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Total Organic Carbon and Total Nitrogen in Sediments and Soils: A Comparison of the Wet Oxidation – Titration Method with the Combustion-Infrared Method

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Abstract

Total organic carbon (TOC) and total nitrogen (TN) are the most important components of sediments and soils as they can be used to distinguish marine and terrestrial sources of organic matter, environmental depositional conditions, pollution indices and soil quality and productivity indicators. In this paper we present datasets of measurements of TOC and TN in sediments applying high temperature (720°C) catalytic combustion (Pt/Al₂O₃) oxidation method, as well as measurements of soil certified references materials (CRM). The detection of TOC and TN was performed using an infrared or a chemiluminescence detector, respectively. We validate the methods studying the range of measurement, the repeatability, reproducibility and precision. TOC results are compared with these measured by the widely used modified Wakley-Black titration method of Gaudette et al. (1974). This comparison indicated that the catalytic combustion method and Wakley-Black titration method have a very good correlation for low total organic carbon content (less than 5%), as well as for high organic carbon content (till 40%), while for sediments with higher organic load the catalytic combustion method is more accurate.

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1. Introduction

An important parameter for the environmental status estimation of terrestrial and aquatic ecosystem is the total organic carbon (TOC) and total nitrogen (TN) content, in soils and sediments. The soil and sediments organic carbon and nitrogen are mainly derived by decomposition of the plants and animals or plankton or anthropogenic sources such as chemical contaminants, fertilizers or organic rich waste.

Regardless of the source the portion of TOC and TN affect, especially in aquatic systems, the faunal communities (Carroll et al., 2003; Schaanning, 1994), the primary production in an ecosystem as well as the eutrophication status

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(Nixon, 1995). The sediments and soils concentrations of the organic carbon are correlated very well with organic contaminants and for this reason can be used as a tool for the estimation of the level of contamination - toxicity (Di Toro, 1991; MacDonald, 2010). The sediments TOC and TN ratios can be used as biomarkers, to distinguish the marine or terrestrial sources of organic matter as well as aerobic/anoxic and sulfate reduction conditions and thus give a qualitative indication of the redox status (Froelich et al., 1979; Raiswell, R. et al., 1987; Harnett et al., 1998). Moreover, organic matter and nitrogen content ratios have been used widely as biomarkers for the reconstruction of sedimentological depositional environments and the environmental changes of the past (Dean, 1999,1974; Avramidis et al., 2013, 2014). In sedimentology the presence of the organic matter is an important constitute for the study of recent aquatic bottom sediments as it consists an index for the sediments depositional environments (Avramidis et al., 2015; Panagiotaras et al., 2012). In agriculture, soil total carbon (TC), soil organic matter (SOM) and soil total nitrogen (STN) are the major determinants for soil fertility and indicators of quality, and are closely related to soil productivity. Soil is the most important and largest C reservoir in the world, thus Carbon Pool (CP), is important to both soil productivity and its ecosystem functions; C sequestration and the global C cycle (Al-Kaisi et al., 2005, Qadir et al., 2006, Elbasiouny et al., 2014).

For the TOC determinations several methods have been developed which some of them need compositional and complicated analytical instruments and others are inexpensive chemical methods, but all of them with advantages and limitations. In the instrumental methods are included the LECO (Folger, 1972), the RockEval pyrolysis (Espitalié et al. 1977), the Lost on Ignition (LOI) and the Combustion-Infrared method (APHA, 2005; DIN EN 15936 2009). The most inexpensive and widely used method is the Wakley-Black wet oxidation - titration method (Wakley and Black, 1934), which has been validated and compared with LECO by Gaudette et al., (1974) and later by Beaudoin (2003). A comparison of the measurements of TOC between LECO and Combustion-Infrared method, using recent lake sediments have been reported by Wang et al. (2012) with very good correlation.

In the present paper Total Organic Carbon (TOC) and Total Nitrogen (TN) were simultaneously determined in sediment and soil samples, applying the high-temperature (720°C) catalytic combustion (Pt/Al₂O₃) oxidation method and were validated (APHA, 2005; DIN EN 15936 2009; ASTM, 2008). Method characteristics such as range of measurement, repeatability, reproducibility and precision were determined. Moreover, the results of sediment TOC of the Combustion-Infrared and Combustion-Chemiluminescence method were compared with wet oxidation – titration method of Wakley and Black (1934). For the above purposes certified references materials (CRM/TOC-TN) and a dataset of sediments which have been collected from two Greek coastal lagoon environments were studied.

2. Materials and Methods

For this study the samples were collected from two coastal environments of western Greece, Prokopos Lagoon and Keri Lake. A total number of 38 samples were analyzed for their TOC and TN content while two different certified reference materials were used for the validation. All the samples were analyzed by using the Combustion-Infrared and Combustion-Chemiluminescence method using a Shimadzu TOC analyzer (TOC-VCSH) coupled to a chemiluminescence detector (TNM-1 TN unit) (APHA, 2005; DIN EN 15936 2009; ASTM, 2008), as well as the wet oxidation method of Wakley and Black (1934).

