

Nutrient Leaching from Reservoir Bottom Sediments

Natalia Junakova*, Magdalena Balintova

Technical University of Kosice, Faculty of Civil Engineering, Institute of Environmental Engineering, Vysokoskolska 4,
042 00 Kosice, Slovakia
natalia.junakova@tuke.sk

Erosion is one of the most important pathway of sediment entries into river systems. Sediments as a pollutant is harmful by itself and is even more so when combined with contaminants, such as heavy metals, nutrients, pesticides and other organic micro-pollutants. Contaminants also mediate their uptake, storage, release and transfer between environmental compartments. Nutrients - nitrogen and phosphorus - are the chief pollutants of our waterways and their enrichment of surface water bodies is often attributed to nonpoint source pollution from agricultural production areas. The addition of nutrients to surface water bodies accelerates the eutrophication process, what is abnormally high production of algae and aquatic plants. The aim of this contribution is to study the influence of sediment quality on the water quality through the nutrient leaching from sediments to water environment.

1. Introduction

Soil erosion is one of the major cause of soil degradation in Slovakia. When eroded soil particles enter surface waters, damage to water quality occurs. Sediment often carries organic matter, animal or industrial wastes, nutrients, and chemicals. Runoff water also can transport potentially harmful dissolved chemicals from fields to bodies of water (Cook et al., 1994).

The most troublesome nutrient element is phosphorus that may come from such sources as fertilizers, organic matter, and animal manure. Phosphorus is very immobile in most soils and concentrates in the top few centimeters of soil. It is very susceptible to erosion and likely to be present in sediment (Cook et al., 1994). Phosphorus lost from agricultural soils can increase the fertility status of natural waters (eutrophication), which can accelerate the growth of algae and other aquatic plants (Mangwandi et al., 2011). The US EPA has recommended a limit for controlling eutrophication of 0.05 ppm for total phosphorus in streams that enter lakes and 0.1 ppm for total phosphorus in flowing streams (US EPA, 1986). Acceptable levels of phosphorus in surface runoff from agricultural fields have not been established (Ongley, 1996). One way of phosphorus losses from soil is not only runoff and erosion but also leaching.

Nitrogen, in the form of nitrate, NO_3^- , may cause human and animal health problems when concentrations exceed 10 milligrams of nitrogen per liter (44 mg of NO_3^-) (Cook et al., 1994). In waters where nitrogen deficiency limits growth of the ecosystem, added nitrogen stimulates algae growth in the manner described earlier for phosphorus. Nitrogen in the nitrate form can be moved out of the soil profile by leaching. If applied nitrogen or mineralized organic matter (conversion from organic to ammonium) nitrogen would stay in the ammonium form (NH_4^+), then losses would not occur because ammonium attaches to soil and does not leach or denitrify (Sawyer, 2007). Vitosh et al. (1995) gives that ammonium forms of nitrogen have a positive charge and are held by the negative sites on the clay in the soil; therefore NH_4^+ forms of nitrogen leach very little in clay. Ammonium forms can leach in coarse-textured sands and some muck soils. These are the only soils where ammonium leaching may be significant. Lee (1970) states that clay minerals show significant sorption capabilities for some anions such as phosphate while other anions, for example, nitrate, show essentially no sorption tendencies on clay minerals.

In this research the leaching of nitrogen and phosphorus from reservoir bottom sediments detached through water erosion to water environment have been studied.

2. Material and methods

2.1 Study area

This study has been carried out on the sediments taken from the small water reservoir Klusov, situated in Eastern Slovakia, in Bardejov district. The Klusov reservoir is located at an altitude of 343 meters above sea level. Its average depth is 3.5 m, surface area 2.2 ha and its total capacity is about 72,000 m³. It was built for fishing, irrigations, recreation and for retention of high water. The climate in this area is continental with the mean maximum annual temperature varying from -3 °C in January to 20 °C in July. The mean annual precipitation is about 670 mm, with maximum in summer months.

