

# Nitrogen Compounds in the Surface Water Identifying Concentrations and Sources

Jolita Braduliene<sup>1</sup>, Raimondas Grubliauskas<sup>2</sup>

*Environmental protection department, Vilnius Gediminas Technical University, Vilnius, Lithuania*  
*E-mails: <sup>1</sup>jolita.braduliene@vgtu.lt (corresponding author); <sup>2</sup>raimondas.grubliauskas@vgtu.lt*

**Abstract.** The main objective of the surface water monitoring – periodically to conduct water quality testing, to find out the possible sources of pollution in time and to warn population. Water samples for analysis of surface water bodies – rivers Raseika (Raseiniai district, central Lithuania) were taken during the autumn season. The river Raseika belongs to the basin of the river Jura. This river was drained for many times and has a lot of ponds. The treated urban sewage of Raseiniai wastewater treatment plants flows to this river. Also the river Raseika is polluted by population sewage, which are not collected and treated. The river Raseika flows through Dubysa Regional Park area, which was established in 1992 to preserve Dubysa erosive valley landscape, natural and cultural heritage values: the picturesque Dubysa valley; significant geomorphological, hydrographic, cultural, botanical and landscape values, natural ecosystem stability, biota components, unique flora and fauna, natural fish migration routes and spawning grounds.

Six points were selected to carry out the monitoring of the river Raseika. The nitrogen concentrations were mostly not corresponding to the standards. Most of the ascendances were found in samples where the treated urban sewage of Raseiniai city wastewater treatment plants flows in the river.

**Keywords:** surface water monitoring, ammonium, nitrate, nitrite, total nitrogen.

**Conference topic:** Environmental protection.

## Introduction

Nitrogen (N) compounds are among the most important hydrosphere components. Their concentrations largely determine the productivity of water bodies and their state. The wide use of N forms in agriculture and industry and their input with wastewater very often cause water pollution by such compounds (Lozovik, Borodulina 2009).

Nitrogen is a naturally occurring element that is essential to plant growth and crop production. However, nitrate N can cause eutrophication of surface waters primarily by stimulating algae production. In a soil system, nitrate N is continually supplied through the natural processes of mineralization and nitrification of soil organic matter. Other sources of N include fertilizers, animal manures, municipal sewage wastes, agricultural and industrial wastes, atmospheric deposition, and dinitrogen fixation, all of which can be converted to nitrate N through mineralization and nitrification. Nitrate N is mobile and, therefore, can be lost from the soil profile by leaching. Subsequent transport of nitrate N to surface waters occurs through subsurface drainage (tile lines) or base flow. Very little nitrate N is lost from the landscape via surface runoff (Jackson *et al.* 1973; Randall, Mulla 2001; Bagdžiūnaitė-Litvinaitienė 2004).

Nitrates and similar substances assimilating into organism can be provocative to methaemoglobinaemia, interrupt thyroid activities and cause cancer risk (nitrosamines). Nitrates are extremely dangerous to pregnant females, newborn babies and in the first months of babies (Gangolli *et al.* 1994; Jakučionytė *et al.* 2001; Mažeikienė *et al.* 2008).

Nitrogen and phosphorus are two most important elements helping the growth of algae and aquatic plants in rivers, lakes, and shallow embayed areas of the marine environment. For this reason, they are termed eutrophic or life-giving elements. In quiescent surface waters, excessive growth of algae and other aquatic vegetation reduces the sunlight penetration into the water body, thereby inducing stratification and causing oxygen depletion in the lower levels (Vosyliienė *et al.* 2010). This discourages the growth of fish and other natural aquatic life (Vosyliienė, Jankaitė 2006; Vosyliienė *et al.* 2006), causes undesirable tastes and odours, and generally reduces the value of water for domestic, industrial, agricultural and recreational use (Vabolienė *et al.* 2007; Skaisgirienė *et al.* 2009).

