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Turbidity as a Surrogate for the Determination of Total Phosphorus, Using Relationship Based on Sub-Sampling Techniques

Laura Kusari[1]

[1] Faculty of Civil Engineering, University of Prishtina, Hasan Prishtina, Rr. George Bush Nr. 31, 10000 Pristina, Kosovo
E-mail: laura.kusari@uni-pr.edu

ABSTRACT
One of the most challenging issues regarding water quality control is the lack of adequate measurements and lack of data on many water quality constituents. Since water quality is highly variable during time and space, traditional grab sampling often misses extreme events and the result isn't always a representative one. This paper evaluated the usefulness of turbidity measurement as a surrogate for the determination of the Total Phosphorus. Instead of in-situ sensors for real time turbidity measurements, another approach was taken during this investigation. The suitability of using turbidity as a surrogate for TP was investigated using prepared subsamples, each with different concentration of water quality constituents. Laboratory results, with the use of the linear regression techniques, enabled the development of the model that relates the total phosphorus to turbidity. The linear regression equation developed, TP = 0.3942TTU – 3.4279 shows that there is a very good prediction of the total phosphorus based on the turbidity measurement, with the correlation coefficient as good as $R^2 = 0.8782$ and p-value less than 0.5. Even though the equation is site specific, and more investigation is needed, we conclude that it can be used in similar situations, when there is a lack of monitoring programs.

Keywords: diffuse pollution, linear regression analyses, sub-sampling, surrogate relationship, total phosphorus, turbidity, water quality constituents.

INTRODUCTION

According to UNFPA, the world population in 2021 has reached 7,875 million and the forecast is that by the end of the century nearly 11 billion people will be living on Earth. All over the world, the majority lives in urban areas and by the 2019, the share of population living in urban areas increased to 55.7 per cent [United Nations, 2019]. Furthermore, this urbanization has been more pronounced in the developing economies. The changes in world population, associated with the changes in food production and energy consumption have caused substantial changes in hydrological cycle and massive alteration of nutrients, primarily nitrogen and phosphorus on our lands. Urbanization is changing the source of non-point source pollution and its impact on the latter one can be analyzed by the landscape change in catchment.

Although the municipal sewage treatment plant discharges were a leading source of contamination in surface rivers (and still are in areas without waste water treatment plants), currently there is a greater focus on non-point source pollution. Agriculture is an important source of non-point source pollution, because higher levels of nutrients, especially phosphorus and nitrogen are observed in the flow coming from agriculture. This is mainly due to the precipitation, irrigation and the use of pesticides and fertilizers. For this reason, those nutrients have been a study subject for many further studies [Chang, 2004, according to Donaldson, 2005]. Our riverine catchments also have been subject to rapid urban development over the last years and as a consequence are suffering impaired water quality. The quality of surface waters is directly linked to the activities taking place within the catchment, the increased presence of new and un-controlled substances [Miller &

Hutchins, 2017]. Also, we must emphasize the impact of climate changes on surface water quality, as well. As for the Mediterranean basin, the future climate predictions indicate a possible temperature increase of 2–3°C by the 2050 year, which might cause a decrease in the precipitation of about 20–30% [Marchane, Tramblay, & Hanich, 2017]. Recent studies have indicated that changes to land use generate the imbalances in the natural dynamics of riverine ecosystems [Cerqueira, Mendonca, & Gomes, 2020]. Pollutants entering surface waters can have chemical nature or mineral composition and their entrance can be through point sources (PS) or non-point sources (NPS). Pollutants from diffuse sources enter the surface waters in a spread way, like the flows from agricultural surfaces, urban runoff and ground water flow. These sources of pollution are not regulated and are considered the leading remaining cause of water quality deterioration. Those diffuse sources are highly variable and very hard to control; therefore, we can say that NPS pollution today presents a major challenge.

Over the past few decades, our watersheds too, have experienced land cover change. It is well known that land cover determines the type and quantity of non-point source (NPS) pollutants that enter the surface waters and thus land cover influences water quality. Furthermore, stream banks are incised and eroding at accelerated rates due to urbanization. This excess stream bank erosion reduces water quality through the transport of sediment-bound pollutants. River flowing through the area of agricultural land are also being polluted as a result of inappropriate use of fertilizers. The rivers are transporting nutrients from land to coastal areas and it is of utmost importance to identify the nutrient sources.

