VALIDATION OF A SIMPLE SPECTROPHOTOMETRIC METHOD FOR THE DETERMINATION OF TOC IN SEDIMENT SAMPLES OF VAINI LAGOON, ALBANIA

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11th International Scientific Conference on Energy and Climate Change

WETLANDS

Areas where water covers the soil, or is present either at or near the surface of the soil all year or for varying periods of time during the year, including during the growing season

(EPA)

DIFFERENT FROM.....

LAKES

There are 2 types of wetlands

Two general categories of wetlands are recognized:

COASTAL OR TIDAL WETLANDS

and

INLAND OR NON-TIDAL WETLANDS.

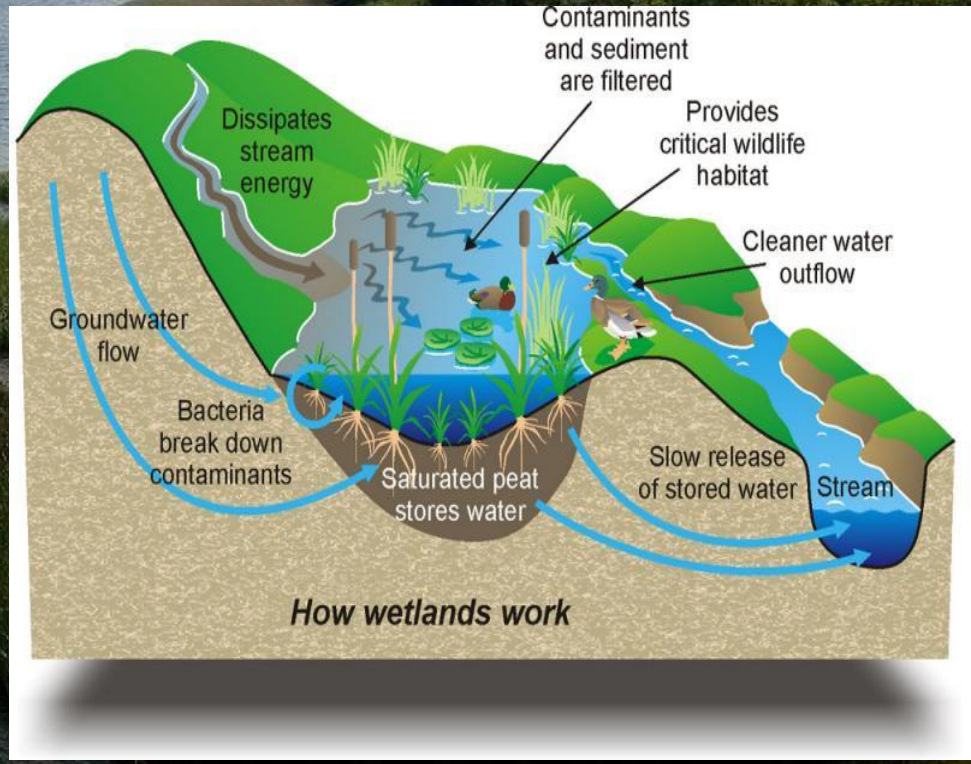
IMPORTANCE OF WETLANDS

FILTER OUT SEDIMENTS AND CHEMICALS

PROVIDE FOOD AND SHELTER TO WILD LIFE

STORE EXCESS WATER

ABSORB NUTRIENTS

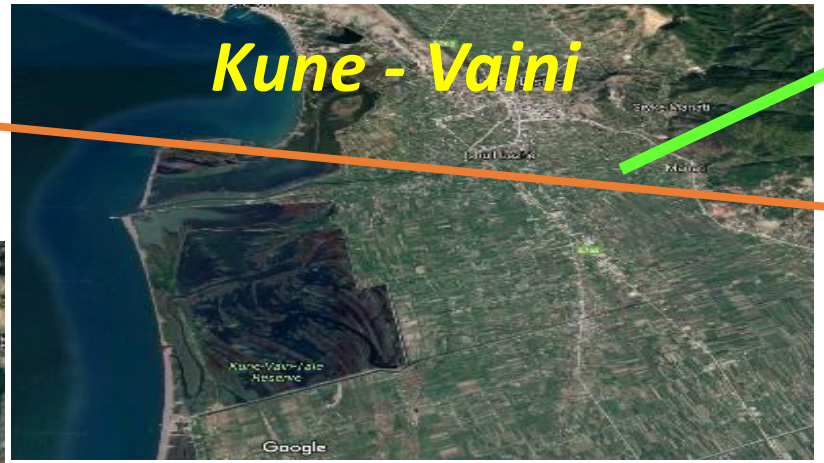


ALBANIAN WETLANDS

The most important transitional habitats, coastal wetlands and lagoons extend along the coastline of the Adriatic Lowlands

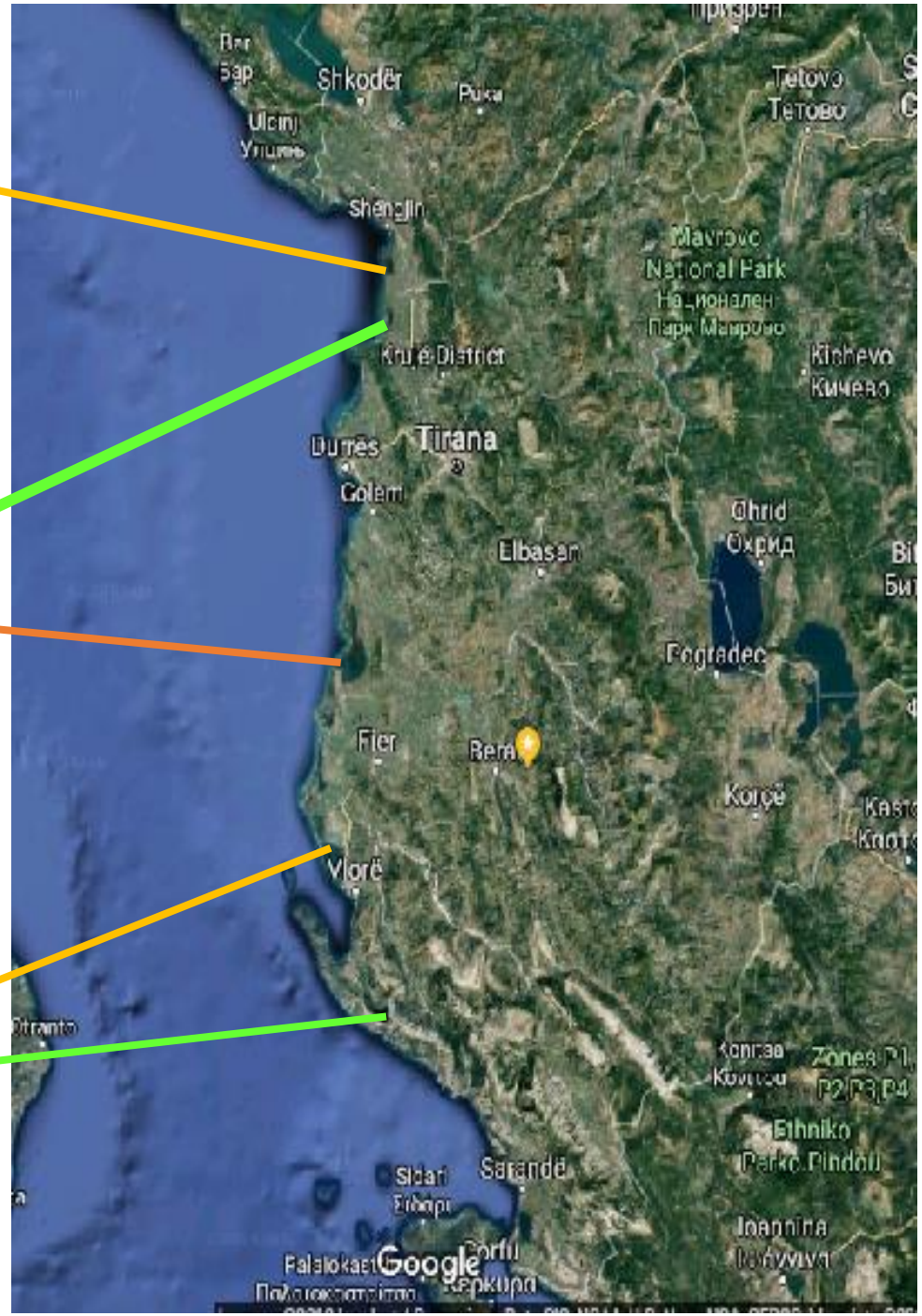

Karavastaja Lagoon
Divjaka-Karavasta National Park
Google


Viluni Lagoon
Google


Kune - Vaini
Kune-Vain-Lalzi Reserve
Google


Butrinti Lagoon
Butrint National Park
Google


Narta Lagoon
Google


Shkodër
Tirana
Durrës
Elbasan
Fier
Vlorë
Sarandë
Korçë
Pogradec
Ohrid
Kukës
Kruje District
Mavrovo National Park
Google

- **Project:**
- **“Climate changes adaption interventions of the Kune-Vaini lagoon system - ecological approach”**

- **The Program will cover the monitoring of three important biotic components: Phytoplankton, Zooplankton, and the development of Aquatic plants (Macrophytes), all in response to Kune-Vaini Project intervention (tidal channel). It will be in parallel with monitoring of Physical and chemical parameters and nutrient profile in Kune-Vaini system**