The wet oxidation technique utilizes exothermic heating and oxidation of organic carbon of the sample with potassium dichromate and concentrated H₂SO₄ and the titration of excess dichromate with 0.5N ferrous ammonium sulphate solution to a sharp one drop end point. In this procedure 10 ml of 1 N K₂Cr₂O₇ solution is added to 0.2 to 0.5 g dried sample in a 500 ml Erlenmeyer flask and are mixed by swirling. Twenty (20) ml of concentrated H₂SO₄ are added and mixed gently. The mixture is allowed for 30 minutes and after is diluted to 200 ml volume of distilled water and 10 ml of 85% H₃PO₄, 0.2 g NaF and 15 drops of diphenylamine indicator are added. The solution is back titrated with 0.5 N ferrous solution (Gaudette et al., 1974).

For the Combustion-Infrared and Combustion-Chemiluminescence method (TOC – TN) 0.200 g of pulverized sample is weighted in a Erlenmeyer flask and is suspended in a 200 mL diluted hydrochloric acid solution (HCl 0.22 mol/L). The suspension is dispersed and homogenized using a dispersion drive for three minutes at a speed of 17000 to 18000 rpm. After the dispersion the suspension is transferred to the equipment sampler and the measurement starts immediately.

The principle for the TOC method is that a microportion of the sample is injected into a heated reaction chamber packed with an oxidative catalyst, which in our case is Pt/Al₂O₃. The water is vaporized and the organic and inorganic carbon is oxidized to CO₂ and water. The CO₂ is transported in the carrier gas streams (purified air) and is measured by means of a non dispersive infrared analyzer (NDIR analyzer). Because in this way Total Carbon (TC) is measured, Inorganic Carbon (IC) is measured separately. The origin of inorganic carbon is CO₂ and carbonate salts dissolved in water. Acidifying the sample with HCl acid at pH <3 all the carbonate salts are transformed to CO₂. All the quantity of CO₂ is transported in the carrier gas streams and is measured by the NDIR analyzer. Then TOC is obtained by difference (TOC = TC-IC).

The principle for the TN is that a microportion of the sample is introduced into a stream of inert purified air flowing through a quartz pyrolysis tube. Oxidative pyrolysis converts chemically bound nitrogen to nitric oxide (NO). The gas stream is dried and the NO is contacted with ozone (O₃) producing metastable nitrogen dioxide (NO₂*). As the NO₂* decays, light is emitted and detected by a photomultiplier tube. The resulting signal is a measure of the total chemically bound nitrogen in the sample.

3. Results and Discussion

3.1 Total Organic Carbon (TOC) and Total Nitrogen (TN)

The results of the analyzed samples by wet oxidation – titration and the combustion-infrared methods were compared with regression analysis. We present the results separating them into two main categories: (a) low concentration (<5%) and (b) high concentration of TOC (>5%). The results of the regression analysis are shown in Table 1. The comparisons of the two data sets (low and high concentrations) are presented in Figures 1a and 1b while all samples scatter diagram and comparison is shown in Figure 2. For both comparisons was not taking into account the correction factor of Wakley (1947), following the comparison method which Gaudette et al., (1974) applied, without to use a correction factor for the wet oxidation results.

Table 1. The results of the regression analysis, between wet oxidation and chemiluminescence methods.

Range of measurements Concentration Area	Number of samples	Intercept		Slope		R-square
		Value	Error	Value	Error	
Low <5%	21	-0.037	0.146	1.081	0.043	0.968
High >5%	17	0.038	1.088	1.263	0.058	0.967
All samples <50%	38	-0.566	0.341	1.289	0.026	0.984

The comparison of the two different methods with the regression analysis indicates a very good correlation, with regression coefficients greater than 0.965 to all range of concentration areas. In low concentration area (<5%) the intercept point is -0.037 and the regression coefficient R²= 0.968 for a sample population 21 and significance level p<0.001 (Table 1; Fig. 1a). In high concentration area (>5%) the intercept point is 0.038, the regression coefficient R²=0.967 for a population of 17 samples and significance level p<0.001, while the comparison of the whole samples (samples number 38) indicate a very good correlation of the two methods with R²=0.984 (p<0.001) and intercept - 0.566 (Table 1; Fig. 1bc).

3.2 Validation of TOC-TN determination-Data analysis

For the validation of TOC determination two Certified Reference Materials (CRM), the first one with low and the second one with high TOC concentrations, were used. The first one was the AgroMat – Compost CP-1 with concentration of 28% and the second one was IRMM-443-7, Eurosoil 7 with concentration of 5.62%. Eurosoil 7 was also used for TN validation with 0.48% certified TN value. The range of measurements was dictated by the range of the water samples that could be analyzed by this system and are in both cases (TOC and TN) from 0.05% till 100% (Bekiari and Avramidis, 2014). Methods precision was determined in terms of repeatability and reproducibility and quantified by the repeatability and reproducibility standard deviation S_r and S_R, respectively (Table 2). Repeatability

data were obtained by replicate analysis of fifteen portions from both CRM the same day by the same analyst. Reproducibility data were collected by analyzing over a period of two months the same CRM, by two different analysts. Repeatability and reproducibility data are presented in Table 2.

