstream/downstream arrangement of the sub-catchments. The intensity of load of total Nitrogen has been visualized in different colours for each sub-catchment.

The (Figure 49.) shows gross load of total Nitrogen (kg) from the sum of all pollution sources, broken down by sub-catchments and in relation from the most downstream point of the Kolubara catchment.

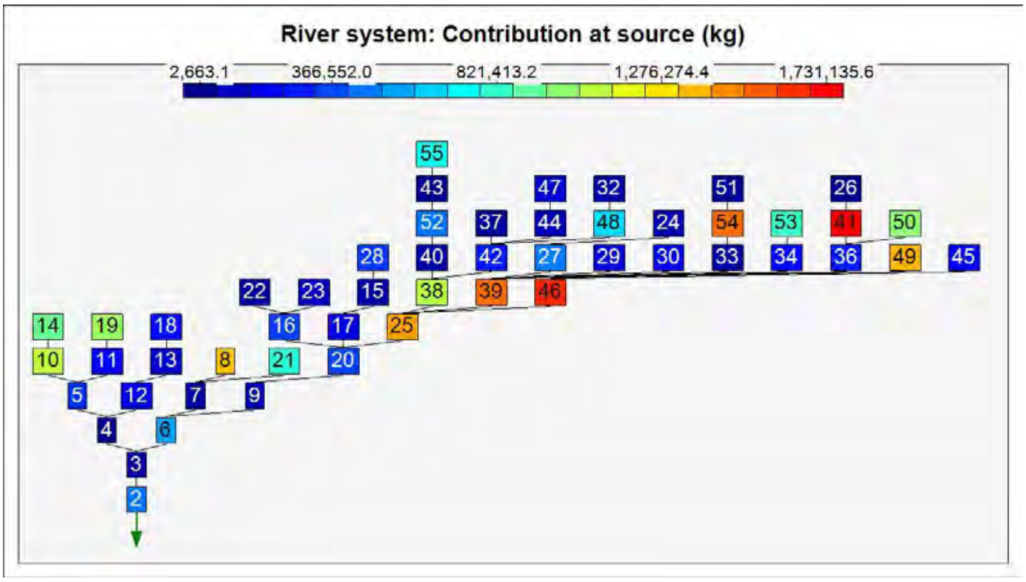


Figure 49. Contribution at sources

The (Figure 50.) shows net load of total Nitrogen (kg) from each sub-catchments in relation from the most downstream point of the Kolubara catchment