- *Importance of studying sediments organic matter*

- **Sediments contain natural organic matter (“humus”- like material)**

- **Organic contaminants bind strongest to natural organic matter in the sediment**

- **Binding strength depends on compound AND on organic content of the sediment**

- ***METHODS OF TOC DETERMINATION IN SOILS AND SEDIMENTS***

- ***Soil and sediment total organic carbon (TOC) determinations are requested with contaminant analyses as part of an ecological risk assessment data package.***

- ***TOC contents may be used qualitatively to assess the nature of the sampling location (e.g., was a depositional area) or may be used to normalize portions of the analytical chemistry data set (e.g., equilibrium partitioning).***

- **SOURCES AND FORMS OF CARBON IN SOILS AND SEDIMENTS**

  - **In soils and sediments, three basic forms of carbon may be present.**
    - **(1) elemental C,**
    - **(2) inorganic C, and**
    - **(3) organic C.**

- **The quality of organic matter in sediments is critical to the partitioning and bioavailability of sediment-associated contaminants.**

- Methods of TOC determination

- **Total Carbon = Inorganic Carbon + Organic Carbon**

- **If pH < 7.4**

- **Total Carbon = Organic Carbon**

- Methods of TOC determination

- **The basic principle for the quantitation of total organic carbon relies on the destruction of organic matter present in the soil or sediment although there are a few non-destructive techniques identified in the literature that are currently under development.**
  - **The destruction of the organic matter can be performed chemically or via heat at elevated temperatures.**

- **QUALITATIVE METHODS**
- **nuclear magnetic resonance (NMR) spectroscopy**
- **diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy.**

- Methods of TOC determination

- **SEMI-QUANTITATIVE METHODS**
- The two primary semi-quantitative methods are:

- **(1) loss-on-ignition and**
- **(2) hydrogen peroxide digestion.**

- Methods of TOC determination

QUANTITATIVE TECHNIQUES FOR THE DETERMINATION OF TOTAL ORGANIC CARBON

- **destructive and non-destructive techniques are available for the determination of TOC and total carbon in soils and sediments**

- **(1) wet oxidation followed by titration with ferrous ammonium sulfate or photometric determination of Cr^{3+}**
- **(2) wet oxidation followed by the collection and measurement of evolved CO_2, and**
- **(3) dry combustion at high temperatures in a furnace with the collection and detection of evolved CO_2**
- **An innovative nondestructive technique using non-elastic neutron scattering is also being developed for TOC determination (Wielopolski et al.,**

Optimization of the spectrophotometric method for the determination of TOC in sediment samples of Vaini Lagoon.

- **Principle: According to ISO 14235:1998. Determination of TOC in soils after sulfochromic oxidation.**
  - **$3C + 2K_2Cr_2O_7 + 16H_2SO_4 \rightarrow 3CO_2 + 4Cr^{3+} + 8H_2O$**
  - **Standardized against glucose standard solutions**
  - **Measurements of Cr^{3+} absorption in 585 nm.**

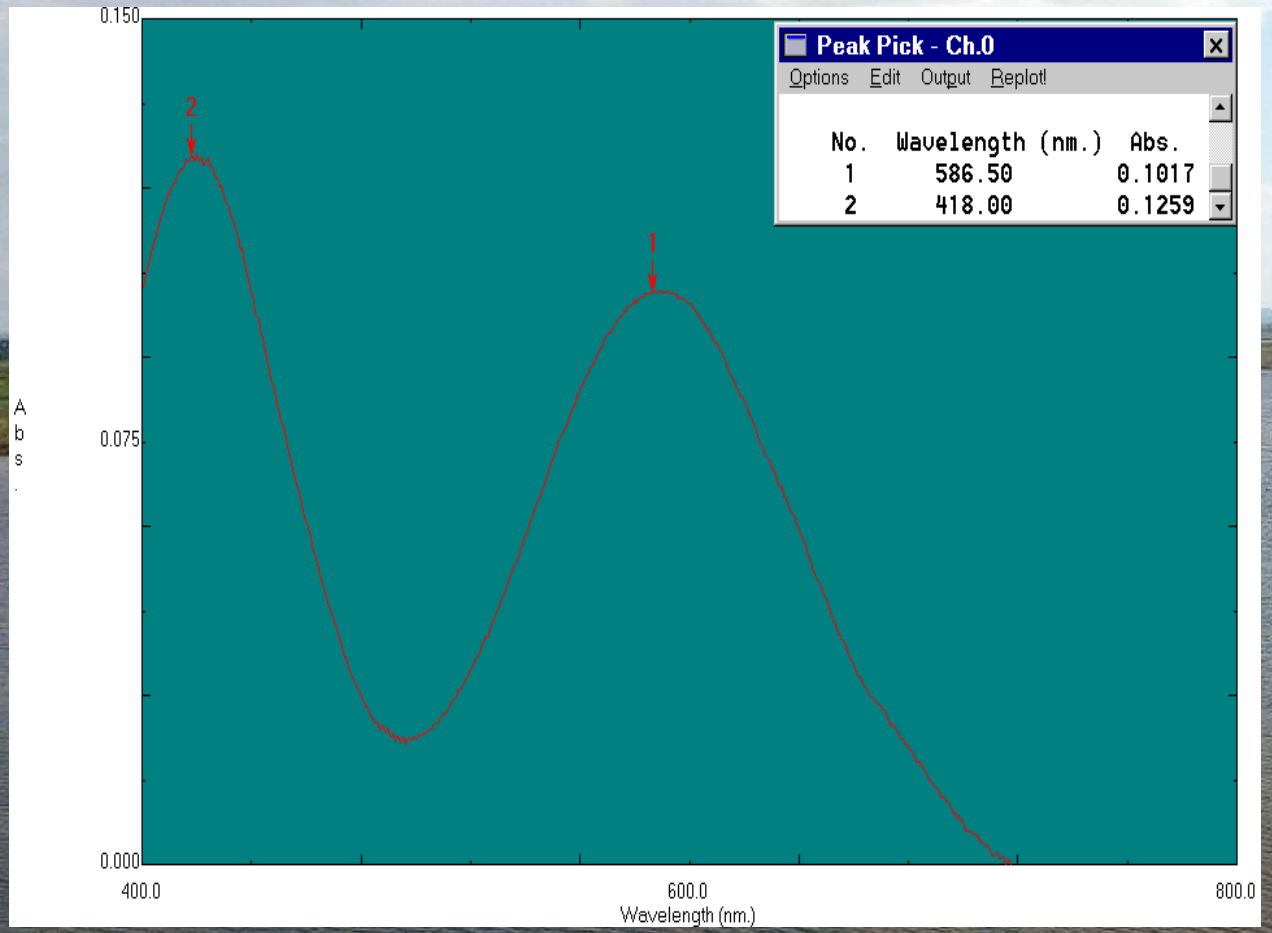
- **5 ml $K_2Cr_2O_7$ 0.27 M + glucose (sample) + H_2SO_4 + Digestion at 150°C for 30' + water till a known volume.**

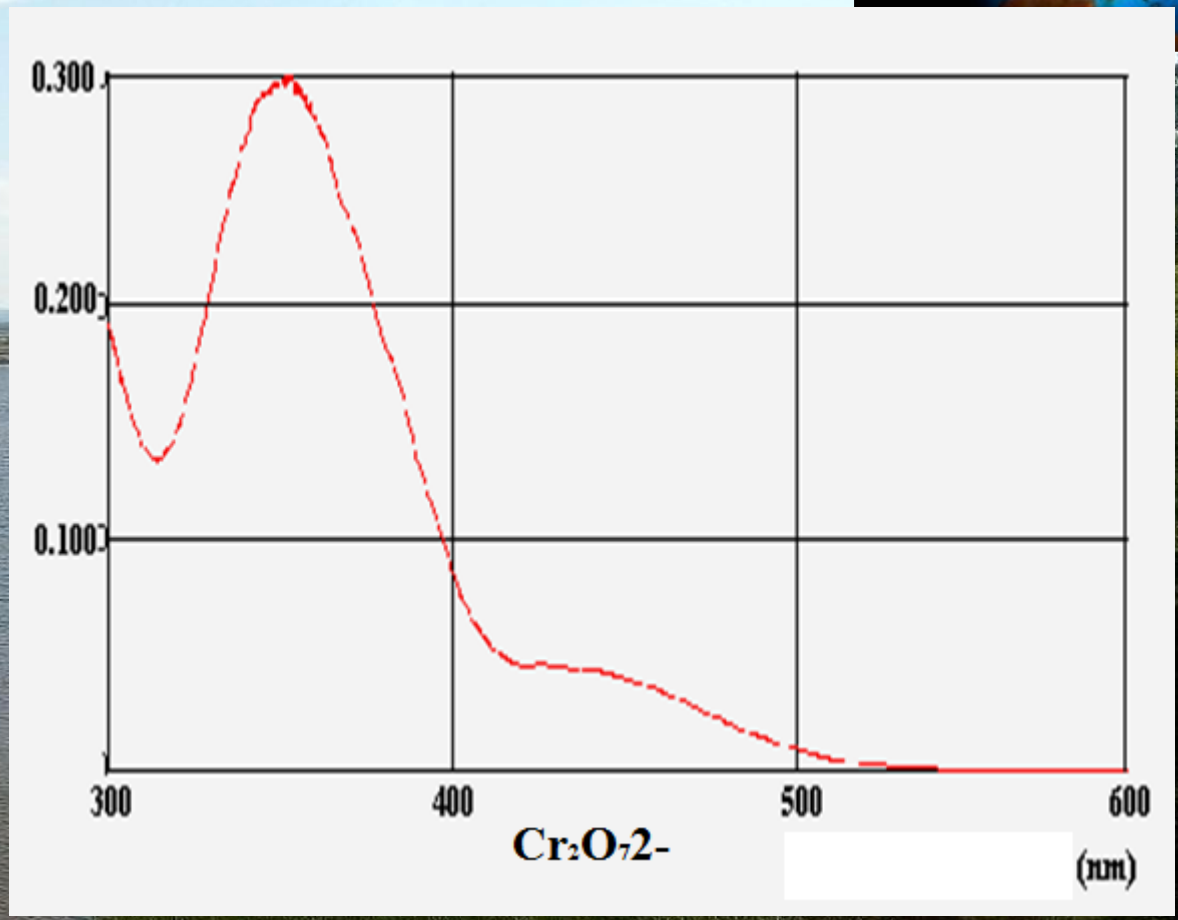
- Optimization of the spectrophotometric method for the determinatio TOC in sediment samples of Vaini Lagoon.