Finally, for both CRM TOC was determined by the wet-oxidation method and the results are compared in Table 3. From these data it is evident that wet oxidation method systematically underestimates the concentration and this is more pronounced in higher organic contents where catalytic combustion method is obviously more accurate.

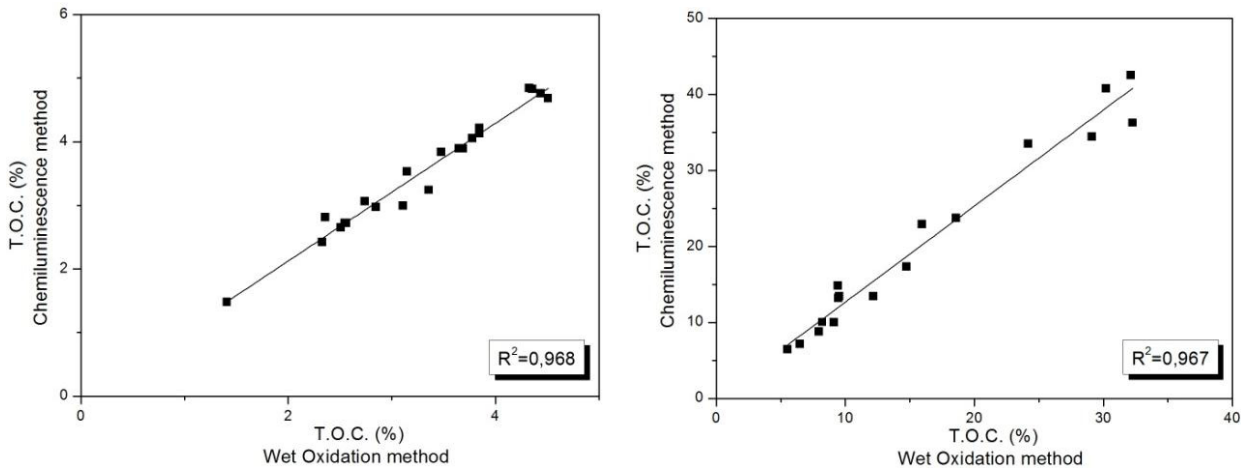


Fig. 1. Scatter diagrams and best fitted lines for: (a) low concentration <5%. values of TOC. (b) high concentration >5%. values of TOC.

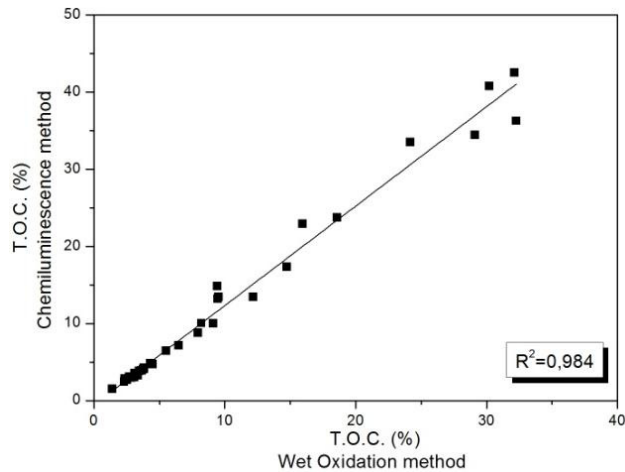


Fig. 2. Scatter diagrams and best fitted lines for all analyzed samples.

Table 2. TOC and TN precision data, repeatability (S_r) and reproducibility (S_R) standard deviation.

Parameter	Certified	Repeatability		Reproducibility	
	Concentration %	X_{mean} (n=15) %	S_r	X_{mean} (n=15) %	S_R
TOC	28%	29%	3.31	29%	3.29
TOC	5.62%	5.60%	0.64	5.60%	0.60
TN	0.48%	0.48%	0.03	0.47%	0.03

Table 3. TOC data for both CRM by the two different determination techniques.

Parameter	Certified Concentration %	Concentration from Combustion Infrared Method %	Concentration from Wet Oxidation method %
TOC	28%	29%	21%
TOC	5.62%	5.60%	4.94%

4. Conclusion

The determination of TOC for 38 aquatic sediments samples and two Certified Reference Materials (CRM), indicated a very good correlation ($R^2 > 0.967$) between the wet oxidation – titration method and the high temperature catalytic combustion oxidation - infrared method. Although the Wakley and Black method was developed in 1934 it seems to be still applicable for a quick estimation of the TOC but with some limitations in the concentration range. The analysis of the CRM materials supports the above assumption and with the titration method to be more accurate in low concentrations while for sediments with higher organic load the catalytic combustion method gives better results.

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