Municipal and industrial wastewater contains significant quantities of nitrogen and phosphorus and therefore the removal of these nutrients has become an important facet of wastewater treatment. Biological removal of these nutrients is preferred to the chemical removal as it results in a lower waste sludge production and has the public perception that biological processes are more “environmentally friendly” than chemical processes (Vabolienė *et al.* 2007; Oldham, Rabinowitz 2002).

## Objects and methods

The following sampling places were selected for the assessment of pollution diffused and generated in the river Raseika: 1R – 4R (above Raseiniai town); 5R – 6R (below Raseiniai town). The work of river cleaning was launched in sampling place 1R. Sampling place 4R covers a pond, sampling place 5R is located in front of wastewater treatment facilities, 6R – behind wastewater treatment facilities. Water samples for research were taken from the surface water body (the river Raseika) in the autumn season twice (on 22 October and 18 November).

An assessment of the quality of water bodies was carried out on the basis of its compliance with the MPCs set by Order No D1-236 of the Minister for the Environment of 17 May 2006 on the approval of the Wastewater Management Regulation and by Order No D1-633 of the Minister for the Environment of 21 December 2005 on the approval of the requirements regarding the protection of surface water bodies in which freshwater fish can live and breed.

Where an assessment of the quality of a salmon or carp water body according to a certain quality indicator determines that the water body meets the established requirements, water sampling or certain indicator measurement can be performed at rarer intervals. If an analysis of the taken samples shows that the quality of a water body does not comply with the set requirements according to at least one indicator and the determined nonconformity/ies is/are not occasional, the environmental monitoring programme has to be corrected with regard of the respective indicator.

Water quality parameters measured according to Lithuanian Government Wastewater Management Regulation. There were measured the following parameters: oxygen saturation (mg O<sub>2</sub>/l), pH, suspended of substance (mg/l), BOD<sub>7</sub> (mg O<sub>2</sub>/l), phosphate (mgP/l), nitrite (mgN/l), nitrate (mgN/l), ammonium (mgN/l), total phosphorus (mgP/l), total nitrogen (mgN/l), colour (mg/l Pt).

Sampling, preservation and analytical protocols were conducted by standard methods for surface waters: EN 25814:1999 Water quality – Determination of dissolved oxygen – Electrochemical probe method (ISO 5814:1990). ISO 10523:2009 Water quality – Determination of pH (ISO 10523:2008, identical). EN 872:2005 Water quality – Determination of suspended solids – Method by filtration through glass fibre filters. EN 1899-1:2000 Water quality – Determination of biochemical oxygen demand after n days (BOD<sub>n</sub>) – Part 1: Dilution and seeding method with allylthiourea addition (ISO 5815:1989, modified). EN 1899-2:2000 Water quality – Determination of biochemical oxygen demand after n days (BOD<sub>n</sub>) – Part 2: Method for undiluted samples (ISO 5815:1989, modified). EN ISO 6878:2004 Water quality – Determination of phosphorus – Ammonium molybdate spectrometric method (ISO 6878:2004). EN 26777:1999 Water quality – Determination of nitrite – Molecular absorption spectrometric method (ISO 6777:1984). ISO 7150-1:1998 Water quality. Determination of ammonium. Part 1: Manual spectrometric method.

The purpose of surface water monitoring is to carry out regular research of water quality (microbiological, parasitological and chemical pollution), to find out the possible sources of pollution in time and to warn people.