- **Interferences**

  - **Spectral – evaluated by means of absorption spectra of C^{3+} and $Cr_2O_7^{2-}$**
  - **Chemical (Cl^- , Fe^{3+}) – evaluated by the Method of Standard Additions**

• Spectral interferences



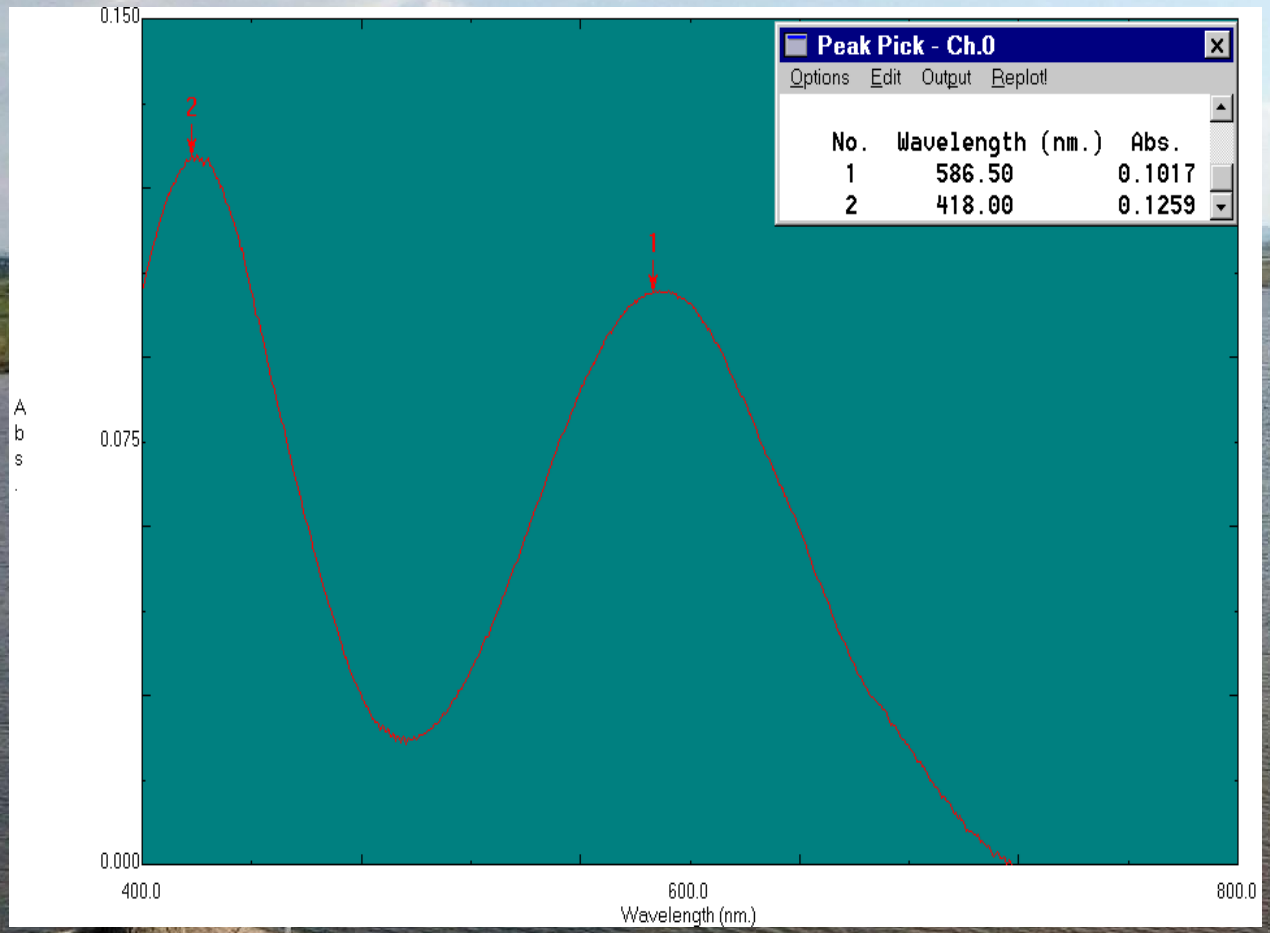


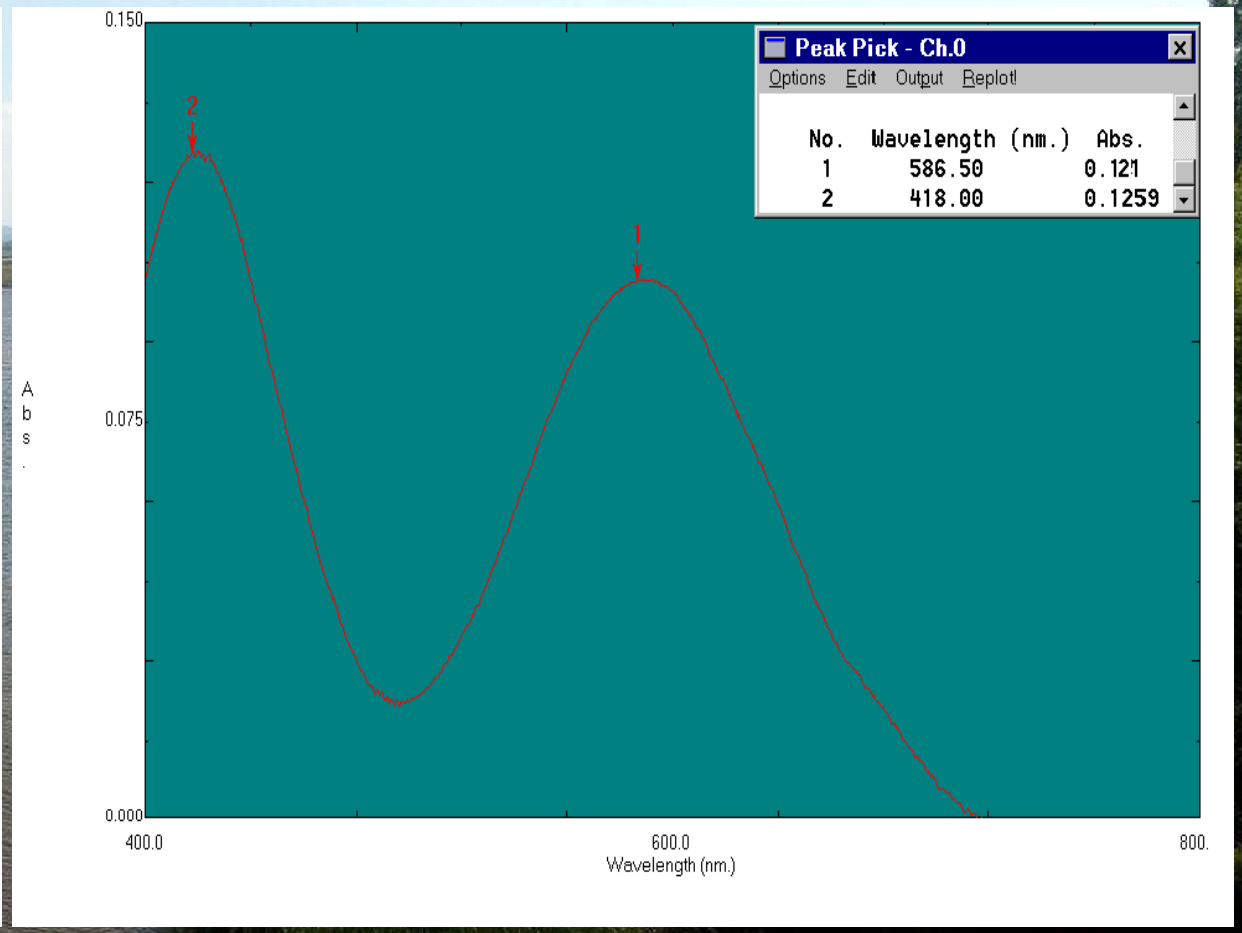
• No overlapping of spectral curves at 585 nm