This diffuse loading is very difficult to measure, it is often missed by the monitoring process mainly because it is usually transported during short term periods of flows in riverine systems. Most monitoring programs are at a bi weekly or even monthly frequency, and therefore the representativeness of samples is very important. There is a possibility of losing detailed temporal resolution and peaks in concentrations, if samples are collected bi- weekly or monthly [Jones, Horburgh, Mesner, Ryel, & Stevens, 2012]. Grab sampling very often does not provide a needed representation of the water quality parameters concentration.

As with many other nutrients, the higher enrichment of phosphorus in water bodies can affect and endanger many forms of aquatic life. Widely spread human activities are altering the phosphorus cycle in nature, causing its deposition in soils and higher potential of its transportation (runoff) through water bodies. Total phosphorus concentrations are low in the mountain areas but are higher in agricultural and urban areas. High total phosphorus concentrations in summer can be linked to sewage effluent while high concentrations in the winter and spring are often associated with sediment losses from agricultural catchments. Increased levels of total phosphorus may result from erosion, discharge of sewage or detergents, urban runoff, rural runoff containing fertilizers and animals.

Therefore, monitoring of surface water quality is very important when considering the transport of nutrients and pollutants that affect the aquatic life. Nonpoint source pollution is difficult to monitor due to the nature of the type of discharge. For instance, an agricultural land use may contribute with different pollutants. The nutrient enrichment or eutrophication is a significant issue that results in water quality deterioration, stimulating excessive growth of plants and algae, high decomposition rates of the accumulated plant biomass, water acidification, decreased oxygenation and overall habitat degradation [Schaffner & Sanchez Colon, 2021; Gonzalez-Rivas, et al., 2020].

Today, the sensors are very helpful when it comes to in-situ measurements for water quality monitoring. Their use saves time and energy and provides a large data base of real time results. Turbidity is easy to meter in-situ through sensors and therefore we can obtain large data sets for short period of time. But, unfortunately even with this technology development over the last years, some water quality constituents still cannot be measured in situ. One of these is total phosphorus. Total phosphorus in streams is higher when there is a high surface runoff, especially if it is associated with erosion and also it is very high during storm events. Due to this high variability in time and space, total phosphorus measurement is time and resource consuming. In order to avoid frequent and costly analyzes, this research investigates the relationship between Turbidity and TP. Turbidity is chosen as a surrogate parameter for TP, because of its easy high frequency measurement. But this high frequency measurements requires the deployment of in situ sensors in our rivers, which will enable a real time measurement of turbidity and also a higher number of measurements compared with traditional grab sampling techniques.

On the other hand, since TP cannot be measured with sensors, the surrogate relationship was chosen for this paper. Another earlier study has demonstrated the use of a turbidity subsampling as a surrogate for TSS [Kusari, 2017]. The relationship between turbidity and TSS was a strong one, since the coefficient of determination was found to be $R^2 = 0.8687$. Knowing that the most of the total phosphorus transported in streams is in the particulate form, this makes the use of TSS and Turbidity a promising surrogate for total phosphorus. But, although the relationship between turbidity and total phosphorus at previous investigations showed a very good value of correlation coefficient, those relationships are site-specific and thus non-transferable between catchments [Stutter, et al., 2017]. Most previous studies on the relationship between turbidity and total phosphorus are based on the high frequency and real time data for turbidity. Even though the most often method for creating high frequency proxy data of turbidity is the deployment of an in-situ sensor in water body, in the present study we used different approach. Instead of a using a frequent turbidity data from sensors, the research used the artificially prepared sub-samples for the development of a relationship between turbidity and TP. Those subsamples provided the needed data for the relationship between turbidity and total phoshorus.

MATERIALS AND METHODS

This research evaluated the use of turbidity data as a proxy for the total phosphorus estimation, in surface waters. The development of a relationship between turbidity and total phosphorus was based on the laboratory analyses of sub-samples, previously prepared with different turbidity and total phosphorus concentrations. The study area was chosen the Sitnica River basin, which covers an area of 2931.71 km^2 with a mixed land cover, consisting of 43% arable land (Figure 1). The river flow is characterized with very high flows during spring reaching up to 328.0 m^3/s and very low during summer as low as 0.50 m^3/s, and an average annual runoff of 13.62 m^3/s.

The sampling location selected for this relationship was Sitnica River, in the vicinity of Vragoli location, with 42.609138 latitude and 21.061295 longitude coordination (Figure 2). Sitnica river is 167 km long as it drains a mixed land use catchment, in the west-central part of Kosova. Water quality is a major environmental problem in this River basin and Sitnica River is amongst the most polluted rivers in Kosovo.