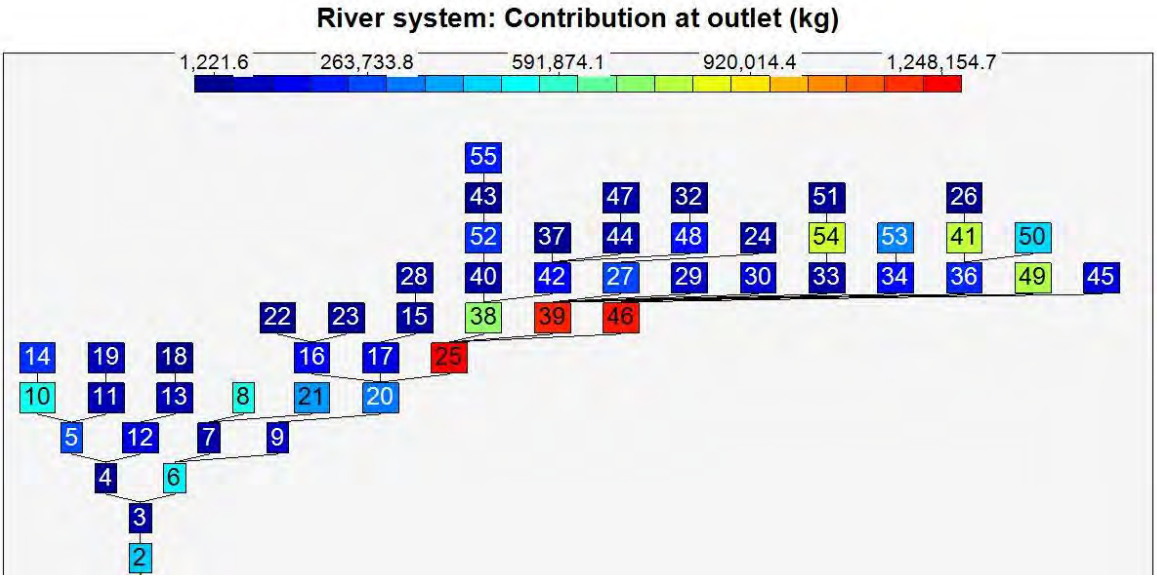


Figure 50. Contribution at outlet

The (Figure 51.) shows relative values of net load of total Nitrogen from each sub-catchment in relation to the most downstream point of the Kolubara Catchment

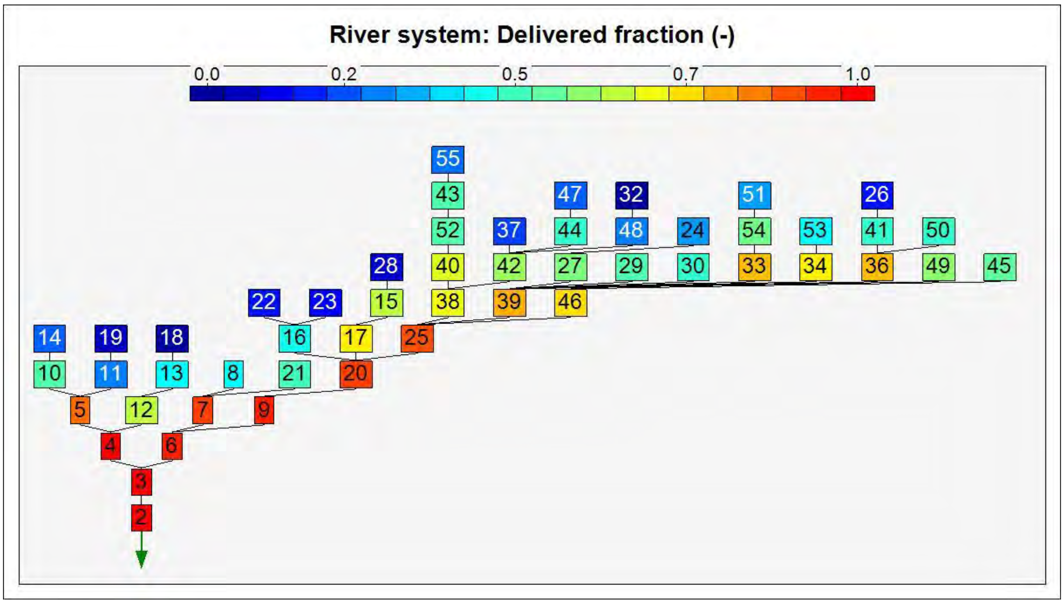


Figure 51. Delivered fraction

The (Figure 52.) shows average values of the retention coefficient for each sub-catchment in relation to the most downstream point of the Kolubara Catchment. The highest retention is in the sub-catchment 18 (accumulation Paljuvi Vis), and sub-catchment 32 (accumulation Garasi).