Table 1. The limit values of water quality indicators for surface water bodies in which freshwater fish can live and breed. Sampling methods and frequency

No	Quality indicator	Limit value		Sampling frequency	Comments
		For salmon water bodies	For carp water bodies		
1.	Dissolved oxygen (mg/l O <sub>2</sub> )	≥ 9 mg/l O <sub>2</sub> (min concentration 6 mg/l O <sub>2</sub> )	≥ 7 mg/l O <sub>2</sub> (min concentration 4 mg/l O <sub>2</sub> )	Once a month	Where O <sub>2</sub> concentration is below the minimum, immediate measures have to be taken to eliminate the causes.
2.	pH	from 6 to 9 (O)	from 6 to 9 (O)	Once a month	–
3.	Suspended matter (mg/l)	≤ 25 (O)	≤ 25 (O)	Once a month	The concentrations of suspended substances can considerably increase as a result of floods.
4.	BOD <sub>7</sub> (mg/l O <sub>2</sub> )	≤ 4	≤ 6	Once a month	–
5.	Phosphorus (mg/l PO <sub>4</sub> )	≤ 0,2	≤ 0,4	4–9 times per year	–
6.	Nitrite (mg/l NO <sub>2</sub> )	≤ 0,1	≤ 0,15	Once a month	–
7.	Ammonium (mg/l NH <sub>4</sub> )	≤ 1	≤ 1	Once a month	–

(O) – deviations from quality indicator values are possible due to extraordinary weather or special geographical conditions.

Table 2. The maximum permissible concentrations (MPC) of dangerous and other controllable substances

No	Substance	MPC to wastewater collection system	MPC to natural environment	MPC in water body- receiver	Limit concentration to natural environment
1.	Total nitrogen	100	30	2,5	12
2.	Nitrite (NO <sub>2</sub> -N)/NO <sub>2</sub>	0,9/3	0,45/1,5	0,03/0,1	0,09/0,3
3.	Nitrate (NO <sub>3</sub> -N)/NO <sub>3</sub>	69/300	23/100	2,3/10	9/39
4.	Ammonium (NH <sub>4</sub> -N)	15	5	1	2
5.	Total phosphorus	20	4	0,1	1,6
6.	Phosphate (PO <sub>4</sub> -P)/PO <sub>4</sub>	–	–	0,0653/0,2	–

/the denominator shows the maximum single-time concentration.

## Results

As Figure 1 shows, the highest oxygen saturation in the river Raseika, 11.33 mgO<sub>2</sub>/l, was determined in the water sample which was taken in place 5R in October exceeding the limit value for carp water bodies by 1.6 times. The lowest O<sub>2</sub> saturation was identified in the sample taken from 1R in November.

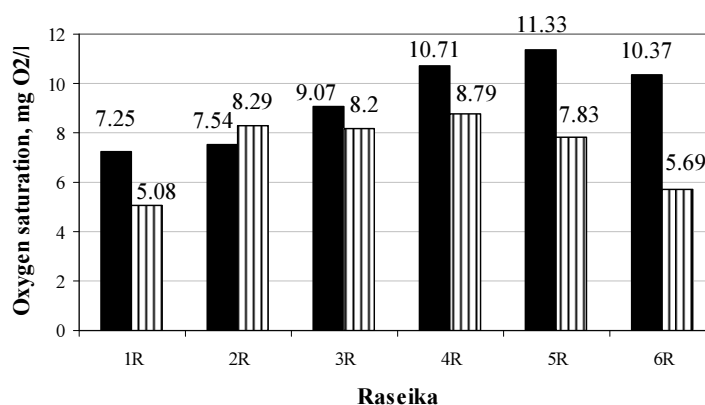


Fig. 1. The oxygen saturation in the river Raseika

Compared to the limit value for carp water bodies ( $\geq 7$  mg/l O<sub>2</sub>), the measured value was by 1.4 times lower; consequently, O<sub>2</sub> concentration was insufficient at that time. In such a case immediate measures are to be taken to increase O<sub>2</sub> concentration. The limit value set for carp water bodies was also not achieved in two investigated samples which were taken from 1R and 6R in November. Within a month O<sub>2</sub> concentration in 1R samples fell by 1.4 times and only in sample 2R increased by 1.1 times. O<sub>2</sub> concentration in 3R sample decreased by 1.1 times, in 4R sample decreased by 1.2 times, in 5R sample decreased by 1.4 times and in 6R sample decreased by 1.8 times. Analysis of the average of all samples shows that oxygen saturation reached 9.38 mg/l O<sub>2</sub> in October and 7.31 mg/l O<sub>2</sub> in November. Within a month O<sub>2</sub> concentration in the river Raseika fell by 1.28 times but still complied with the limit value for carp water bodies.

