COMPARISON OF METHODS FOR DETERMINATION OF SELECTED INDICATORS OF SURFACE WATER QUALITY

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ABSTRACT

Our objective was to find out, if two different methods for determination of water quality indicators– spectrophotometric (SPM) and distillation-titration (DTM) – have comparable results. Distillation-titration method was done according to Peoples at all. (1986) and spectrophotometric method was done according to Hach-Lange methodology. Water sampling was realized in Jizera Mountains on three respectively six sites. Results from both methods were compared within one-way analysis of variance (ANOVA) in combination with Tukey´s test and graphic processing into a chart, which are supplemented by tables. According to fixed standard deviation just two of comparisons of SPM and DTM are above the significant level, so both methods are comparable.

Key words: spectrophotometer, distillation-titration method, analysis of variance, Tukey´s test, mineral nitrogen

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INTRODUCTION

During this research lot of indicators were determined, but this paper is focused just on the mineral nitrogen.

Human perturbation of the nitrogen cycle represents a major example of global geo-engineering. Historically, the limited availability of reactive nitrogen compounds has provided a key constraint to human activities. Although the element nitrogen is extremely abundant, making up 78% of the Earth's atmosphere, it exists mainly as unreactive di-nitrogen (N_2). By contrast, to be useable by most plants and animals, reactive nitrogen (N_r) forms are needed (Sutton, 2011).

Reactive nitrogen, N_r, is defined here as all other nitrogen forms in our system apart from N_2. This includes oxidized nitrogen, mainly NO, NO_2, NO_3; reduced forms of nitrogen: NH_4^+, NH_3 and organic nitrogen: proteins, amines, etc., with different states of oxidation (Erisman, 2011).

The major threat to the quality of surface water is mineral nitrogen (N_{min}). N_{min} is a reactive nitrogen and consisting of ammonia (NH_4^+-N) and nitrate (NO_3^--N) nitrogen (Elbl, et al. 2013). The most dangerous are nitrates, because they are very mobile in the soil. They have a negative charge and soil sorption complex has minimal affinity for negatively charged particles.

Therefore, the authors focused on the determination of N_{min} in surface water. It was determined by Spectrophotometric Method (SPM) and Distillation-titration Method (DTM). Hypothesis that difference between SPM and DTM exist was tested.

The hypothesis is that both SPM and DTM provide comparable results according to sampling and determining of surface water and pollution.

MATERIAL AND METHODS

Water sampling was carried out in the area of Jizera Mountains on three sites, which are possible sources of surface water pollution. On each site two samples were made, one under the source of pollution and second the stream bellow. All samples were transported according to Hach-Lange principles for the handling of water samples (temperature, sun light etc.). Thereafter they were determined in laboratories of Department of Agrochemistry, Soil Science, Microbiology and Plant Nutrition and Department of Applied and Landscape Ecology.

Determination of mineral nitrogen by spectrophotometric method

Spectrophotometric method was performed according to Hach-Lange Method 10071 – Persulfate Digestion Method for spectrophotometer DR/4000.

An alkaline persulfate digestion converts all forms of nitrogen to nitrate. In well aerated water, most of the mineral nitrogen is in the form of nitrate. (Tyson, 2011) Sodium metabisulfite is added after the digestion to eliminate halogen oxide interferences. Nitrate then reacts with chromotropic acid under strongly acidic conditions to form a yellow complex with an absorbance maximum at 410 nm.(Hach-Lange Methodology).

Determination of mineral nitrogen by distillation-titration method

Concentration of mineral nitrogen was measured using distillation-titration method by Peoples et al. (1986). Elbl et al. (2013) described this method as follows: Ammonium nitrogen was determined by distillation-titration method in an alkaline solution after the addition of MgO. Nitrate nitrogen was determined in the same manner using Devard´s alloy. The value of N_{min} was calculated as the

sum of the detected ammonium and nitrate forms. Concentration of NH_4^+-N and NO_3^--N was calculated:

$$\text{mg } NH_4^+ \text{ or } NO_3^- - N = \left(\frac{\text{normality of standart HCl}}{0.03571}\right) \times 0.5 \times \text{titration} \quad (1)$$

Statistical analysis

Potential differences in values of mineral nitrogen were identified by one-way analysis of variance (ANOVA) in combination with Tukey´s test. The means differences was significant at the level 0.05 ($P<0.05$). All analyses were performed using Statistica 10 software. The results were processed graphically in the program Microsoft Excel 2010.