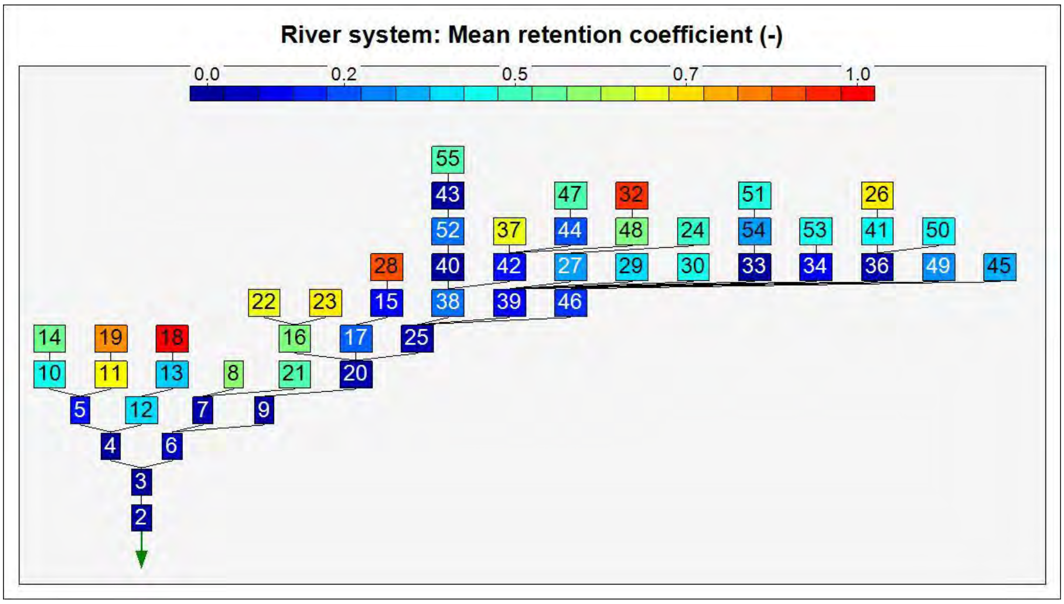


Figure 52. Mean retention coefficient

b) **Output results for total Phosphorus**

The (Figure 53.) shows output results obtained after making the query *Internal load,* i.e. gross and net mass flows of total Phosphorus broken down by each sub-catchment. The magnitude of retention of total Phosphorus in each sub-catchment can be observed from the difference between gross and net mass flow.

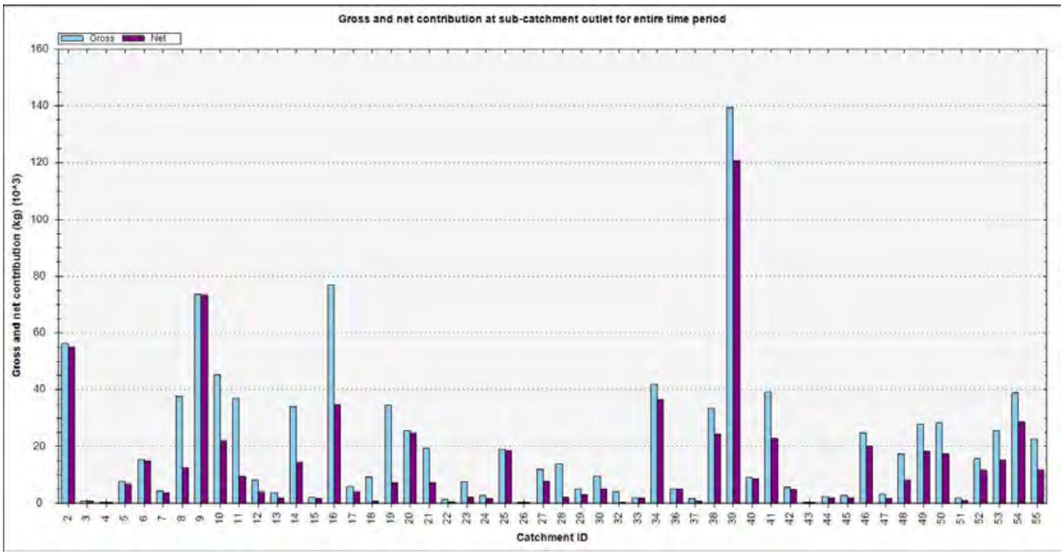


Figure 53. Gross and net mass flow at the outlet of sub-catchments

The (Figure 54.) shows output results obtained after making the query *Sources*, i.e. gross contributions of total Phosphorus from individual sources (Arable, Forest, Urban, Major point sources, Households) at the sub-catchment level. The red colour prevails at the chart: this is the load from major point sources, where discharge points of urban sewage systems are located (sub-catchment 2-

Obrenovac, sub-catchment 9- RB Kolubara processing, sub-catchment 16-Lazarevac, sub-catchment -34 Mionica, sub-catchment 39-Valjevo)