• Spectral interferences

- *Clean Cr^{3+} standard*

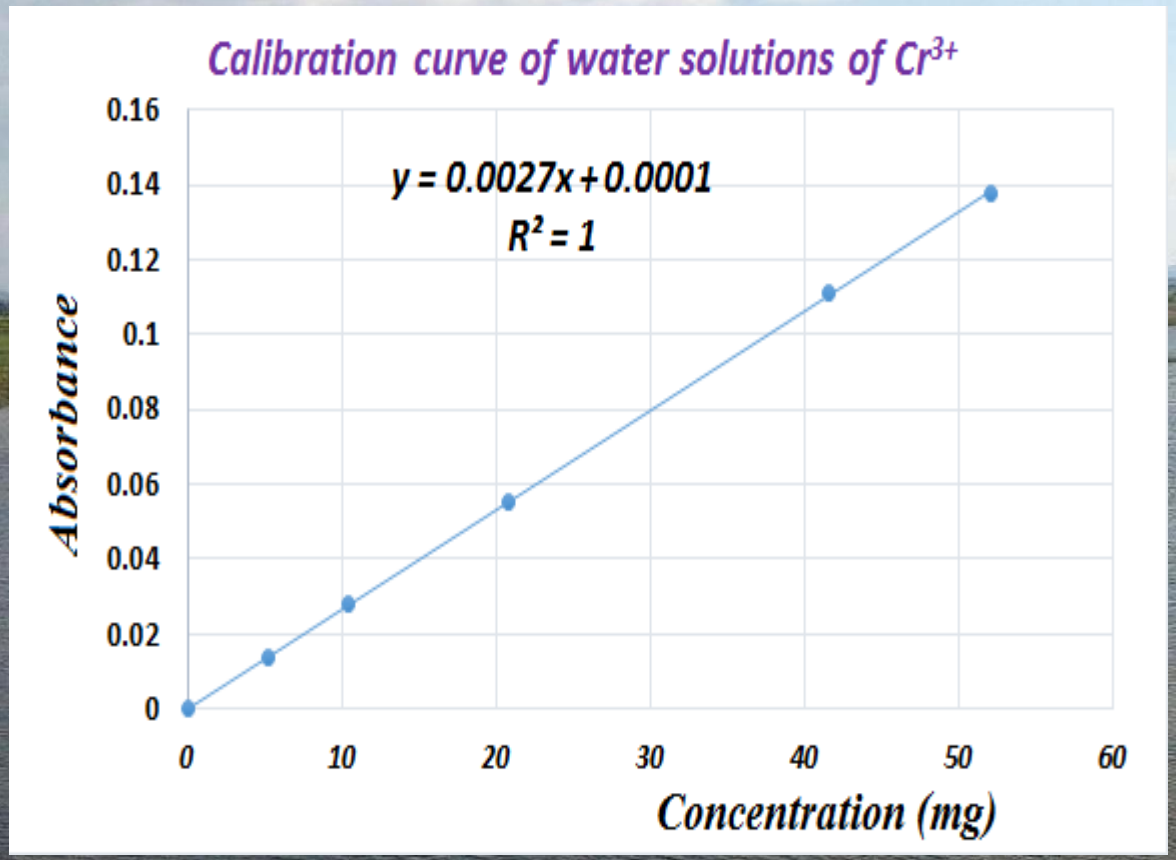
After reaction of Cr2O72- with C

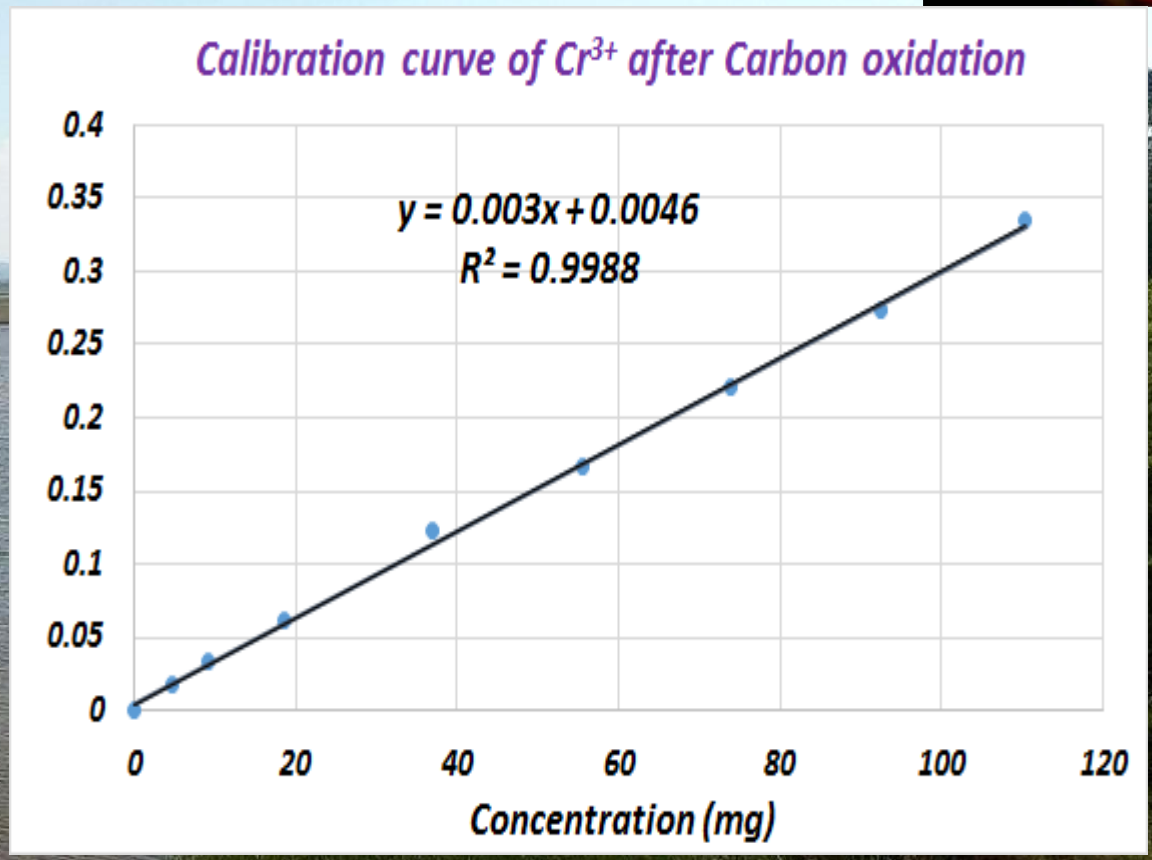




• No shift of optimal wavelength

- Calibration curves of C^{3+}

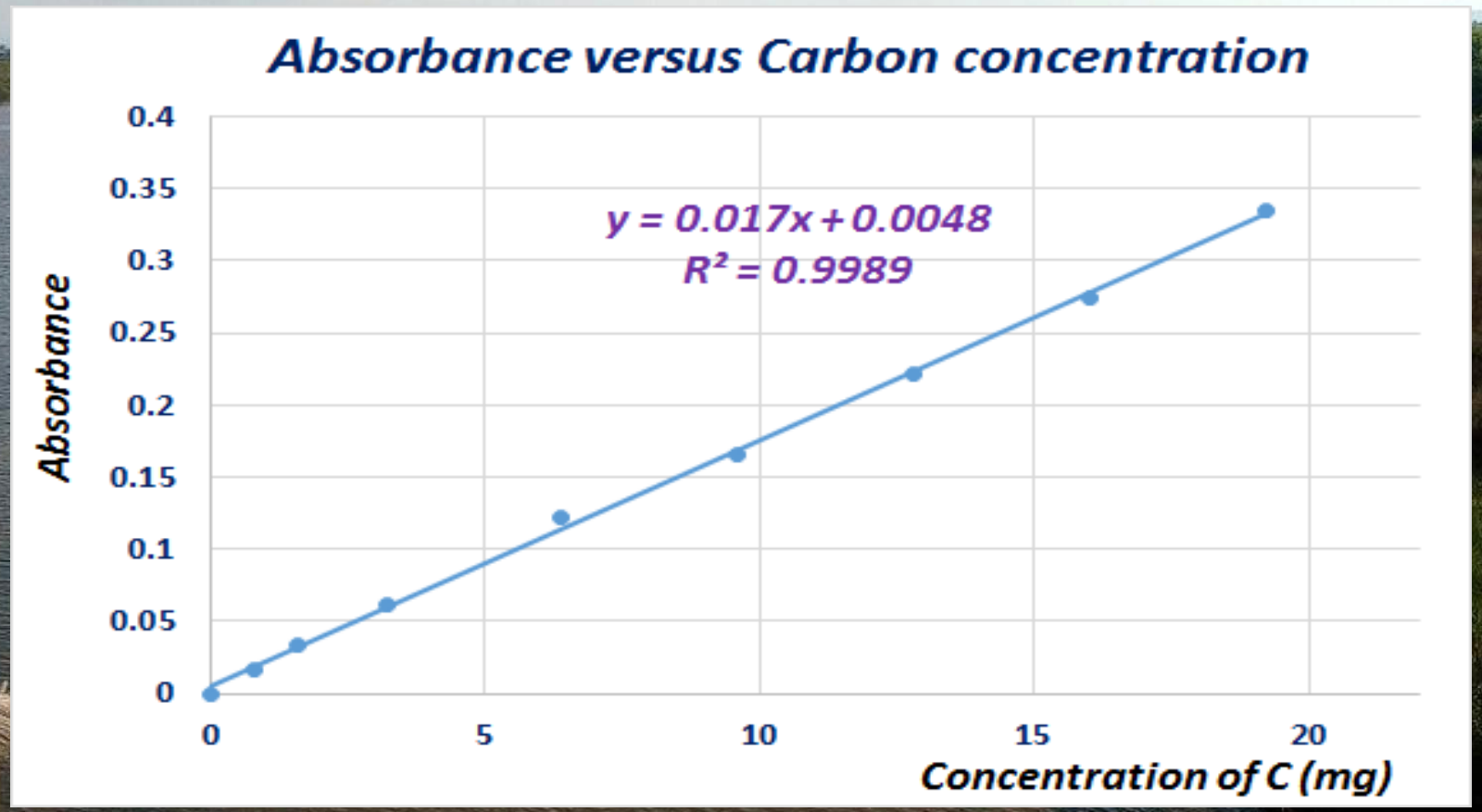




- *Sensitivity changes 11.1%:*
- *Recommended treatment of standards the same way as samples.*