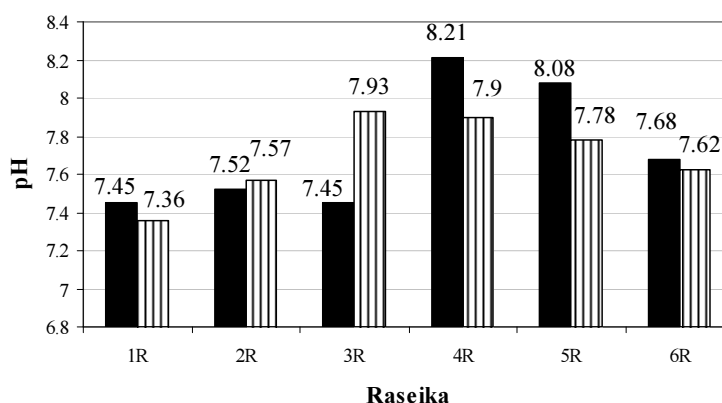


Fig. 2. The pH in the river Raseika

As Figure 2 shows, the highest pH in the river Raseika was identified in water sample 4R which was taken in October. The lowest pH value was determined in water sample 1R taken in November, but it still complied with the limit value (from 6 to 9) for both carp and salmon water bodies, like in all other samples. Samples 4R and 5R had an alkaline medium. According to assessment of the pH averages of all investigated samples the average in October was 7.73 and decreased to 7.69 in November. The medium of water (either alkaline or acid) predetermines the speed of biological and biochemical processes occurring in water, the development of aquatic plants, the migration forms of chemical elements water aggressiveness with regard to metal structures, concrete, etc.

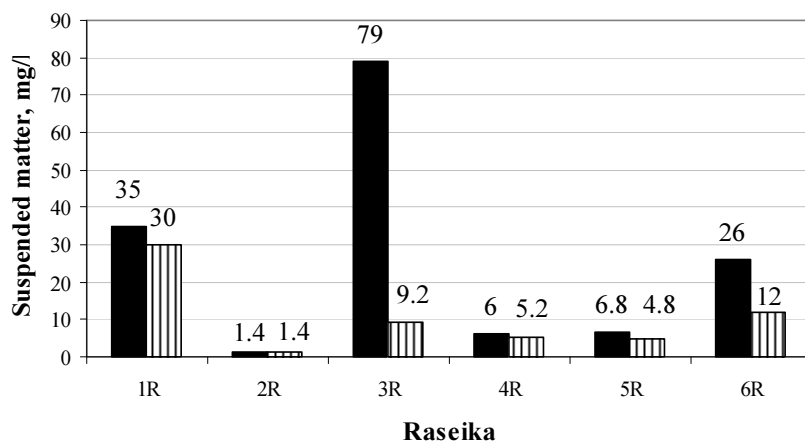


Fig. 3. The suspended matter in the river Raseika

As data in Figure 3 show, the suspended matter in samples 1R, 3R and 6R from the river Raseika were changing unevenly within a month. The largest content of suspended matter was determined in water sample 3R which was taken in October and exceeded the limit value (25 mg/l) by 3.12 times. The reason for this irregularity has not been determined. The lowest amounts of suspended matter (1.4 mg/l) were determined in 2R samples which were taken behind the section of river cleaning work. According to assessment of the average of the suspended matter of all samples, it was 25.7 mg/l in October and 10.4 mg/l. in November.