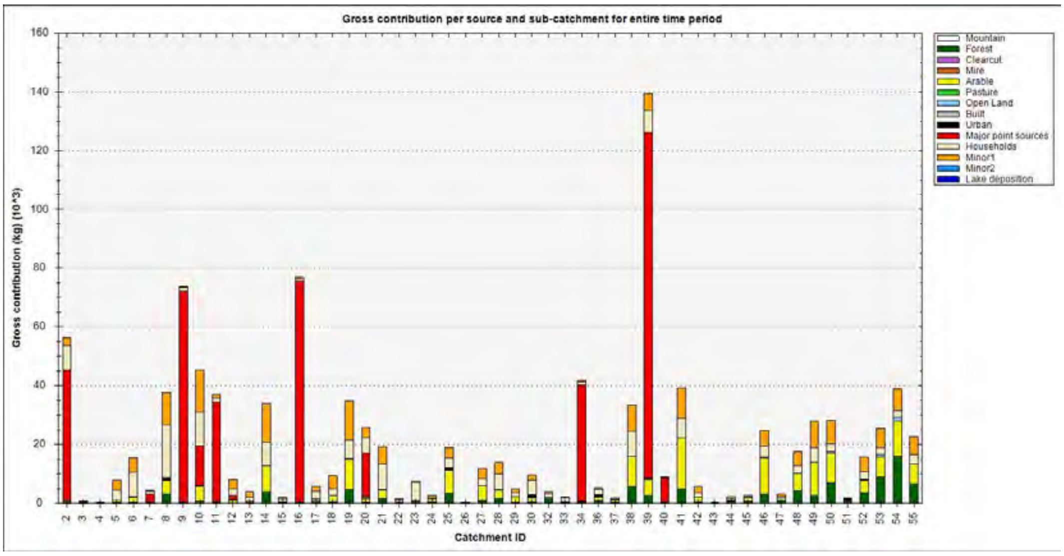


Figure 54. Gross contributions of total Nitrogen from individual sources, broken down by sub-catchments

After making the query *Apportionment* for the chosen sub-catchment relative values of mass flow of total Phosphorus are obtained from individual sources (Arable, Forest, Urban, Major point sources, Households) at the outlet from the chosen sub-catchment, including the impacts from all upstream sub-catchments.

The (Figure 55.) illustrates the impacts of all pollutants on the most downstream point in the Kolubara catchment (at the confluence of the Kolubara and the Sava river). Around 50% pollution of total Phosphorus originates from major point sources, while only 7.1% is due to forests as diffuse pollution source

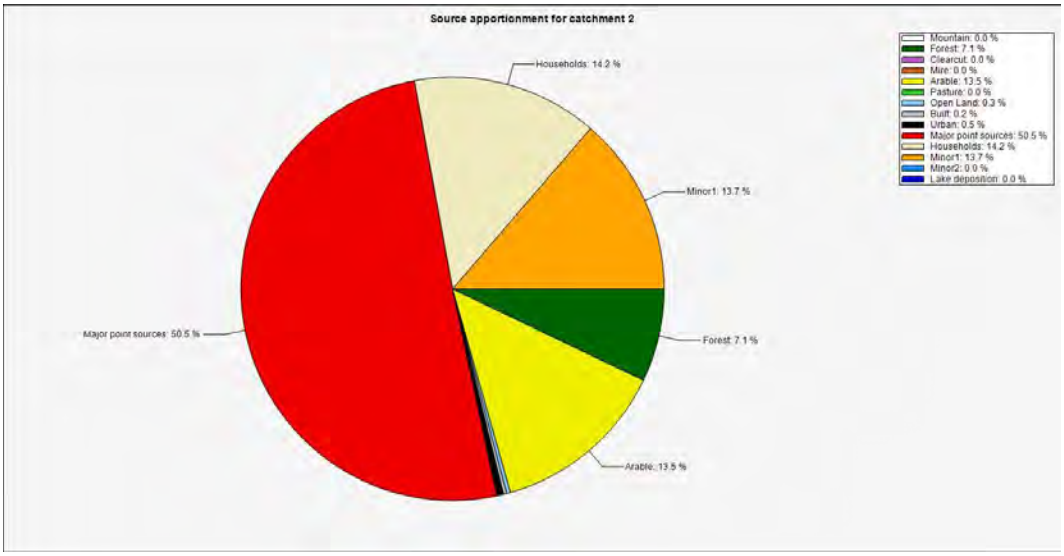


Figure 55. Relative values of mass flow of total Phosphorus from individual sources at the outlet of the Kolubara catchment

The (Figure 56.) illustrates the impacts of all pollutants on the most downstream point of the sub-catchment 51 (the confluence of the Kozlica river and Bukovska river), which was selected as a small experimental catchment predominantly covered by forests. 64% pollution comes from forests, as expected.