Calibration curve. Absorbance vs. C concentration

Nr	1	2	3	4	5	6	7	8	9
ml Glucoze 4%	0	0.05	0.1	0.2	0.4	0.6	0.8	1	1.2
mg C/100 ml	0	0.8	1.6	3.2	6.4	9.6	12.8	16	19.2
Abs 586.5	0	0.017	0.033	0.062	0.122	0.166	0.221	0.274	0.334



Validation:

LOD and LOQ

Nr. of Blank Solution	1	2	3	4	5
Absorbance	0.003	0.002	0.005	0.003	0.003

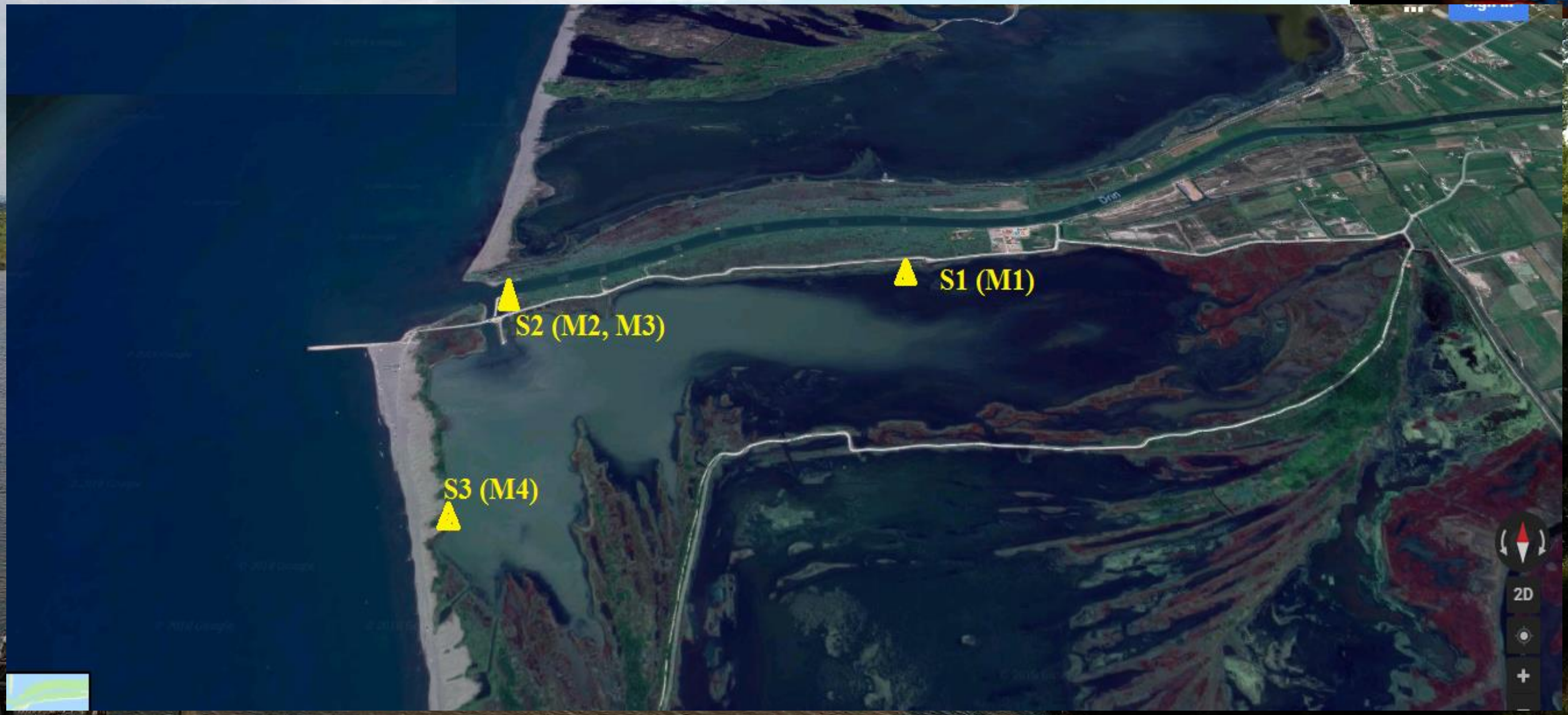
$$S_{LOD} = Aav + 3SD_A$$

$$S_{LOQ} = Aav + 10SD_A$$

A_{av}	Standard Deviation	S_{LOD}	S_{LOQ}	LOD mg C	LOQ mg
0.0032	0.0011	0.0065	0.014	0.10	0.55