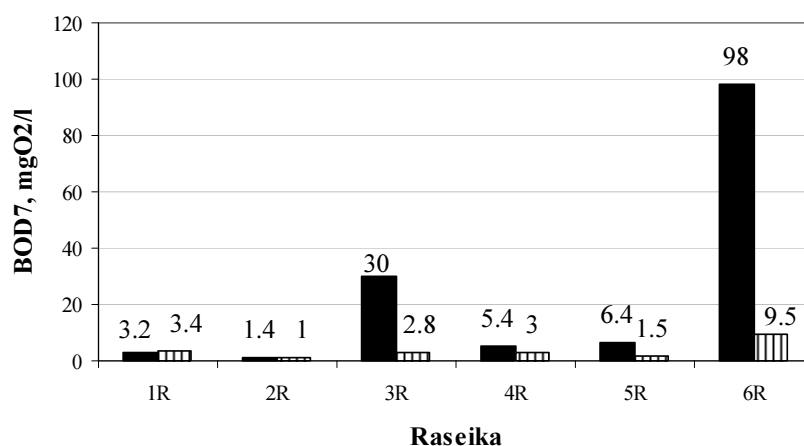


Fig. 4. The highest BOD<sub>7</sub> in the river Raseika

As results presented in Figure 4 show, the highest BOD<sub>7</sub> in the river Raseika was identified in samples 3R (30 mg O<sub>2</sub>/l) and 6R (98 mg O<sub>2</sub>/l) which were taken in October and which exceeded the limit values by several ten times. The least BOD<sub>7</sub> consumptions were recorded in 2R sample which was taken behind the section of river cleaning work. As the analysis of samples taken in November shows, the situation regarding pollution was significantly improved. As recorded during investigations, the limit values were exceeded by 2.38 times for salmon water bodies and by 1.58 times for carp water bodies only in 6R sample (9.5 mg O<sub>2</sub>/l) which was taken from wastewater treatment facilities. River-water pollution with organic matter reduces the chemical, biological and microbiological quality of water and has an adverse effect on the biologic variety of the aquatic environment.

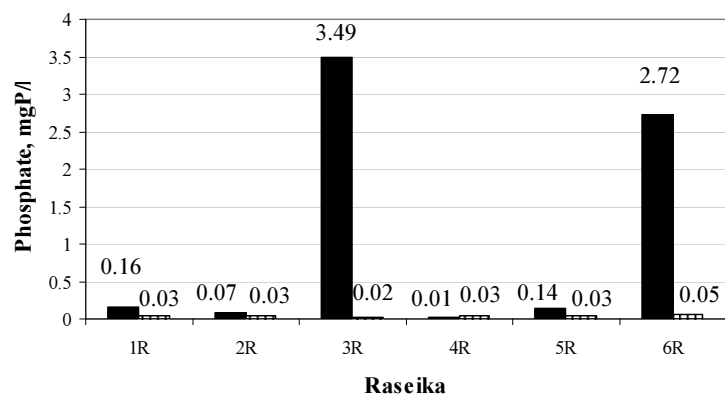


Fig. 5. The phosphate in the river Raseika

As Figure 5 shows, the amounts of phosphate significantly differing from the total level were determined in water samples 3R (3.49 mgP/l) and 6R (2.72 mgP/l) which were taken in October. Other samples under investigation did not go beyond the limit values.