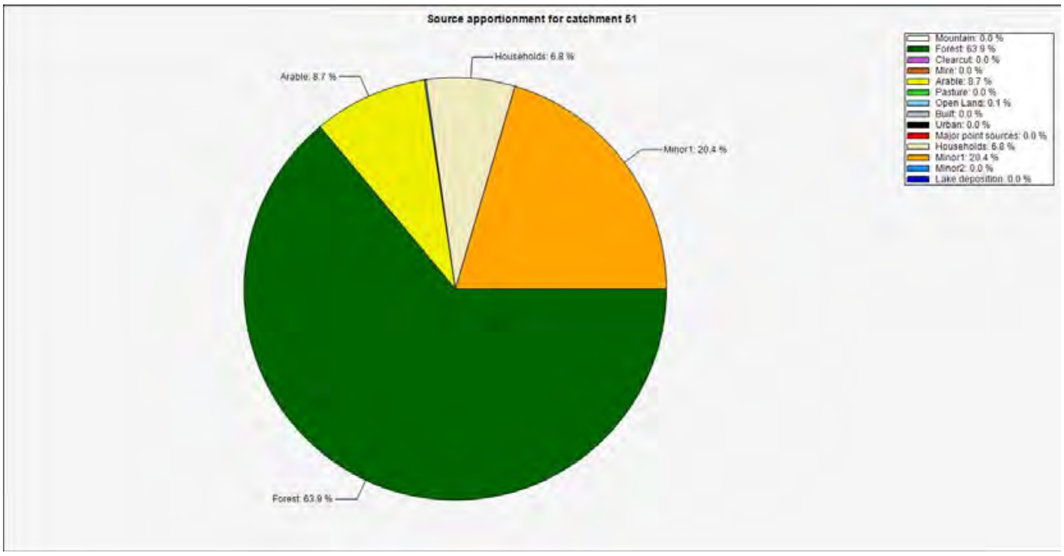


Figure 56. Relative values of mass flow of total Phosphorus from individual sources at the point where Kozlica river joins the Bukovska river (experimental catchment)

Output results obtained after making the query *Catchment control* are shown in a tree diagram, with defined inter-relations and upstream/downstream arrangement of sub-catchments. The intensity of load of total Phosphorus has been visualized in different colours for each sub-catchment.

The (Figure 57.) shows gross load of total Phosphorus (kg) from the sum of all pollution sources, broken down by sub-catchments and in relation from the most downstream point of the Kolubara catchment. Most gross load of total Phosphorus originates from the sub-catchment -39 where the discharge point of the Valjevo sewage system is located.