SAMPLE ANALYSIS

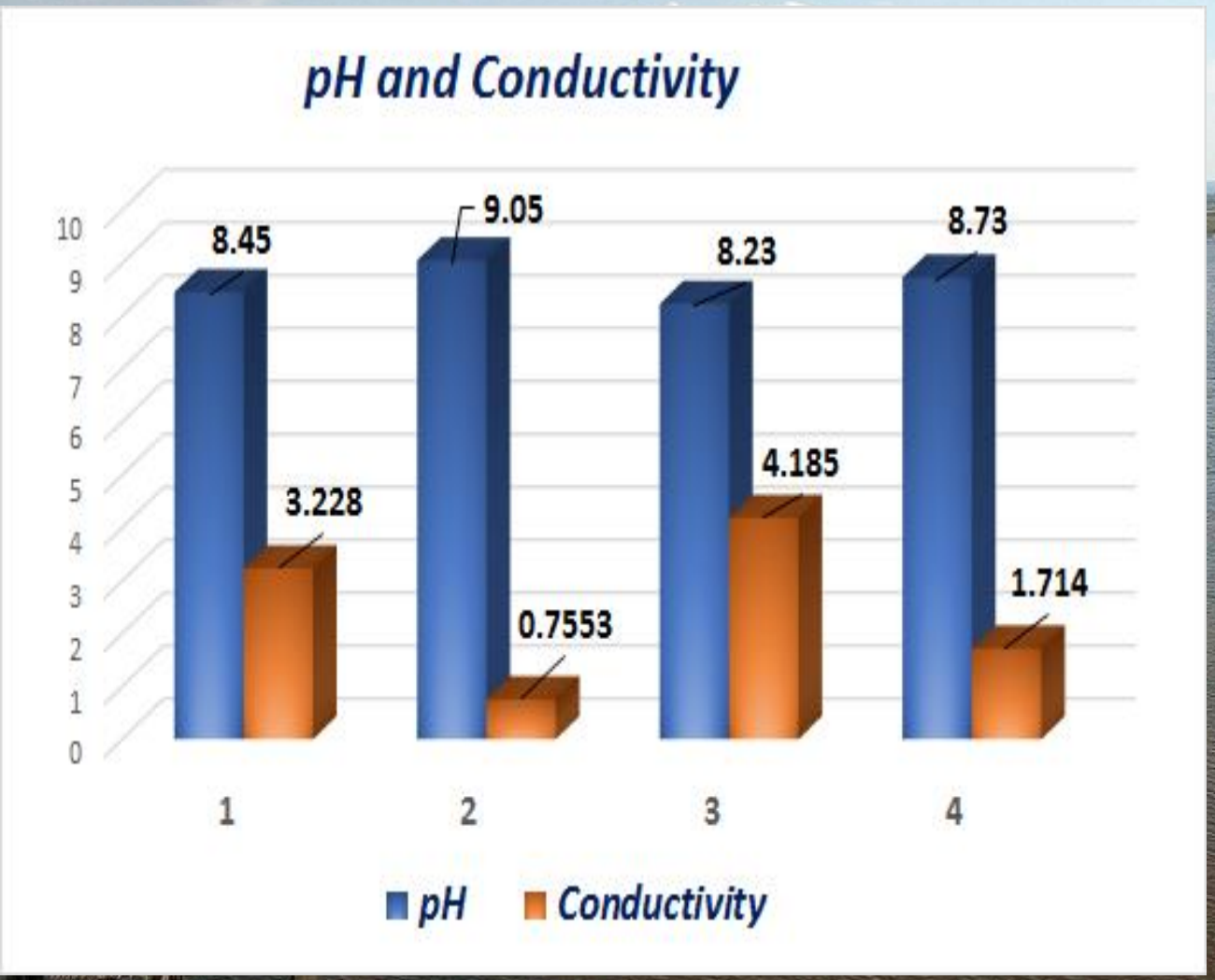
SAMPLING STATIONS

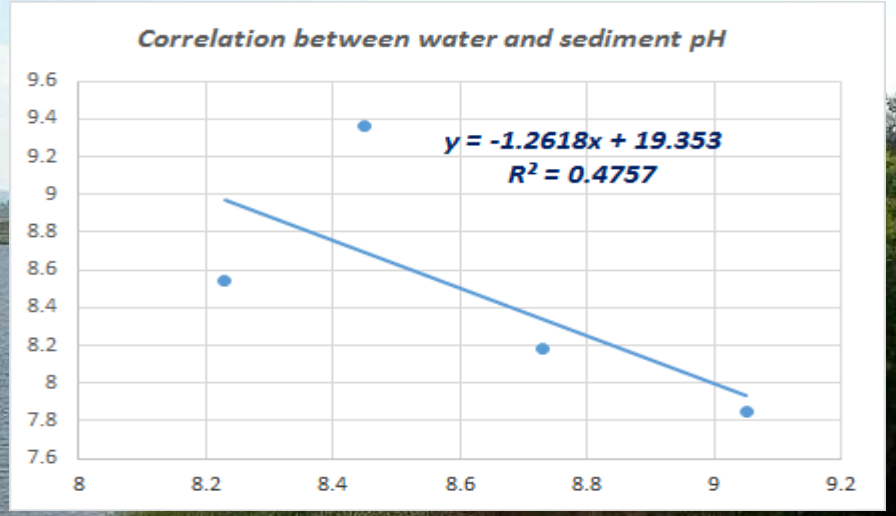


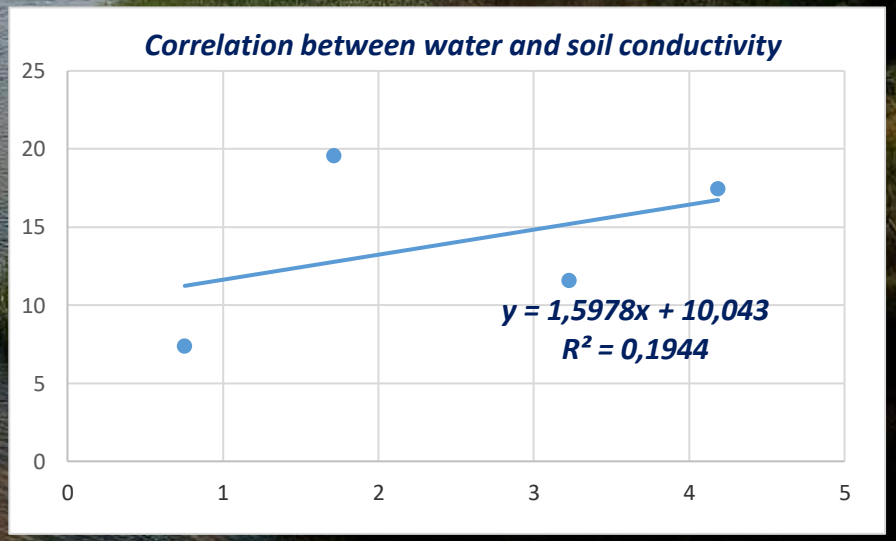
SAMPLE ANALYSIS

Sample pretreatment: EPA, 2014. Soil sampling procedure

Physic-Chemical parameters: ISO 10390:1994 and ISO 11265:1994



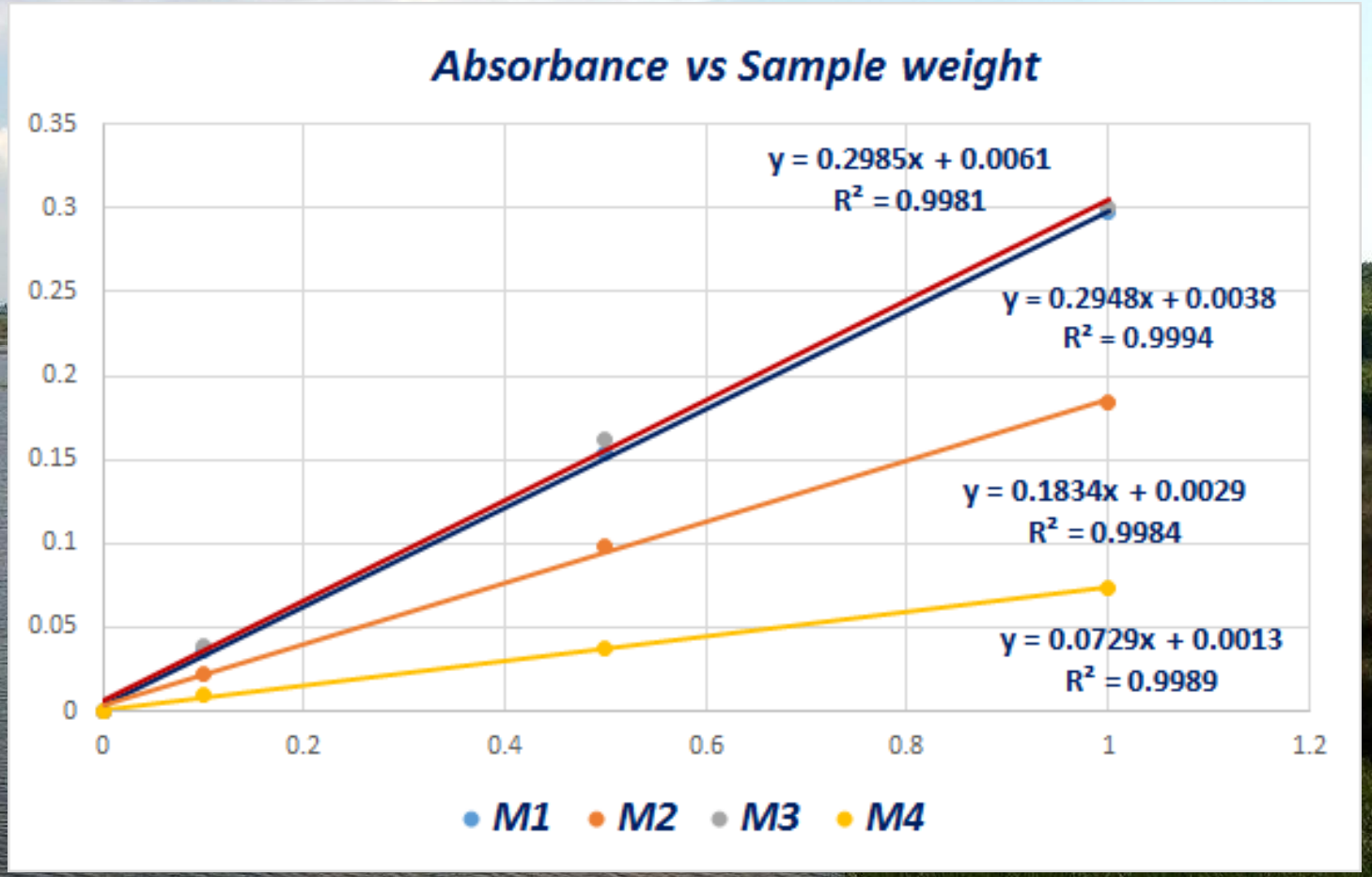




SAMPLE ANALYSIS

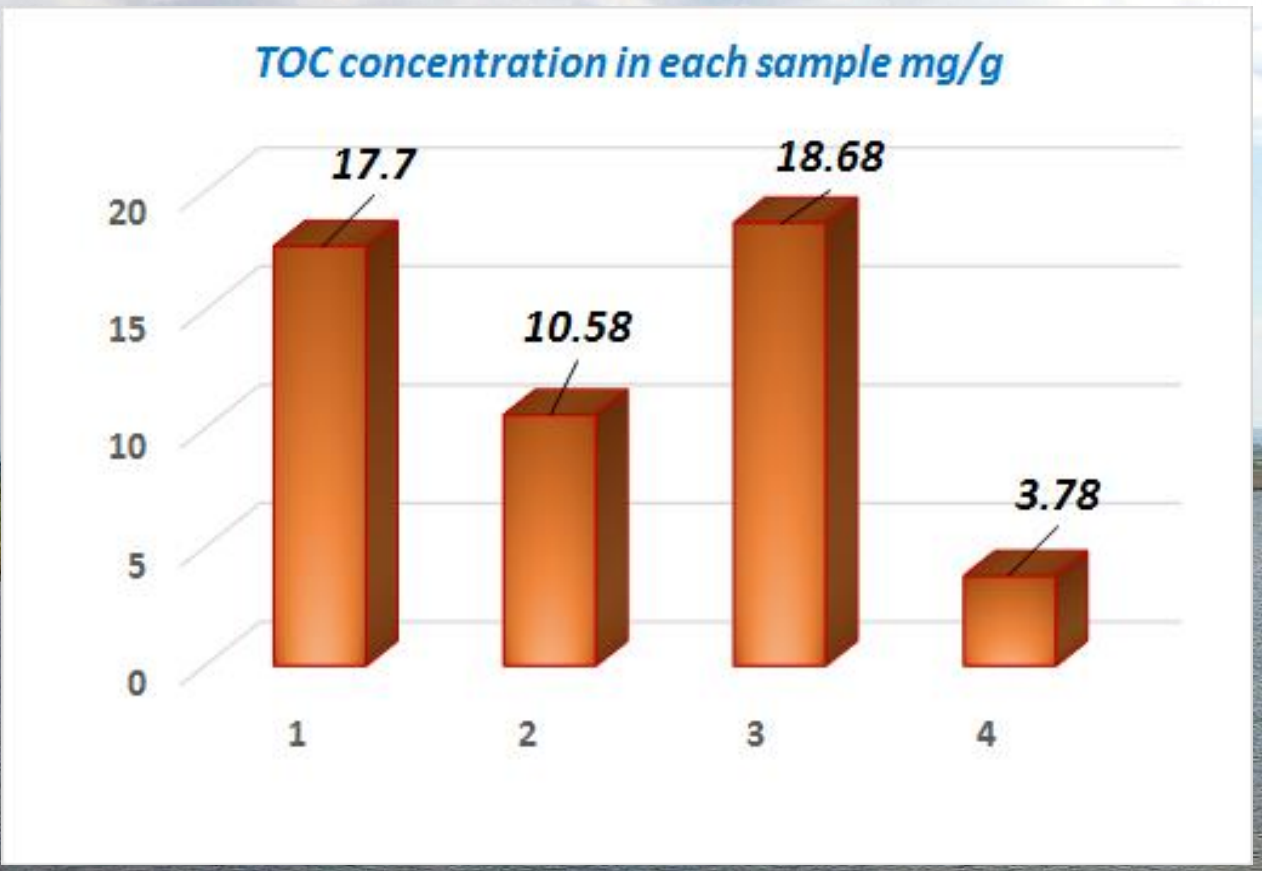