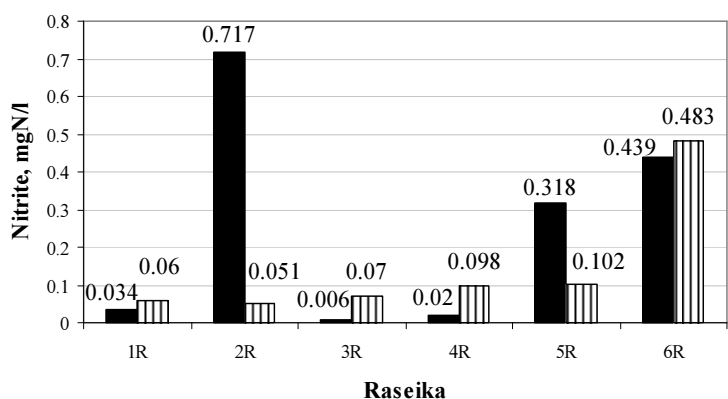


Fig. 6. The nitrites in the river Raseika

As Figure 6 shows, a very big amount of nitrites in the river Raseika (0.717 mgN/l) was determined in water sample 2R which was taken in October. Compared to the limit value for surface water bodies (Table 1) the recorded value exceeded it by 7.17 times, while compared to the MPC to the natural environment (Table 2) the exceedance reached 1.59 times. As the obtained results show (6R sample) wastewater treatment facilities do not clean off nitrites from wastewater to the required level and therefore further monitoring investigations are needed.

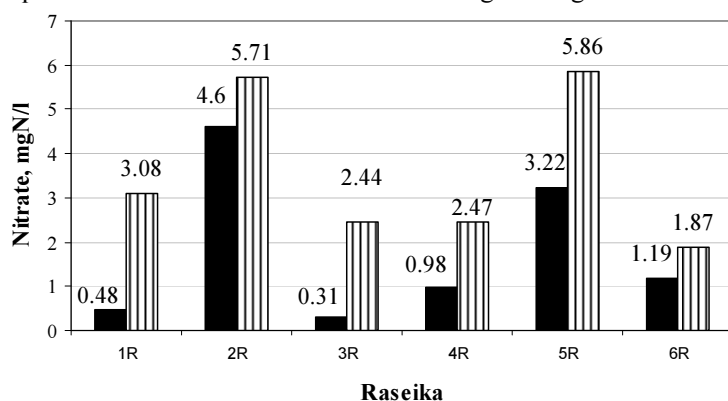


Fig. 7. The nitrates in the river Raseika

An inorganic pollutant of the major concern is nitrate ion ( $\text{NO}_3^-$ ). The main potential source of nitrates to the river Raseika is wastewater generated by agriculture. As Figure 7 shows, uneven distribution of nitrates was determined in the river Raseika. An increase in nitrate content was recorded in the samples taken in November compared to those taken in October. However, as regards the norms presented in Table 2, the values of the MPC were not exceeded. The content of nitrates in all the samples from the river Raseika investigated in October 2014 was 1.80

mgN/l and increased up to 3.57 mgN/l in November. An analysis of the results received from samples 5R and 6R shows that wastewater treatment facilities efficiently clean nitrates from wastewater as a significant decrease in their content was recorded after treatment.

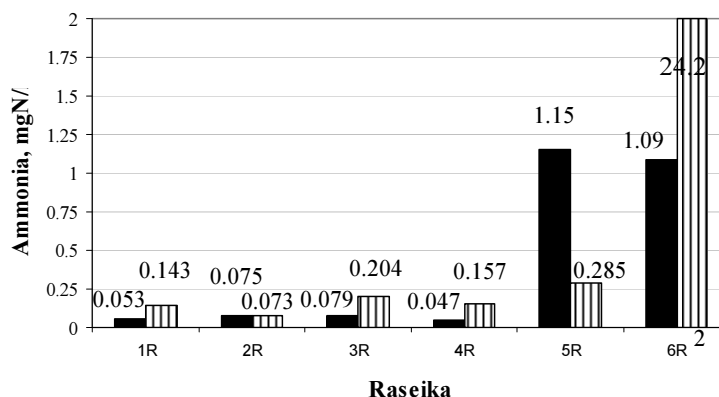


Fig. 8. The ammonia in the river Raseika

As the results of ammonia investigations in the river Raseika show (Fig. 8), the problem areas are those 5R (in front of wastewater treatment facilities) and in particular 6R (behind wastewater treatment facilities). Attention should also be paid to place 3R as the amounts of suspended matter, phosphates and BOD<sub>7</sub> exceeding norms were recorded therein. It can be stated that diffuse pollution enters the river Raseika in sampling place 3R.