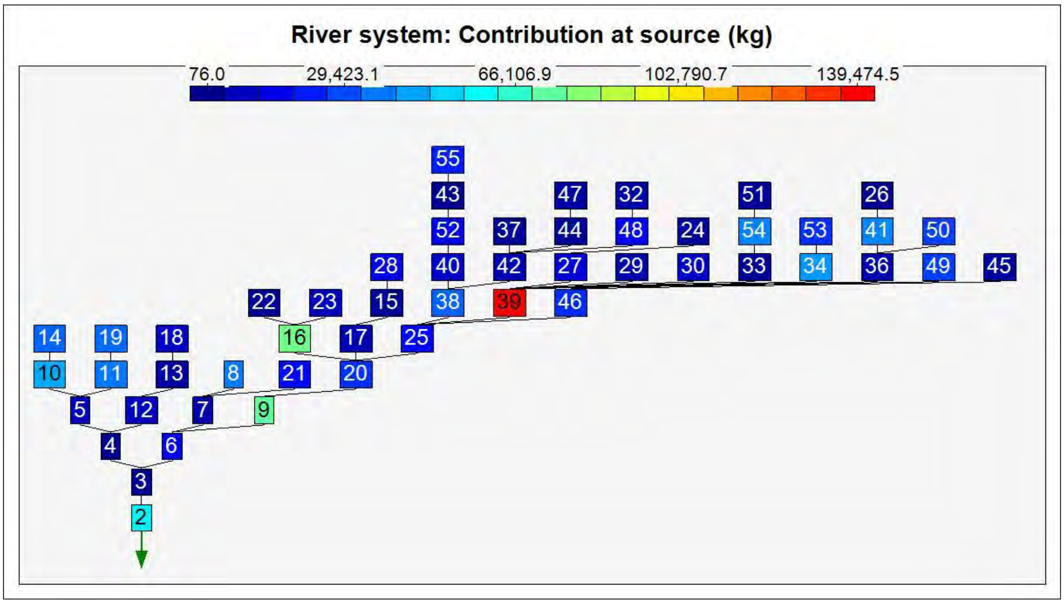


Figure 57. Contribution at sources

The (Figure 58.) shows net load of total Phosphorus (kg) from each sub-catchment in relation to the most downstream point of the Kolubara catchment

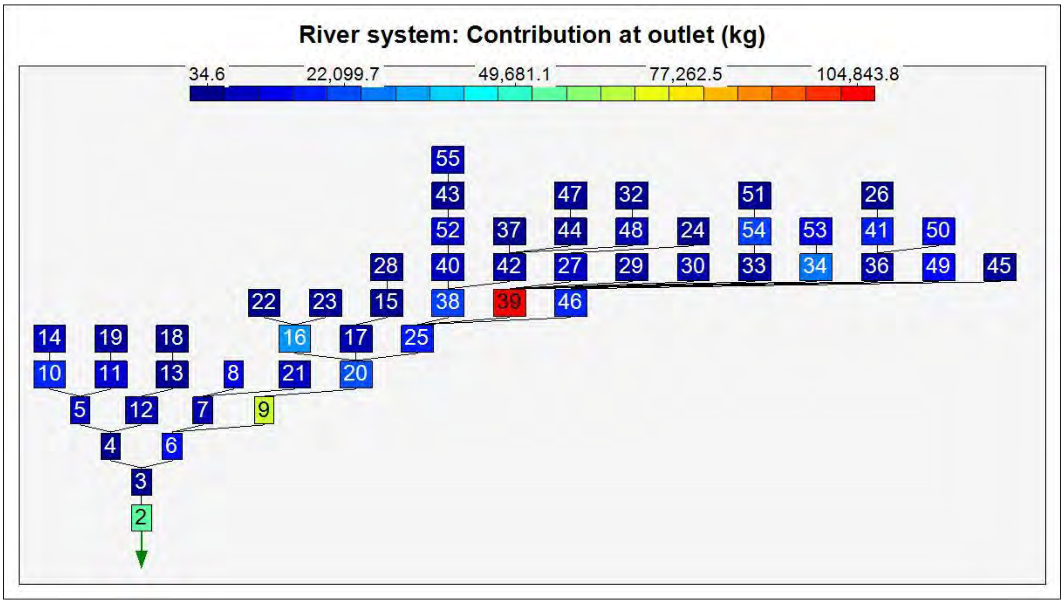


Figure 58. Contribution at outlet

The (Figure 59.) gives relative values of net load of total Phosphorus from each sub-catchment in relation to the most downstream point of the Kolubara catchment.