3 different portions from each sample treated – measured at 586.5

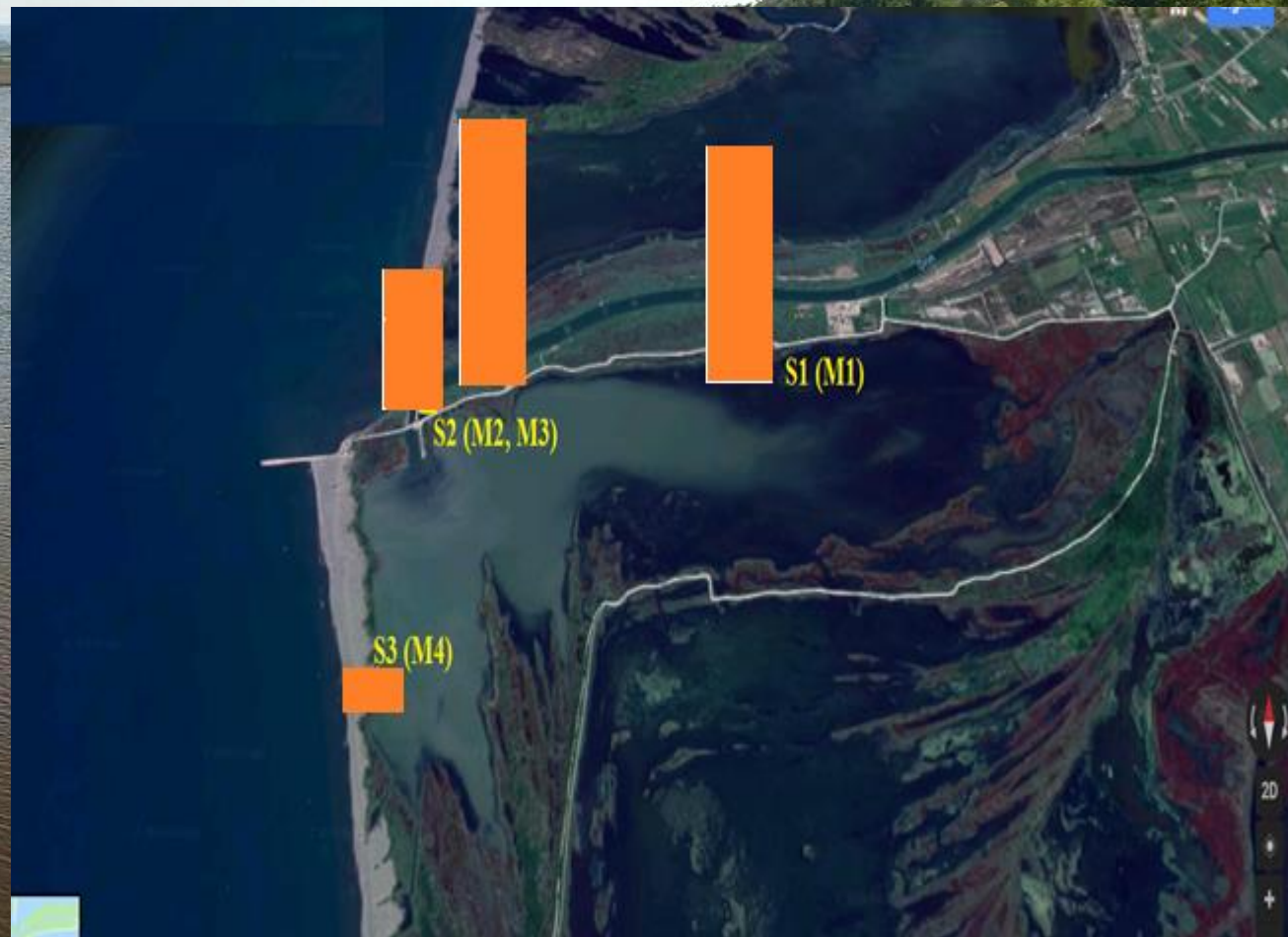
0.2; 0.5; 1.0 g



Good correlation, good repeatability, no matrix interferences

SAMPLE ANALYSIS





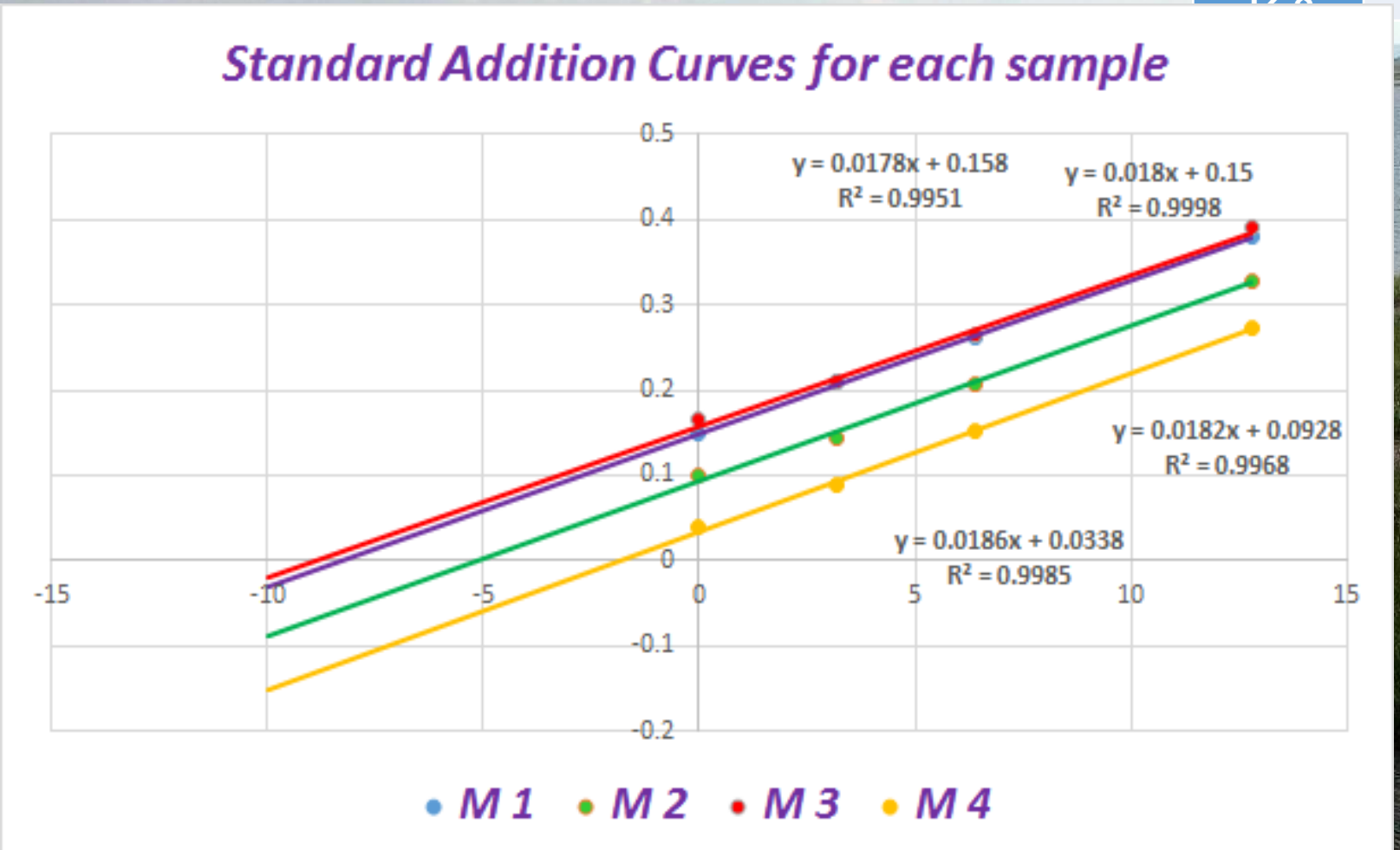
M1, M3 – Loamy , clay mostly

M2, M4 – Sandy sediment

SAMPLE ANALYSIS – METHOD OF STANDARD ADDITION

Sediment sample spiked with glucose solution.

