RELATING NUTRIENT RATIOS TO MUCILAGE EVENTS IN NORTHERN ADRIATIC

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Abstract:

The north western part of the northern Adriatic exhibits eutrophic to mesotrophic characteristics with recurrent algal blooms and quite unpredictable mucilage events. To contribute to the understanding of the mucilage events in the northern Adriatic, a machine learning algorithm for induction of regression trees was applied to a data set comprising physical and chemical parameters, measured at six stations on the profile from the Po River delta (Italy) to Rovinj on the western Istrian coast (Croatia). A model describing the connection between the TIN/PO_4 ratio, considered as a necessary factor and sometimes even a trigger for mucilage events, and the environmental conditions in northern Adriatic was elaborated. The model for TIN/PO_4 ratio confirmed the assumption that the mucilage events are connected with the changes of this ratio in the system. This indicates that at certain levels of P limitation (TIN/PO_4 signal indicate) mucilage event frequency increases. The model also reveals which triggers are responsible (salinity and temperature) for the changes of the TIN/PO_4 ratio as well as their threshold values. As contrasted to to the TIN/PO_4 ratio, the mucilage events could not be attributed to the TIN/SiO_4 ratio.

1 Introduction

Mucilage events have been documented several times during the past two centuries in the northern Adriatic (NA), while their frequency has significantly increased since 1988 [1]. In fact, these events occurred in the past in intervals of approximately 10-50 years, but in the last eighteen years the phenomenon has recurred with a higher frequency with variable intensities and durations (1988, 1989, 1991, 1997, 2000-2004, 2007, 2010) [2 - 8]. For the development of the mucilage phenomenon, large variations of nutrient fluxes and their ratios, in conditions of freshened waters in the NA and water column stratification, rather than the absolute amount of the nutrient inputs are more important [9]. Orthosilicate (SiO_4) does not play a significant limiting role in phytoplankton growth so that it is probably not essential for the development of the mucilage phenomenon in the NA [10].

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The Po River, with an average flow rate of 1 500 m^3/s is the most important source of nutrients in the region with a load of around 170×10^3 t/year of the total nitrogen and 8×10^3 t/year of the total phosphorus, [11]. These discharges generated strong trophic gradients that were refined by dividing the NA into eutrophic, mesotrophic, and oligotrophic regions where only the western coastal waters are considered as eutrophic [12].

The changes in nutrient ratios in the surface layer of the NA, influenced by Po River discharges, coincided with an increased frequency of mucilage events (formation of macroaggregates up to several meters in the upper water column and surface or subsurface organic layers [2]).

There is a large consensus that the mucilage phenomenon is generated by synergic combinations of several factors (i. e. [4]). One of the most significant is the change of Total inorganic nitrogen/Orthophosphate (TIN/PO_4) ratio which can increase the phytoplankton excretion of polysaccharide mucus, the matrix of the mucilaginous material i. e. [9, 13]. Phytoplankton productivity in the NA is most likely to be phosphorous (P)-limited and confirmed with bioassay studies and analyses of dissolved inorganic nutrients [14, 15]. This limitation is probably due to the high inorganic TIN/PO_4 ratios (> 25) of riverine inflows, much larger than the Redfield ratio of 16, considered optimal for phytoplankton growth [16]. Consequently, the particulate matter is P depleted with highly variable particulate-N/particulate-P ratios between 6 and 49 [17, 18]. Along with phosphorus, silica, or orthosilicate (SiO_4) may be a limiting nutrient and thus triggering stressing behavior of the phytoplankton-the mucuous excretion, known as mucilage. In the second part of this study, the Total inorganic nitrogen/Orthosilicate (TIN/SiO_4) ratio was also tried to connect with the mucilage events.

Deserti and others investigate the connections between the mucilage and the change of the climatic conditions [19]. The descriptive analysis pointed out that the mucilage events can be grouped in three main clusters: (1) 1920-1930; (2) 1983-1991 and (3) 1997-2002.

To assess these hypotheses, we performed an exhaustive analysis of the measured data in the NA on long term data (1972-2007). Most commonly, data analyses were performed with classical and recently with advanced statistical approaches, such as principal component analysis (PCA) [20, 21]. Although these techniques provide very useful insights into the data, they are sometimes limited in terms of interpretability. On the other hand, a branch of machine learning (ML) methods were proven to produce descriptive models, which generally allow for easier interpretation [22 - 25].