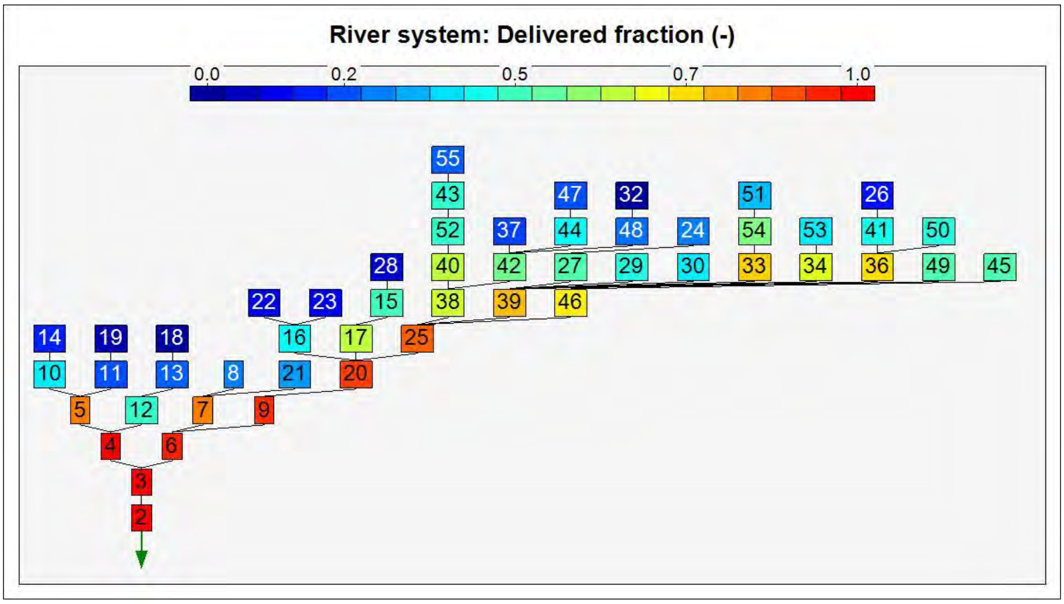


Figure 59. Delivered fraction

The ([Figure 60.](#)) gives average values of the retention coefficient for each sub-catchment in relation to the most downstream point of the Kolubara catchment. Most retention occurs in the sub-catchment 18 (Paljuvi Vis accumulation), and sub-catchment 32 (Garasi accumulation).