Majority of land in vicinity of the reservoir has a slope more than 8 % what can indicate increased erosivity in this area. Soil types of the watershed are, in general, planosols, cambisols and albic luvisols. From the soil texture point of view, medium heavy soils (sandy loam) occur in this area, and according to the content of skeleton in the soil, slightly stony soils lead.

The land use of the catchment was found to be mixed type. The upstream part and middle part of the Tisovec catchment is an area mainly covered with forest (39.2 %) and pastures (21.7 %), while the lower part is an arable land (21.4 %) mainly used for cereals (spring barley, winter wheat), corn silage and winter oilseed rape growing. The rest of the land area is for other uses.

In 2004, Slovak Water Management Enterprise realized the siltation measurements of this reservoir. According to the measuring it was detected that reservoir siltation processes during 19 years (1986-2004) resulted in the reduction of its useful capacity about 33 %. Therefore this reservoir was drained completely (from 2005 to 2007). We make use of this fact for the sediment collection due to sediment quality monitoring.

2.2 Sampling procedure

Composite sediment samples were taken from some localities by the reservoir dyke, especially due to deposition of finest particles preferentially attaching the nutrients - samples S1-S4. The others were collected along the reservoir - S1,S2,S3,S6-S10 (Figure 1).

From each sampling locality, one composite sediment sample was taken to plastic bucket. The weight of the composite samples represented about 3 kg. In laboratory conditions, the samples were air dried at room temperature, any coarse lumps were crushed and samples were homogenized.

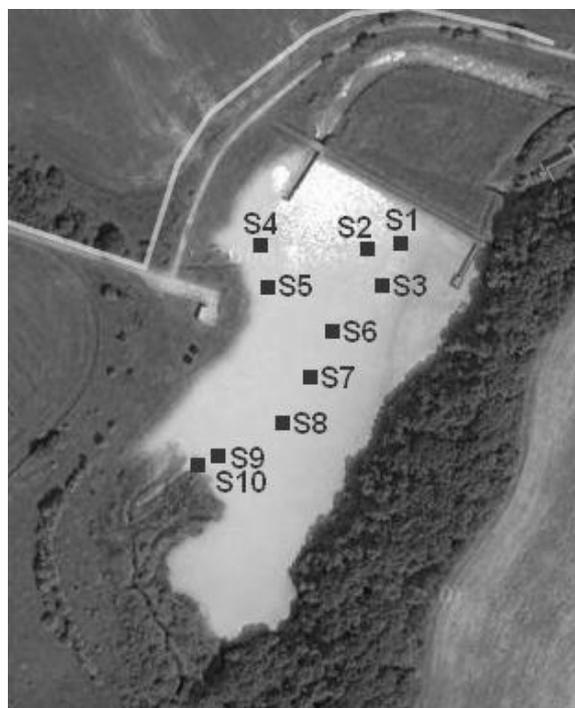


Figure 1: Location of sediment sampling sites

2.3 Sediment characterization

The particle size distribution (PSD) of the sediment samples was performed using a Malvern Mastersizer 2000 (Malvern Instruments, 2007) with a Hydro 2000S wet dispersion unit, capable of analyzing particles between 0.02 and 2000 μm . The refractive index used for the sediment samples was 1.503 (clay minerals). Sediments were suspended in water with a refractive index of 1.330. The samples were run at 2800 rpm on the sample stirrer and cell pump respectively. Agglomerates were broken up by the action of the ultrasonic, turned on for 5 min after sample addition.

Infrared spectroscopy with Fourier transformation (FTIR) was used for the sediment samples characterization in terms of functional groups qualitative analysis. FTIR measurements were performed using a Spectrometer Alpha-T (Bruker, Germany) with ATR technique allowing the direct measurements of powder samples without KBr tablets preparation. Measurements were carried out in transmittance mode, in the range 400 – 4000 cm^{-1} with resolution of 4 cm^{-1} .