Spike (mg C)	Sample (g)	A M1	A M2	A M3	A M4
0	0.5	0.150	0.099	0.165	0.038
3.2	0.5	0.209	0.145	0.210	0.088
6.4	0.5	0.263	0.206	0.265	0.152
12.8	0.5	0.381	0.329	0.390	0.273



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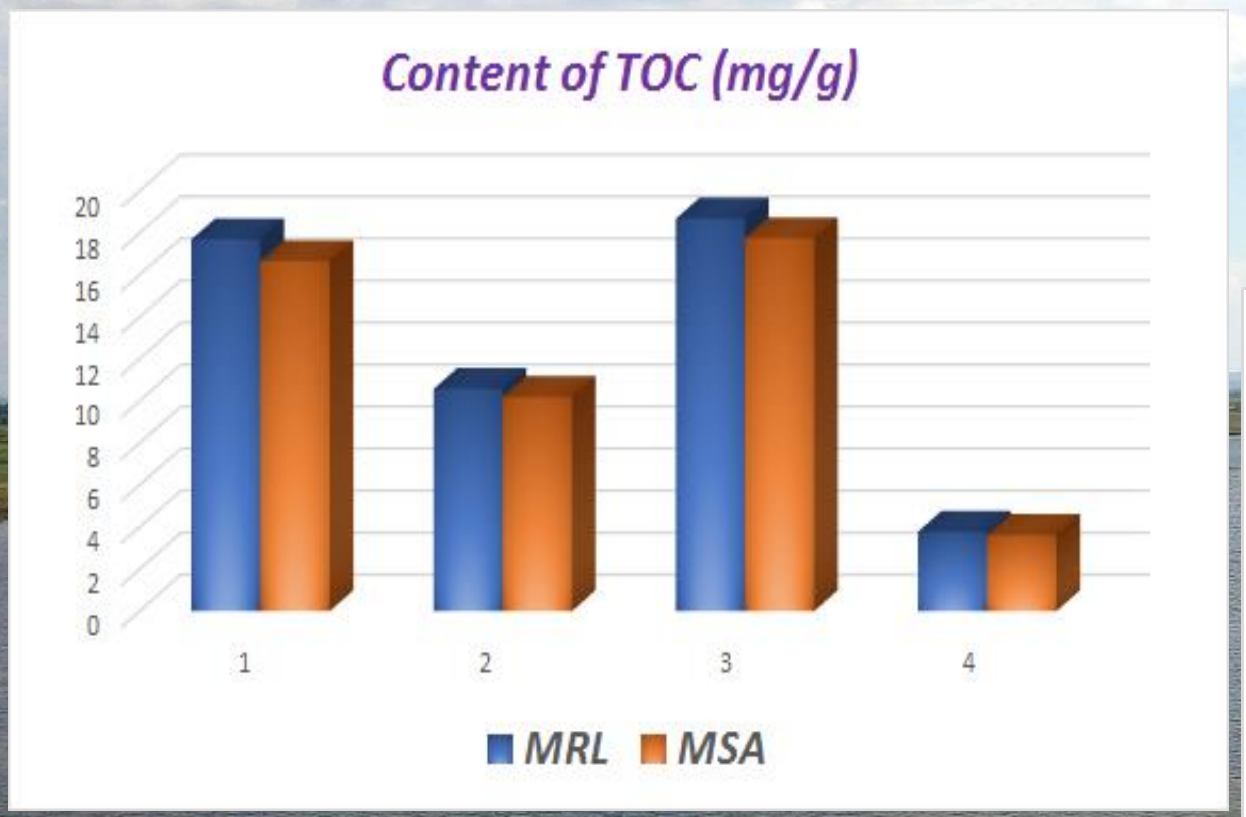
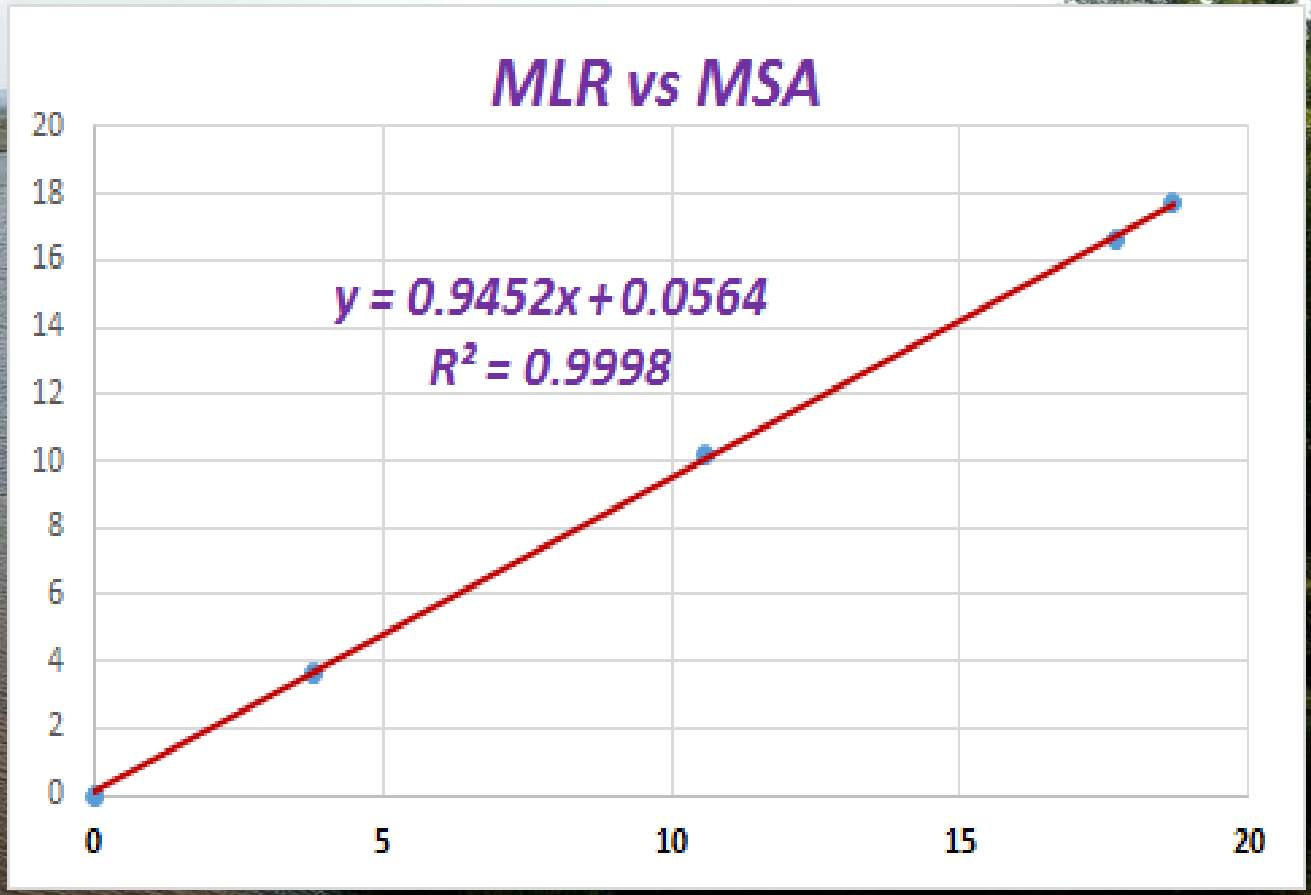
COMPARISON OF RESULTS





COMPARISON OF RESULTS

Student's Test

$$\pm t = (\bar{x} - \mu)\left(\frac{\sqrt{n}}{s}\right)$$

Sample	Result MLR mg/g	SD (MLR)	Result MSA mg/g	t_{exp}	$t_{krit\ (95\%,2)}$
M1	17.70	0.59	16.66	3.05	4.3
M2	10.58	0.48	10.20	1.37	4.3
M3	18.68	1.36	17.75	1.18	4.3
M4	3.78	0.32	3.63	0.81	4.3

No significant differences between results

CONCLUSIONS AND RECOMMANDATIONS

TOC can be determined successfully by using SF VIS method, after the sulfochromic

oxidation of sediment samples

Important:Standards should be treated the same way as the sediment samples

Method of linear regression gives accurate results, no significant differences compared to MSA

TOC content depends on the texture of the sediment: sandy sediments contain less OC than loamy sediments.

TOC content in deep sediments is higher than in the surface.

GOOD NEWS

THE CANNAL OF COMMUNICATION WITH SEA WAS OPENED LAST WEEK.

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THANK YOU

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