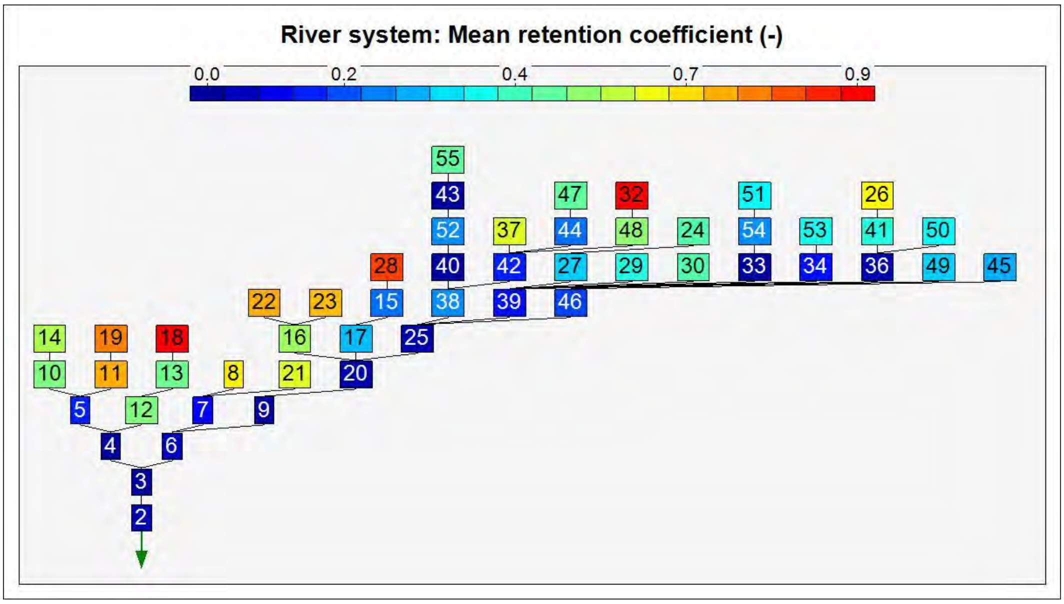


Figure 60. Mean retention coefficient

10. CONCLUSIONS AND RECOMMENDATIONS

The Kolubara River Catchment was chosen as a pilot catchment for testing the mathematical model for nutrient load from diffuse and point sources. Data and platforms from previous international cooperation projects related to the catchment area, such as „the Report on the Features of the Kolubara River Catchment (2007)“ and „Kolubara Catchment Pilot Management Plan (2010)“, were a good basis to put forward a proposal for continuing cooperation with the Swedish Environmental Protection Agency (Swedish EPA). The *FyrisNP model* developed at the Swedish University of Agricultural Sciences in Upsala was used for simulation of water quality and nutrient load (total Nitrogen and total Phosphorus) in the Kolubara Catchment (*Department of Aquatic Science and Assessment at Swedish University of Agricultural Sciences*, Uppsala). The Model simulates the transport of load nutrients (Nitrogen and Phosphorus) at the catchment level, by calculation of contributions of upstream sub-catchments' load, broken down by pollution sources. After a qualitative analysis of input data and platforms used in *FyrisNP model* was performed for the Kolubara Catchment and the relevant results were obtained, the following conclusions were made:

- The contribution from individual pollution sources in the Kolubara Catchment to total Nitrogen load on the most downstream point (the confluence of the Kolubara into the Sava river), shows that about 80% pollution is caused by agricultural surfaces as a diffuse source of pollution.
- The contribution from individual pollution sources in the Kolubara Catchment to total Phosphorus load on the most downstream point (the confluence of the Kolubara into the Sava river), shows that around 50% pollution occurs due to major point sources, while only 7.1% originates from forests as a diffuse source of pollution.
- The contribution of all polluters to total Nitrogen load on the most downstream point of the Ocaga River (at the point it joins the Kolubara River), shows that around 75% pollution is originated by a major point source, the sewage system of the town of Lazarevac, which is released in the Ocaga River.
- The influence of all polluters on the most downstream point in the Kozlica River Catchment (the Kozlica joins the Bukovska River, and the latter joins the Kolubara) shows that around 64% pollution is due to forests, which was expected for the catchment area with a predominant part of the surface under forests.
- The results of simulation of nutrients load by using the *FyrisNP model* have shown that at this stage of the research input data is obtained in the order of magnitude which accounts for further application of this model and its extension to other catchments in Serbia.

- The reliability of the results of nutrient load obtained by using the *FyrisNP model* for the Kolubara Catchment has shown that this model should be used in the process of adoption and application of the Nitrates Directive (*Council Directive 91/676/EEC*). The application of this model should be an integral part of the *Water Management Plan* (Article 33 par. 2, *Law on Water*, Off. Gazette RS 30/10). The assessment of diffuse pollution of soil and water from agricultural areas are main objectives for period 2010-2019. according to National Environmental Protection Programme („Off. Gazette RS 12/10).

The application of the *FyrisNP model* to the Kolubara Catchment has shown that the existing numerical and spatial data collected and processed by different institutions and state authorities are not available in a qualitative and quantitative form for direct use as input parameters for the model. *FyrisNP model* was developed and is used in Sweden and it is adapted to a country with highly developed agricultural statistics and reliable data on concentrated pollution sources. Experience gained in the course of data collection and processing, as well as simulation, shows that the model's potential exceeds the quality and quantity of input data and that with the view to its successful application and obtaining more reliable output data, the following recommendations should be taken into consideration:

- Establish permanent monitoring of quality and quantity of water in small experimental catchments four times a year at a minimum, in all vegetation seasons and under any hydrological conditions (low, medium and high waters). Thus the relevant data about *leaching concentrations of Nitrogen and Phosphorus* will be obtained for different types of soil and crops.

- In order to improve the assessment of *leaching concentrations of Nitrogen and Phosphorus* depending on the type of the soil it is necessary to include further research aimed at producing a more precise map of the soil texture in the Kolubara Catchment, and the entire territory of Serbia.

- More precise data about spatial distribution of the crops, broken down by sub-catchments, may be obtained by using satellite and aero-photo images, which increases the precision of the input data. In order to obtain data by using such platforms additional budget is required.

- In order to make a more precise assessment of the model as regards data related to the use of mineral and organic fertilizers, broken down by type and quantity, statistical accounting is required about their spatial and time dynamics of use.

- The establishment of a reliable national register of communal and industrial sewage systems, as concentrated polluters, is a precondition for a more precise assessment of concentrations and of the net and gross mass flow of total Nitrogen and Phosphorus by using the *FyrisNP model*.

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