Sampling sites were visited during autumn, in the late October, under stable environmental conditions. Therefore, samples were not taken after rainstorms or extremely high discharge events. Water samples were collected manually from each study site, using 1000 ml plastic samplers. The first sample was taken near the concave river bank, a location with higher turbidity then the rest of the river. The second water sample was taken 200 m downstream of river flow, approximately in the middle of a river profile, where turbidity of the river seemed to be very low. Both water samples were used for the careful preparation of 10 sub-samples from 120ml,

Figure 1. Sitnica River Basin - Kosovo map

Figure 2. Sampling location – Sitnica River

with mixtures consisting of different water pollutant concentration. From the first water sample, after its stirring to ensure consistency, 100 ml of water were extracted and poured into the first subsampler of 120 ml volume. By now, we had the first sub sample with the same concentration as the first water sampler (1000 ml).

Now, from the second water sample of 2000 ml (from the one taken downstream of a river), 100 ml of water were extracted and poured in the first water sample (1000 ml). By now, the first water sample has again 1000 ml of water, but now with different content/concentration. The procedure for the preparation of the second sub-sample is the same, again we extracted another 100 ml from the first water sample (1000 ml) and poured in the second sub-sample. By now, we have two 100 ml subsample. A procedure is continuous, every time taking 100 ml from the second sample and filling the first sample, so that it has always 1000ml of water. Extracting 100 ml of water from the first and preparing the next-third sub-sample. This procedure helped us create 10 subsamples of 100 ml each, which were taken immediately to the Hydro Meteorological Institute for the needed laboratory analyses [Kusari, Development of Water Quality Matrix through Surrogate Modeling, 2018]. All analyses were performed with the standard methods at the Laboratory of Hydrometeorological Institute of Kosovo. The results obtained by laboratory measurements provided the needed data for the development of the single line regression model relating turbidity and TP.

The use of turbidity as a proxy for total phosphorus was examined through the results obtained from sub-samples. This relationship was developed with the use of linear regression analyses. The linear regression is in form $y = (\alpha x + \beta)$ and its strength was evaluated as the regression R^2. Subsequently, we estimated the values of total phosphorus based on the turbidity readings, using the resultant surrogate relationship between turbidity and total phosphorus. There was a good linear relationship between the two parameters and turbidity and total phosphorus were significantly related, with a regression $R^2 = 0.8782$. Even though this relationship was developed for the selected location, it can be validated in the future for near site portability.

RESULTS AND DISCUSSION

The managing of the water resources is a major concern in our country and the assessment of surface water quality is needed in this regard. Knowing the actual resources and limitations in the country, it is crucial to select the best sampling strategy. Between increasing of sampling frequencies and the use of possible surrogates, we suggest the second one. In order to evaluate the possible relationship between two parameters, we have conducted an experiment of creating sub-samples from different water mixtures and the use of this results for further analyses. Correlation between total phosphorus in y-axis and turbidity in x-axis is developed by the use of a linear regression model. The dependable variable is total phosphorus and this depends on the turbidity (the independent variable) (Figure 3). The summary output of the linear regression analyses for turbidity and total phosphorus is as in the following Table 1.

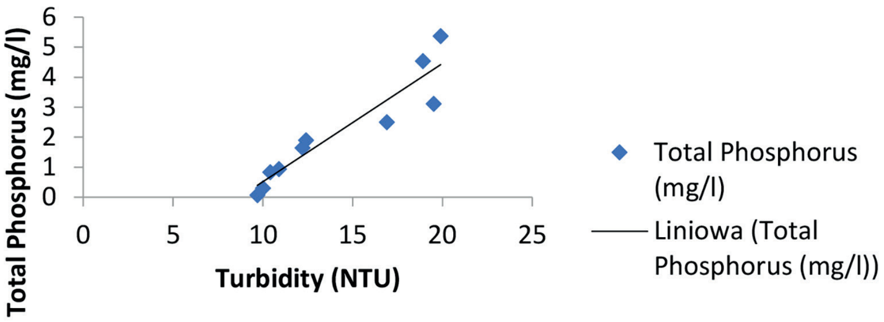

Figure 3. The plotted data of the measured turbidity and total phosphorus, measurements from sub-samples

Table 1. Summary output of the linear regression analyses for turbidity to total suspended