In this study we apply regression-based ML method, induction of regression trees for knowledge discovery in the data set. The first objective of this study is to build a model for TIN/PO_4 ratio that will indicate and explain the following: (1) confirm or reject the relationship between the change in TIN/PO_4 ratio and the occurrence (temporal) of the mucilage events in the NA and (2) if the above relationship is confirmed, explain which environmental variables and how they influence the change of the TIN/PO_4 ratio and consequently to the mucilage events. The second objective was to relate mucilage events with the TIN/SiO_4 ratio, if possible.

2 Data description

The data set comprises physical and chemical parameters. Data were collected at six stations (SJ108, SJ101, SJ103, SJ105, SJ107 and RV001) on the profile from 12 Nm off the Po River delta to 1 Nm off Rovinj on the western Istrian coast by the Center for Marine Research (CMR) in Rovinj, Croatia (Fig. 1). This transect is 92 km in length, with station depths of 37 m and is considered representative for the shallowest part of NA delimited by the line Cape Kamenjak-Rimini [26, 27] approximately down to the 50 m isobaths with a surface area of about 19 000 km^2 and a volume of 635 km^3 [28]. Marked trophic gradients are often established between the predominantly mesotrophic northwestern part of this region with its southeastern part, which is under the influence of oligotrophic waters originated in the central Adriatic.

The water column was sampled with 5 l Niskin samplers at 0.3, 5, 10, and 20 meters, and at 2 meters above the bottom from 1972 to 2007 with near monthly frequency. Nutrient analyses (ammonium-NH_4, nitrite-NO_2, nitrate-NO_3, orthophosphate-PO_4 and orthosilicate-SiO_4) and pH were performed aboard the research vessel immediately after sample collection. The analyses were performed by methods widely used in oceanographic research [29], using Beckman DU and Shimazu UV mini-1240 and UV-1800 spectrophotometers with 10 cm cells and Radiometer pH meters. Temperature was measured with reversing thermometers, salinity by Beckman RS 7c or Yeo-Kal MKII high precision salinometers in the ashore laboratory. TIN was calculated as the sum of NH_4-N, NO_2-N, and NO_3-N.

Daily Po River flow data measured at Pontelagoscuro (Fig. 1) from January 1966 to December 2007 were obtained from the Agenzia Regionale Prevenzione e Ambiente dell'Emilia Romagna, Servizio Idrometeorologico, Parma. The data used for building the model are depicted in Table 1. For the modelling experiments, the entire span of the historic data was used. At each station, the measured parameters for the top 11 m of the water column were averaged because upper water column is more related to eutrophication in which mucilage is developed. Additionally, we obtained information about the temporal occurrence of the mucilage events (CMR Rovinj int. data; Fig. 3-5).

Table 1. Data used for modelling TIN/PO_4 and TIN/SiO_4 ratio

Symbol	**Interpretation**	**Unit**
Flow	Po River flow	m^3/s
Year		
Month		
Temp	Temperature	°C
SAL	Salinity	
Dene	Density excess	kg/m^3
pH	pH	
TIN/PO_4 *	**Tot. In. Nitrogen /Orthophosphate**	
TIN/SiO_4 *	**Tot. In. Nitrogen/ Orthosilicate**	