The mineral composition of sediments was identified with diffractometer Bruker D2 Phaser (Bruker AXS, GmbH, Germany) in Bragg-Brentano geometry (configuration Theta-2Theta), using the 1.54060 Å CuK α radiation, Ni K β filters and scintillation detector at a voltage of 30 kV and 10 mA current. Scan conditions were identical for all samples, recording times about 2 h, a step size of 0.04° (2 θ) and step time of 3 s. The XRD patterns were processed using the software Diffrac. EVA v. 2.1. The ICDD PDF database (ICDD PDF – 2 Release 2009) was utilized for the phase identification.

2.4 Chemical analysis

For the purposes of water quality monitoring a measuring sediment quality was made. Bottom sediment samples were analyzed for total nitrogen by elemental analysis (EA) and for total phosphorus using inductively coupled plasma-atomic emission spectrometry (ICP-AES) technique.

For study of the nitrogen and phosphorus interactions between surface water and sediment several leaching experiments were conducted in laboratory conditions.

Leaching of N_{total} and P_{total} from sediments samples to water has been tested in water leachate prepared in proportion of sediment sample to distilled water = 1:10. The pH of distilled water was 7.07. After 24 h derived leachates were subsequently filtered and analyzed for content of N_{total} and P_{total} . The mineralization of samples was carried out in digital reactor block DRB 200 (Hach Lange) and for the determination of total N and P Portable Colorimeter DR 890 (Hach Lange) was used. Multifunction device MX 300 X-matepro (METTLER TOLLEDO) was used to determine the pH of leachates.

3. Results and discussion

The particle size distribution of sediment samples has been different in dependence on sampling locality. Analysis shows (Table 1), that the sample S1 has 99.92 % and sample S2 99 % fraction of particles under 63 μm . Sediment granularity rises with the increasing distance from the dam, what declares samples S3 (with the 95 % proportion of particles < 63 μm) up to S10 (with the 67 % proportion of particles < 63 μm). It can be state that bottom sediments in the Klusov water reservoir are predominantly fine particles responsible for transporting a significant proportion of many nutrients and contaminants.

The chemical analysis results of the sediment samples are given in Table 1. The nutrient concentrations in sediments are diverse due to irregular sediment deposition in the reservoir and increase with the proportion of fine-grained particle fraction.

Table 1: The chemical analysis results of the sediment samples (S1-S10) and their PSD analysis

Sample No.	d (0.9) μm	N_{total} (%)	P_{total} (%)
S1-06	22.111	0.260	0.112
S2-01	26.813	0.240	0.113
S3-00	30.742	0.240	0.112
S4-13	55.936	0.230	0.066
S5-21	49.420	0.220	0.066
S6-24	48.937	0.220	0.067
S7-12	46.577	0.180	0.061
S8-20	57.283	0.170	0.049
S9-18	91.583	0.120	0.048
S10-08	108.270	0.110	0.031

Infrared spectroscopy (Figure 2) was realized for all sediment samples. Transmittances associated with symmetric and asymmetric vibrations of silicate and quartz functional groups were observed at 995, 777,

693 and 517 cm^{-1} . All samples have shown the identical behavior which declares the inorganic origin of sediments.

Silicates in form of muscovite and quartz were identified by XRD analysis as major phase minerals in analyzed sample (Figure 3).