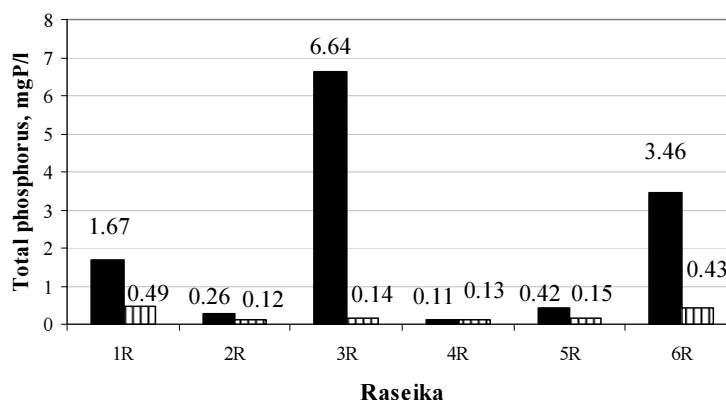


Fig. 9. The total phosphorus in the river Raseika

The total phosphorus is regulated by MPCs (Table 2). Samples from research places 3R (6.64 mgP/l) and 6R (3.46 mgP/l) differed from other samples taken from the river Raseika in October (Fig. 9) but the MPC to the natural environment was exceeded by 1.33 times only in place 3R. The average of the total phosphorus of all samples taken in November is 0.24 mgP/l.

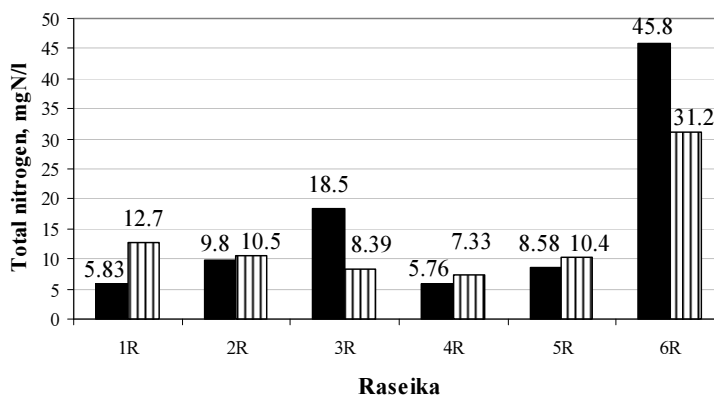


Fig. 10. The total nitrogen in the river Raseika

The total nitrogen is also regulated only by the MPCs (Table 2). The highest amount of the total nitrogen in the river Raseika was determined in water sample 6R (45.8 mgN/l) which was taken in October. The MPC to the natural environment was exceeded by 1.5 times (Fig. 10). In the meantime the total nitrogen concentration in the sample taken in November only by 1.04 times exceeded the MPC. As the analysis of the average of the investigated samples shows, the total nitrogen content in October was 15.71 mg/l, and in November – 13.42 mg/l. These concentrations exceed the limit concentration to the natural environment (12 mg/l).

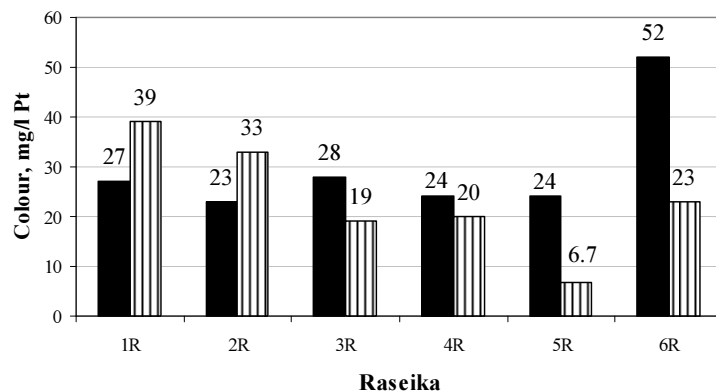


Fig. 11. The colour intensity in the river Raseika

As Figure 11 shows, the biggest colour intensity according to the scale in the river Raseika was determined in water sample 6R which was taken in October. The lowest colour intensity was recorded in water sample 5R taken in November. The average of colour intensity of all the samples investigated in October was 30 mg/l Pt, and decreased to 23 mg/l Pt in the samples taken in November. The colour of surface waters depends on humus substances and iron compounds contained in them. Water colour can also be predetermined by wastewater from various industrial plants.