* *Molar ratio.*

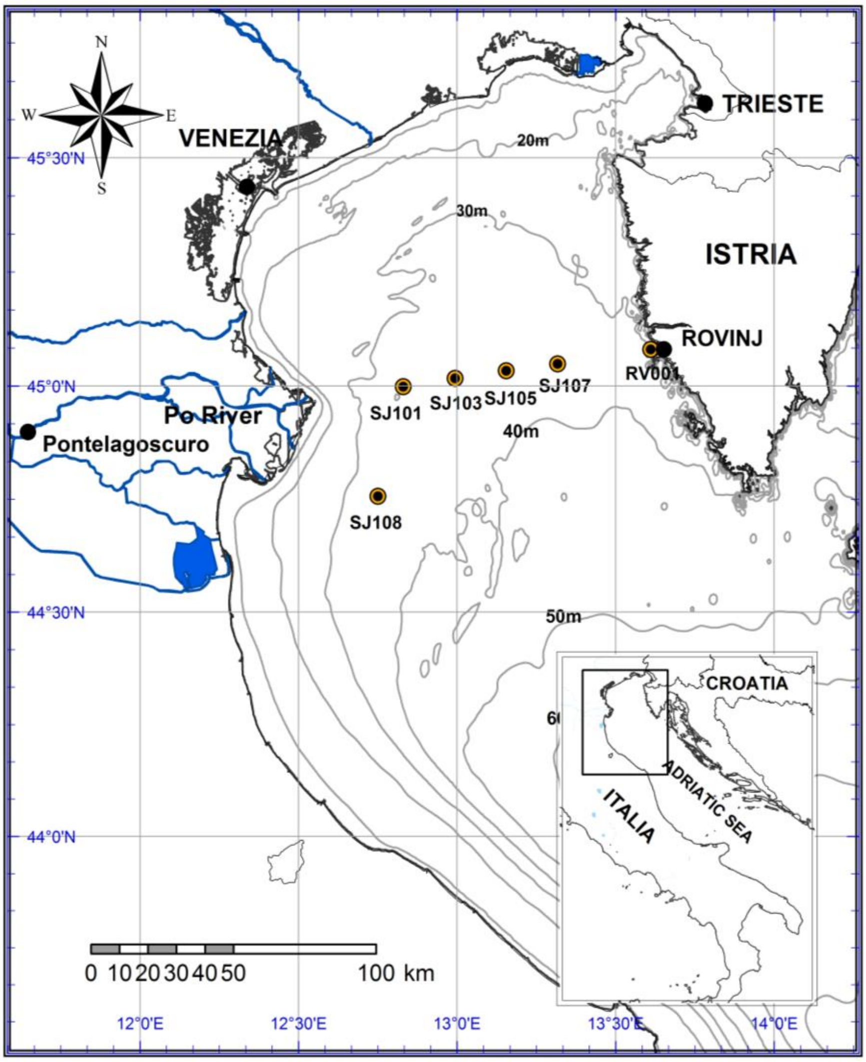

Figure 1. Geographic position of measurement stations.

3 Modeling methods

The aim of this paper is focused on identifying the nutrient status through their ratios that could be related to the onset of mucilage events on the basis of the measured parameters and the use of ML tool WEKA to build up the model for TIN/PO_4 and TIN/SiO_4 ratios presented in the form of regression trees.

Given a data set of examples in a form (*a1, a2,…, an, x*), where *ai* are values of the *n* attributes also independent variables or descriptors and *x* in the value of the dependent variable (also called a target variable, or class), Regression trees can be induced from the data to predict the value of the class based on linear regression principle.

Unlike the simple linear regression, which calculates one equation (one weight vector) for the entire data set, piecewise or *tree-structured regression* divides the data set to several subsets to which *uniform class value* or *linear equation* can be applied. The division to subsets is based on tests of the values of the input attributes, which are put as nodes in a regression tree. Thus, regression trees are hierarchical structures composed of nodes and branches where the internal nodes contain tests on the input attributes. Each branch of an internal test corresponds to an outcome of the test, and the predictions for the values of the target variable (the class) are stored in the leaves, which are the terminal nodes in the tree (see also Section 6). If the leafs contain a single value for the class prediction, then we are talking about simple regression trees, while if linear equation is used for prediction in the leaf, we are speaking of (regression) model trees.

One of the mostly used algorithm for induction of regression trees is the M5 algorithm [30], based on the TDIDT (top-down induction of decision trees) algorithm [31]. For our experiments, a variation of the M5 algorithm was used, called M5P implemented in the software package WEKA [32].

After the tree is constructed from the training (learning) set of data, it is necessary to assess the model quality, i.e., the accuracy of prediction. This can be done by simulating the model on a testing set of data and comparing the predicted values of the target with the actual values. Another option is to employ cross-validation. The given (training) data set is partitioned on a chosen number of folds (n). In turn, each fold is used for testing, while the remainder (n-1 folds) is used for training. The final error is the averaged error of the all models throughout the procedure.

The size of the error between the actual and the predicted values can be calculated by several measures to evaluate the model accuracy: root mean-squared error, mean absolute error, root relative squared error, relative absolute error and correlation coefficient (R).

4 Modeling experiment

For the experiments, we employed the machine learning algorithm M5P for regression trees integrated in the WEKA modelling software (MS). The experiments were designed to first elaborate a model for TIN/PO_4 ratio. We set the ratio TIN/PO_4 as dependant variable, while Po River flow rate, year, month, sea water temperature, salinity, density and pH were given as independent variables (Table 1). Due to the lack of Po River water chemical composition data, flow rates were used as a rough measure of the eutrophication pressure to the investigated ecosystem combined with nutrient concentrations in the sea as a measure of the eutrophication degree.