RESULT AND DISCUSSION

The results obtained from statistic analysis were graphically presented into a bar chart with variance (see Fig. 1).

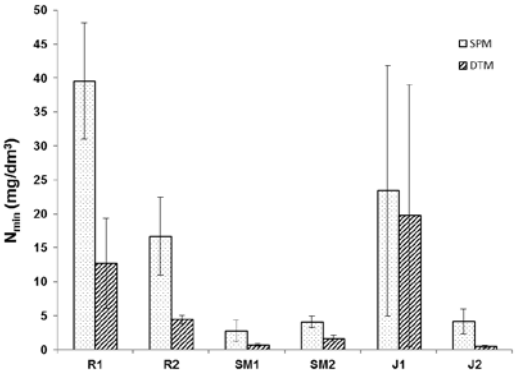

Fig. 1 Detection of mineral nitrogen (mean values ± SE) by Spectrophotometric Method (SPM) and Distillation Titration Method (DTM)

Tab. 1 Concentration of N_{min} in surface water (weighted average with SE are presented)

Experimental site	SPM N_{min} (mg·dm^{-3})	±SE	DTM N_{min} (mg·dm^{-3})	±SE
R1	39.56455	8.563011	12.686251	6.634694
R2	16.69292	5.729757	4.4426765	0.598908
SM1	2.70403	1.602431	0.6927785	0.148057
SM2	4.06599	0.883209	1.6453468	0.43363
J1	23.39018	18.45494	19.75629	19.29913
J2	4.138191	1.82096	0.4739162	0.163059

Comment for Table 1: Weighted average ($\bar{x}$) of nitrate nitrogen with SE (standard error) are presented. These parameters were calculated from five measurement (n = 5) by Statistica 10 software for each experimental site (Elbl et al., 2013).

Tab. 2 ANOVA for individual methods and experimental sites (weighted average with SE are presented)

Experimental site	Method	95% Confidence interval		F	p
		lower bound	upper bound		
R1	SPM	15,7898	63,33928	6.157	0.03804
	DTM	-5,7346	31,10711		
R2	SPM	0,7846	32,60128	4.521	0.06616
	DTM	2,7798	6,10551		
SM1	SPM	-1,7450	7,15309	1.562	0.24669
	DTM	0,2817	1,10385		
SM2	SPM	1,6138	6,51818	6.052	0.03931
	DTM	0,4414	2,84930		
J1	SPM	-27,8489	74,62930	0.018	0.89512
	DTM	-33,8267	73,33926		
J2	SPM	-0,9176	9,19399	4.030	0.0796
	DTM	0,0212	0,92664		

Comment for Table 2: 95 % confidence interval (+-) and probability (p-value) are presented. F is a measure of test accuracy (Elbl et al., 2013).

Tab. 3 Comparison of SPM and DTM by Tukey´s test

Number of cell	Experimental site	Methods	Mean difference	
			(1)	(2)
1	R1	SPM		**0,038192**
2		DTM	**0,038192**	
1	R2	SPM		0,066329
2		DTM	0,066329	
1	SM1	SPM		0,246843
2		DTM	0,246843	
1	SM2	SPM		**0,039466**
2		DTM	**0,039466**	
1	J1	SPM		0,895253
2		DTM	0,895253	
1	J2	SPM		0,079722
2		DTM	0,079722	

Comment for Table 3: The means differences is significant at the level 0.05 (P<0.05). These differences are shown **in bold**. Methods (SPM and DTM) were compared always for one experimental site (Elbl et al., 2013).

CONCLUSIONS

The results from comparing both methods confirm the hypothesis. So it is obvious that results from sampling and determining of water quality indicators set by spectrophotometric method have the

same predictive value as distillation-titration one. The next step would be comparing of obtained results with the actual legislation. This could be a tool for Management of Protected Landscape Area of Jizera Mountains, how to guide e. g. recreational facilities and activities in that area. (ZÁKOUTSKÁ, 2013)

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