<table>
<tr><td colspan="18">Summary output</td></tr>
<tr><td colspan="18">Regression statistics</td></tr>
<tr><td colspan="9">Multiple R</td><td colspan="9">0.9371</td></tr>
<tr><td colspan="9">R Square</td><td colspan="9">0.8782</td></tr>
<tr><td colspan="9">Adjusted R Square</td><td colspan="9">0.8629</td></tr>
<tr><td colspan="9">Standard Error</td><td colspan="9">0.6570</td></tr>
<tr><td colspan="9">Observations</td><td colspan="9">10</td></tr>
<tr><td colspan="3">Parameter</td><td colspan="3">df</td><td colspan="3">SS</td><td colspan="3">MS</td><td colspan="3">F</td><td colspan="3">Significance F</td></tr>
<tr><td colspan="3">Regression</td><td colspan="3">1</td><td colspan="3">24.9019</td><td colspan="3">24.9019</td><td colspan="3">57.6879</td><td colspan="3">6.333E-05</td></tr>
<tr><td colspan="3">Residual</td><td colspan="3">8</td><td colspan="3">3.45332</td><td colspan="3">0.43166</td><td colspan="3">-</td><td colspan="3">-</td></tr>
<tr><td colspan="3">Total</td><td colspan="3">9</td><td colspan="3">28.3552</td><td colspan="3">-</td><td colspan="3">-</td><td colspan="3">-</td></tr>
<tr><td colspan="2">Parameter</td><td colspan="2">Coefficients</td><td colspan="2">Standard Error</td><td colspan="2">t Stat</td><td colspan="2">P-value</td><td colspan="2">Lower 95%</td><td colspan="2">Upper 95%</td><td colspan="2">Lower 95.0%</td><td colspan="2">Upper 95.0%</td></tr>
<tr><td colspan="2">Intercept</td><td colspan="2">-3.42789</td><td colspan="2">0.7596</td><td colspan="2">-4.5123</td><td colspan="2">0.00197</td><td colspan="2">-5.1796</td><td colspan="2">-1.6760</td><td colspan="2">-5.1796963</td><td colspan="2">-1.6760974</td></tr>
<tr><td colspan="2">Turbidity (NTU)</td><td colspan="2">0.39416</td><td colspan="2">0.0518</td><td colspan="2">7.5952</td><td colspan="2">.33E-05</td><td colspan="2">0.2744</td><td colspan="2">0.5138</td><td colspan="2">0.27449485</td><td colspan="2">0.51384276</td></tr>
</table>

As noted from the summary output (Table 1), the developed regression model for the subsamples is as following:

$$TP = 0.3942TTU - 3.4279 \qquad (1)$$

where: TP - Total phosphorus (mg/l); TTU - Turbidity (NTU)

From the summary output, the value of R^2 ranges from -1 to +1, meaning that near to +1 indicates the strongest positive linear correlation between two parameters compared and near to -1 indicates the strongest negative linear correlation. In our case, the general relationship between turbidity and total phosphorus, considering all the results gained from sub-samples, produced an R^2 value of 0.878 and p-value below 0.5, which makes this a significant correlation. This correlation shows that turbidity is significantly correlated to TP, and this result is consistent with other studies where the R^2 values ranged from (0.25–0.95), according to previous studies [Villa, Folster, & Kyllmar, 2019; Lannergard, Ledesma, Folster, & Futter, 2019].

CONCLUSIONS

Conventional methods of surface water quality monitoring are associated with some problems or restrictions regarding the limited number of samples during the year, the values of annual loads of different parameters and the lack of sampling during extraordinary event flows as well as relatively high sampling and manual analyses cost. This uncertainties with conventional methods can be avoided by surrogate relationship while monitoring surface water quality. The aim of this study was to evaluate the use of turbidity as a proxy for the determination of total phosphorus. In general, the use of turbidity as a tool in determining the other water quality constituents can offer many benefits for the research on surface water quality. The work presented could possibly contribute to the easiest measurement of TP in a given location. In this regard, turbidity was found to be a good predictor for total phosphorus. Since turbidity is an easy to measure constituent, the relationship between turbidity and total phosphorus will provide a convenient approach to evaluate the surface water quality directly from field-based measurements, without having to carry out intensive laboratory experiments It can also be used in evaluating pollution loads for pollutants and thus understand the catchment's response to unpredicted pressures. The prediction of total phosphorus based on turbidity measurements would provide the needed information in managing water resources. It is of an utmost importance to quantify the total phosphorus concentration and flux in the rivers, to help identify the nutrient sources and support the water resource management.

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