To test the model accuracy, we employ the cross validation procedure, i.e., the data sets from all stations were used to build and cross-validate the TIN/PO_4 ratio model.

The second part of these modelling experiments was to test the hypothesis that SiO_4 does not play a significant limiting role in phytoplankton growth-consequently, it is probably not essential for the development of the mucilage phenomenon [10]. In this case, instead of SiO_4 we test TIN/SiO_4 ratio, which was the target variable.

5 Results and discussion

The goal of the first model is to give an insight in how TIN/PO_4 ratio is changing in the ecosystem, and what the most influential factors for this change are as this ratio is recognized as one of the more important and necessary factors if not a trigger for the mucilage devolopment [4, 33].

Massive mucilage events, characterized by formation of aggregates of various shapes and dimensions (few milimeters up to several meters) in upper water column and kilometer long gelatinous surface fronts, occurred during summer with various durations (1-3 months) throughout the NA in 1988, 1989, 1991, 1997, 2000-2004, 2007, 2010 [2 - 8]. Notably, only during the 1988, 1989 and 2004 events, when winds blowing from the sea to the land dominated, the coast has been contaminated by gelatinous material for weeks.

Given the historical data from five stations (Table 1, Fig. 1), a TIN/PO_4 model presented in Fig. 3, was constructed. The data from the station SJ108 were finally excluded from the analysis as they significantly contributed to lower accuracy of the model. This indicates that the ecosystem behaviour at this station differs (e.g. is more influenced by Po River discharges) compared with the rest of the investigated profile and cannot be modelled sufficiently well with the available data set. Thus, the generality of the model cannot be extended to this part of the NA area, but only to the area covered with the stations from RV001 to SJ101 (Fig. 1).

The accuracy of the model is given by the correlation coefficient (R) between the modelled and measured values of the TIN/PO_4 ratio. The correlation coefficient for selected model (Fig. 2) using a cross-validation method is 0.52 with probability of $p < 0.0001$.

The selected model (Fig. 2) shows that the first change in TIN/PO_4 ratio occurred after 1982, followed by the changes before 1995, around 2000, and finally around 2004. The model confirms that the mucilage events are grouped in three main clusters: (1) 1920-1930 (not presented in model); (2) 1983-1991 and (3) 1997-2002 [19]. The model indicates that the ratio was close to constant (30) before 2000 and at high temperatures (> 19.6 °C). At lower temperatures (see the sub-tree for Year < 1999.5, left side); we can note some dynamics in the average ratio values. In the period before 1982. the ratio was close to the constant (between 32 and 46) but slightly influenced by the Po River flow rate. In the period between 1982 and 1995 (left side of tree marked with red circles, and at temperatures lower than 19.6 °C, marked with orange rectangle), salinity (SAL marked with blue ellipse) has triggered a change in the ratio values. At lower salinities (less than 36.9), the ratio was higher (around 93), otherwise ratio was around 60.