### Conclusions and discussions

The biggest exceedance was recorded in samples taken below Raseiniai behind wastewater treatment facilities (6R). Measurement place 3R can be treated as the place of diffuse pollution which generates due to non-treated and/or poorly treated household wastewater. However, pollution of surface waters with nitrogen, phosphoric compounds and organic materials, even at low level, worsens the ecological condition of water bodies. Fairly large amounts of biochemical substances in the river Raseika is predetermined not only by the discharge of household and industrial waste waters but also by pollution caused by rain (surface) wastewater, snow-melting and soil-leaching waters.

Factors predetermining the quality of river-water can be divided into direct and indirect. Direct factors (rocks, soil, biota, human economic activities) either supply soluble chemical compounds to water or take them from it. Indirect factors create conditions for the interaction of substances and water and include climate, relief, water regime, vegetation, hydrological and hydrodynamic conditions, etc. (Poszyler-Adamska, Czerniak 2007). The issue of inflow of biogenic materials to surface waters is one of the most important when assessing the functioning of water eco-systems. Anthropogenic activities have a smaller influence on the quality of surface waters than the physical-chemical properties of the soil of a river basin and atmospheric pressure regime. The colloid composition of soils accumulates nitric compounds. The amounts of the total nitrogen leached from sand are by 4 times bigger than that washed out from soils of heavy mechanical composition. The intensity of dynamics of the amounts of leached out phosphorus is very low with respect to all soils as small amounts of this element are discovered in nature (Pauliukevičius 1998). R. Tumas carried out a comparative analysis of the formation of the chemical water condition of Lithuania's small rivers, which showed that the chemical regime of rivers formed unevenly, in terms of hydrogenics, in different regions. Rivers in the plains of central Lithuania where surface waters account for the major share in the formation of a river flow are most polluted with biogenic materials. In western Lithuania the comparative out-wash of chemical substances from the river basins of this region is somewhat lower than in central Lithuania while the lowest is in eastern Lithuania (Tumas 2001, 2002). Biota is also a factor having a direct influence on water quality. It actively participates in all hydrochemical processes when precipitation water moves along a river basin and within soil. The impact of biota on the chemical flow receives different evaluations. As maintained by some scientists, biota regulates the concentrations of chemical substances via reversible links. According to others, the migration of chemical elements along the top part of the Earth crust is either directly impacted by biota or occurs in the environment whose geochemical peculiarities are predetermined by biota. In this case the regulation of chemical substances in rivers would make only a minor share of the mechanism. Still other scientists consider biota to be a factor having a versatile impact on the chemical flow, however (Sakalauskiene *et al.* 2002).

R. Tumas analysed the conditions for the development of biocenoses in Lithuania's rivers with different levels of biogenic pollution. The author searched for correlation between abiotic factors of flowing water and hydrobionts by envisaging the future tendencies for hydrobiont development. As determined by performed investigations, the lowest amounts of the total nitrogen concentration were in the rivers of east Lithuanian region: 0.6–2.1 mg/l (the average of the period 1993–1998), while the highest ones were recorded in central Lithuania: 2.9–4.8 mg/l (by over two times). In the region of western Lithuania: 2.6–3.9 mg/l. The distribution of the total phosphorus was more even: 0.04–0.16 mg/l; 0.06–0.18 mg/l and 0.08 mg/l, respectively (Tumas 2001, 2002; Povilaitis 2008).

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