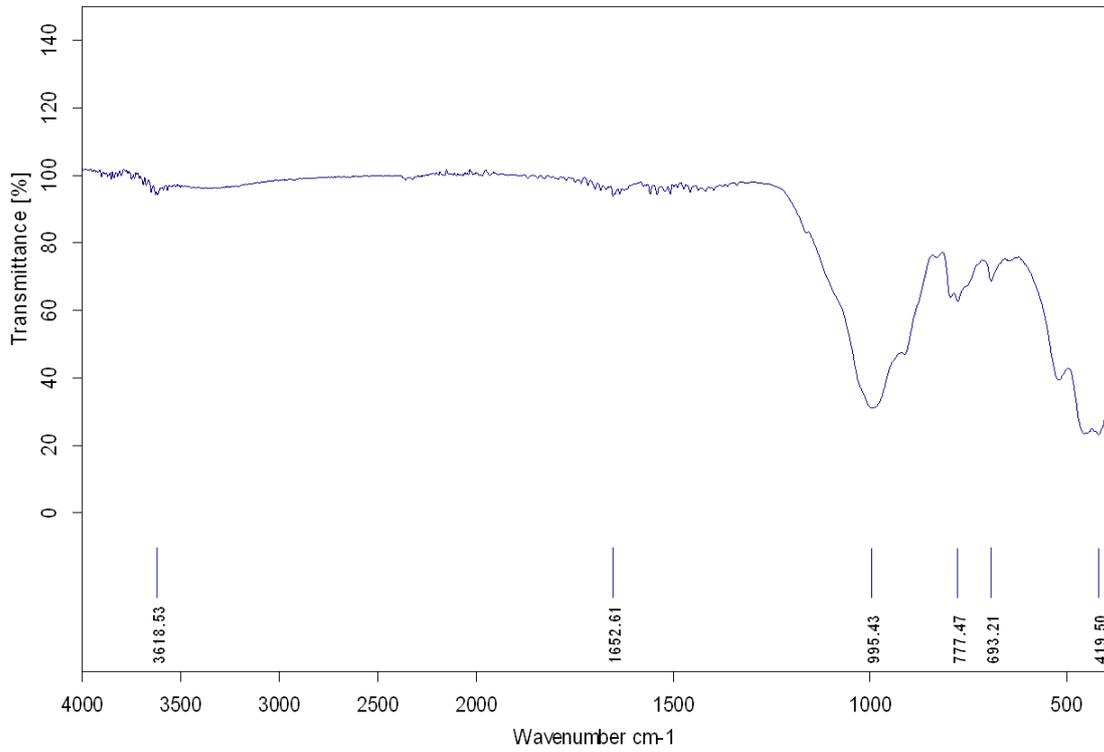


Figure 2: Typical FTIR spectrum of sediment sample

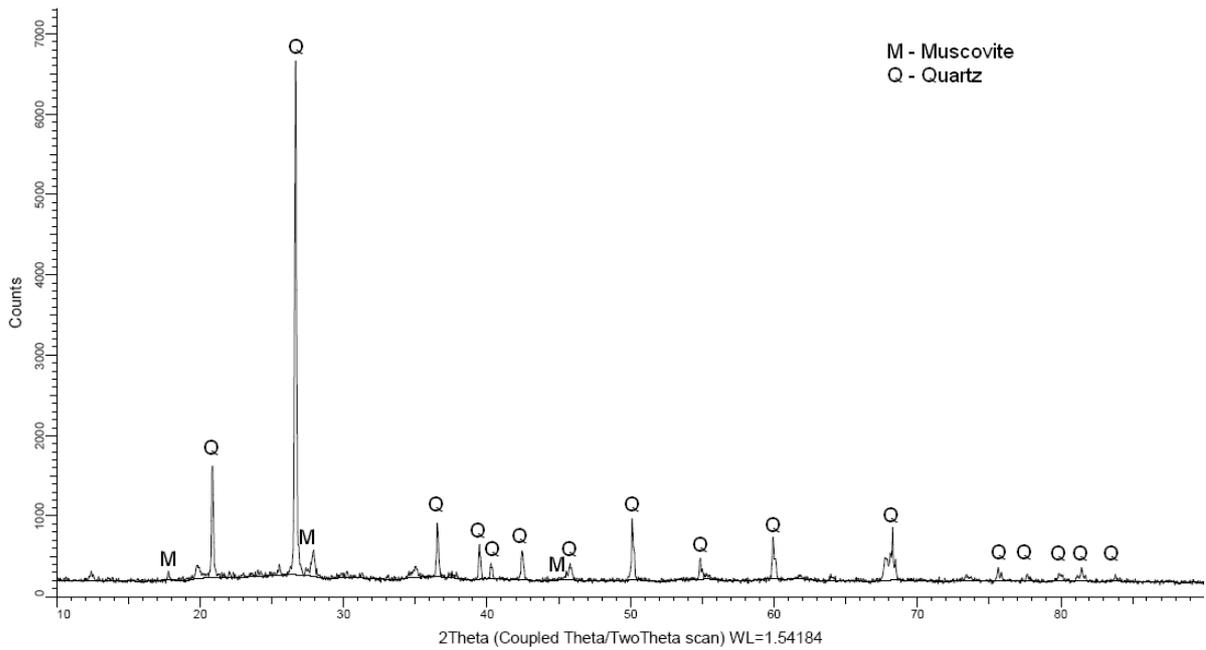


Figure 3: XRD spectrum of sediment sample

The concentrations of total nitrogen and phosphorus leached out from reservoir bottom sediments to water environment are shown in Tables 2 and 3 together with pH values of water leachates that were in range of 7-8.

Table 2: The total nitrogen concentrations in leachates (S1,I-S10,I) and its pH values

Sample No.	N _{total} (mg/l)	N _{total} (%)	pH
S1,I	0.5	0.19	7.66
S2,I	2.3	0.96	7.94
S3,I	1.6	0.67	7.54
S4,I	1.4	0.64	7.74
S5,I	0.1	0.05	7.8
S6,I	< 0.05	< 0.02	7.57
S7,I	< 0.05	< 0.02	7.75
S8,I	< 0.05	< 0.02	7.57
S9,I	< 0.05	< 0.02	7.68
S10,I	< 0.05	< 0.02	7.81

Table 3: The total phosphorus concentrations in leachates (S1,I-S10,I) and its pH values

Sample No.	P _{total} (mg/l)	P _{total} (%)	pH
S1,I	0.71	0.63	7.66
S2,I	0.43	0.32	7.94
S3,I	0.36	0.38	7.54
S4,I	0.30	0.45	7.74
S5,I	0.24	0.37	7.8
S6,I	0.23	0.34	7.57
S7,I	0.20	0.32	7.75
S8,I	0.20	0.41	7.57
S9,I	0.13	0.28	7.68
S10,I	0.17	0.56	7.81

Measuring of the leachate's pH values showed the basic character of the original sediment samples. The experiment results of chemical analysis of total nitrogen and phosphorus concentrations in leachates have shown that proportion of dissolved phase represents less than 0.02 to 0.96 % of total nitrogen and 0,28 – 0,63 % of total phosphorus in the sediment samples. Analyses also declare the dependence of phosphorus leaching on the particle size distribution of bottom sediments, whereas dependence of nitrogen hasn't been observed.

4. Conclusions

Soil erosion causes detaching of the fine particles more than coarse particles into water bodies that may act as a sink or a source of nitrogen and phosphorus in water environment.

Particle size distribution analysis of this study shows that bottom sediments in the Klusov reservoir are mainly fine-grained sediments (silt and clay-sized material < 63 µm in particle diameter). The chemical analyses proved dependence between the total nutrient concentrations in sediments and their particle size. The highest nutrient contents in bottom sediments have been determined in the finest particles of sediments sampled near the dam.

On the other hand, total nitrogen and phosphorus concentrations in leachates have been low. The dependence of total phosphorus leaching on the particle size distribution of bottom sediments has been detected. Total phosphorus concentrations in water leachates decrease with particle size increasing and therefore increasing the amounts of phosphorus in sediments results in increased levels of phosphorus in sediment solution. Dependence of nitrogen leaching on the particle size distribution of bottom sediments hasn't been observed.

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