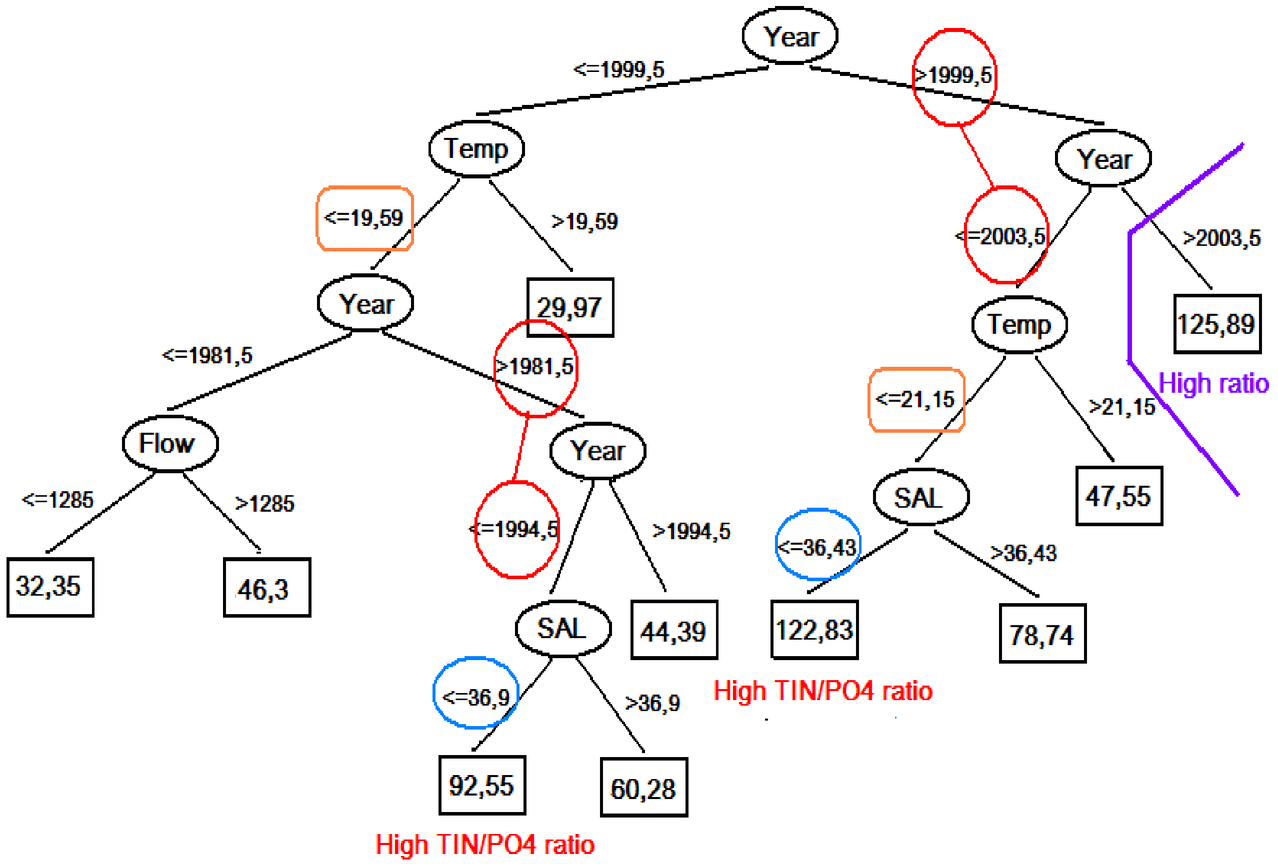

Figure 2. Model for TIN/PO_4 ratio-All data without station SJ108.

For years between 1995 and 2000 (1994.5 and 1999.5), ratio is around 44. The sub-tree for the period after 2000 (right hand side) indicates a change in the ratio between 2000 and 2004 (right side of the tree marked with red circles). The change was triggered by temperature and by salinity. At temperatures lower than 21.1 °C (marked with orange rectangle) and salinity lower than 36.4 (marked with blue ellipse), the average values of the ratio changed from 79 (at SAL > 36.4) to 123 (at SAL < 36.4). At higher temperatures (more than 21.1 °C), the average values of the ratio were 48. After 2004 (far right side of the tree), a change in the nutrient ratio is also observed (126). Changes in the TIN/PO_4 ratio values coincide with the observed mucilage events. Recall that three mucilage events occurred between 1982 and 1995 (1988, 1989, 1991) and five between 2000 and 2004 (2000, 2001, 2002, 2003 event lasted less than one month and was not caught by measurements, so it is not presented in figures and 2004; see above references). This indicates that at certain levels of P limitation, i.e. TIN/PO_4 signals indicate that mucilage events frequency increase.

In 1997 mucilage was also observed, although less visible in the largest part of the NA and it was not considered by the model [6, 34].

Related to previous research of the mucilage phenomena in the NA, the model confirms some of the results, particularly those related to the effects of salinity and temperature on its formation, e.g. that the phenomenon is primarily developed at lower salinity (32-37) and oxygenated surface waters [10]. Recall the threshold values of salinity in the model (Fig. 3) of 36.9, 36.34, etc. [7] showed that a major number of aggregates accumulated in the correspondence with strong pycnoclines with differences in density anomaly of 2 kg m^{-3} or higher, due to temperature and salinity vertical changes.

Observations of mucilage aggregate formations in 2000, 2001, and 2002 made by Russo and others suggest that increased air and sea temperature could play an important role, even a secondary one, in the mucilage phenomenon [1].

Salinity, temperature and other factors influence the growth of planktonic algae in the NA which can contribute to intense blooms in marine coastal waters [35]. In addition to the previous research, the model developed here, reveals the threshold values of salinity (SAL) and temperature (Temp) in the entire observed period (1972-2007) that lead to high values of the TIN/PO_4 ratio as an indicator for mucilage events.

To demonstrate the model results, we present the mucilage events in the period 1988-1991 (Fig. 3) and 2000-2004 (Fig. 4). Please note that this is not an exact representation as the data are taken at different time scales. While temperature and salinity are measured monthly, the mucilage events are only observed in approximate time periods of their appearance (CMR, Rovinj, unpub. data). Still the Figures clearly confirm our results from the model in Fig. 2. In each figure salinity (SAL), temperature (Temp) and TIN/PO_4 ratio values are presented together with their threshold values according to the model in Fig. 2.

In each figure salinity (SAL), temperature (Temp) and TIN/PO_4 ratio values are presented together with their threshold values according to the model in Fig. 2, 3 and 4 clearly indicate that the mucilage events occur when salinity and temperature are below the marked thresholds and above the marked threshold value of TIN/PO_4. It is also evident that events occur in the period when sea-water temperature rises.

Fig. 5 presents the mucilage event in 1997, which was not caught by the model (Fig. 2), possible due to the lack of measured data. According to our opinion, the missed event in 1997 also occurred in the same circumstances like events in 1988-1991 and 2000-2004 (low salinity, temperatures growing and high TIN/PO_4 values) [6].

The second part of the modelling experiments was designed to test possible correlation between the TIN/SiO_4 ratio and the mucilage events. As already suspected, the obtained models in this case have very low correlation coefficients (for example for station RV001 correlation coefficient is 0.16)-thus they confirm the hypothesis that this ratio in general does not trigger the mucilage events.

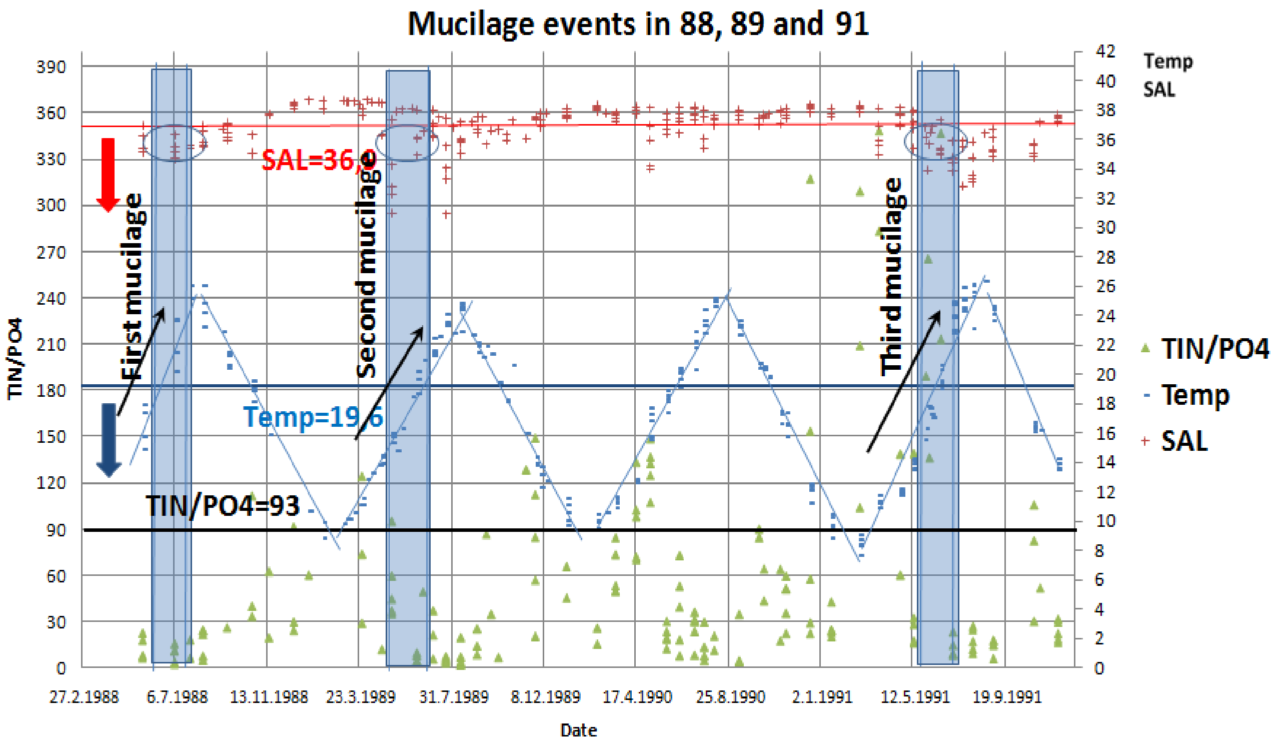

Figure 3. Mucilage events in period 1988-1991.

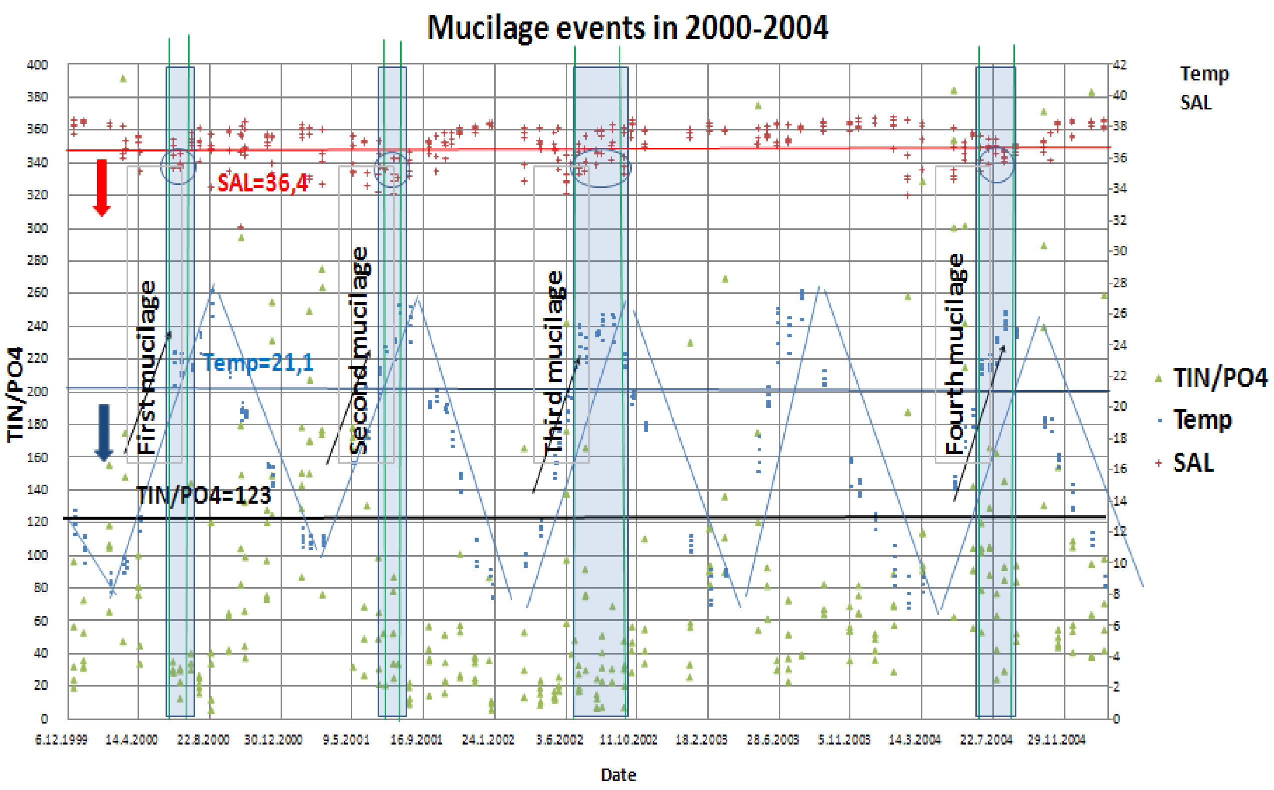

Figure 4. Mucilage events in period 2000-2004.

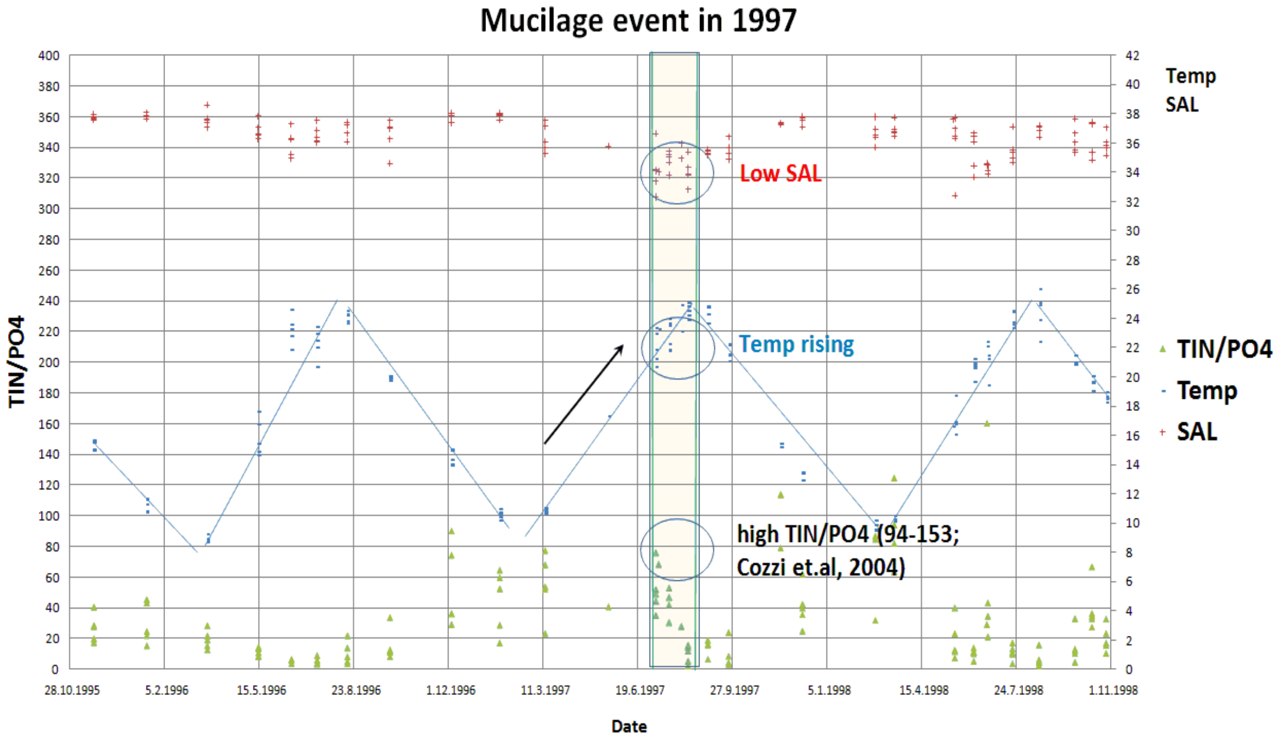

Figure 5. Mucilage event in 1997.

6 Conclusions

In this research machine learning technique was applied to long-term measured data in northern Adriatic in order to possibly induce a descriptive TIN/PO_4 and TIN/SiO_4 ratio model. The first ratio is assumed to be one of the important factors favouring mucilage events, while the common expert opinion for the second ratio is that it is not important.

The model for TIN/PO_4 ratio as given in the Fig. 2 confirmed the assumption that the mucilage events are connected with the changes of this ratio in the system, i.e., the model says that mucilage events coincide with the change of the TIN/PO_4 ratio, see Fig. 3, 4, and 5. This indicates that at certain levels of P limitation (seen through the TIN/PO_4 ratio) mucilage event frequency increases. The model also reveals which threshold salinity and temperature values are responsible for the changes of the TIN/PO_4 ratio. For the period between 1982 and 1995, the major increase (change) in the TIN/PO_4 ratio values occurred at salinity less than 37 and temperatures lower than 19.6 ^{0}C, while for the period between 2000 and 2004, we observe an increase in the ratio of salinity lower than 36.4 and temperature lower than 21.2 ^{0}C. The model also shows that after 2004, the ratio is high mainly because of the reduction of the available orthophosphate in the ecosystem, which is in accordance with findings of Precali and Đakovac, [36]. This phenomenon is contributed to reduced inflows of the Po River into the NA. Namely, in the last decades, rivers flows as well as their nutrient loads have been reduced. The induced models for the TIN/SiO4 ratio have very weak correlation (for example, for station RV001 correlation, the coefficient is 0.16) with the mucilage events, and thus confirm the expert notion that it does not trigger these events.

The focus of our future work will be on building up a model that will completely explain mucilage events.

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