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Research Paper

Water quality assessment of Moro reservoir, Ilorin, Nigeria using organic carbon concentrations in surface water and sediment

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ABSTRACT

The purpose of this study was to use total organic carbon (TOC) and dissolved organic carbon (DOC) in water and sediment samples to assess the water quality of Moro reservoir, Ilorin, Nigeria. The study was conducted from August 2015 to February, 2016. TOC and DOC have a major influence on both the chemical and biological processes that take place in surface sediment and water. TOC and DOC concentrations in water and sediment samples were determined using TOC-VCSH method with ASI-V auto analyzer. All surface waters samples from the reservoir were characterized by increased organic substances concentration levels. TOC and DOC in water and sediment had significant correlation with each other respectively. TOC and DOC concentrations in water samples were in the range of 0.159 to 11.7680 and 0.088 to 10.898 gCl^{-1}, respectively, whereas TOC and DOC concentration in sediments varied between 3.78 to 43.9 and 2.56 to 30.22 $gCKg^{-1}$, respectively which was within range for pollution tolerant benthic macro-invertebrate. High organic carbon content of the reservoir was due to inputs of external organic carbon from run-off, internally produced organic carbon from aquatic organisms' remains and the impoundment itself which allows for accumulation of carbon from the trapping of particles and alteration of flow regime. More than 80% of TOC in sediment samples from the reservoir were above threshold value >10 $gCKg^{-1}$ making profundal sediment azoic; this was due to contaminant associated with organic carbon concentrations and physiological stress factors. From the results it is concluded that the reservoir water is highly polluted and should be managed for human welfare and sustainable use for domestic water supply.

Keywords: Organic carbon, water quality, contaminants, profundal sediment, Moro reservoir.

INTRODUCTION

Improving and protecting water quality, both for human needs and to sustain aquatic ecosystems emerged as a major global challenge in the 20th and 21st centuries. Water quality impairment is a multivariate problem with multiple causes and consequences (Ormerod et al., 2010). Yet, management and restoration efforts often focus on one or a few variables from a limited set that typically includes nitrogen, phosphorus, sediment and habitat structure or flow.

Changing the load or concentration of organic carbon (OC) in lakes and rivers rarely motivates management activities. Exceptions include policies and activities intended to reduce organic matter loading from sewage effluents, prevent manure (organic fertilizer) inputs during periods of intense run-off, increase carbon sequestration or minimize costs associated with dissolved organic carbon

(DOC) removal from drinking water sources. Notably, only two of these cases (point source control and preventing manure spills) involve a goal of improved lake 'health' or 'integrity'. Thus, for management activities that intend to improve or maintain lake status, carbon at best take a back seat to other priorities. Water naturally contains dissolved substances, non-dissolved particulate matter and living organisms; indeed, such materials and organisms are necessary components of good quality water, as they help maintain vital biogeochemical cycles.

Organic matter plays a major role in the aquatic system. It affects biogeochemical processes, nutrient cycling, biological availability, chemical transport and interactions. Organic material can originate from various sources. Organic carbon in aquatic ecosystems is a key indicator of how the catchment functions in terms of biogeochemical nutrient and energy cycling (Fisher et al., 1973; Mulholland, 1997).

Organic matter in aquatic ecosystems ranges from dissolved organic compounds to large aggregates of particulate organic matter. Most of the organic matter, whether dissolved or particulate is detritus (that is, organic matter from dead organisms). Metabolism of the organic matter and interactions of this material chemically and biologically are to a significant extent, governed by the size and chemical composition of the organic matter.

Organic matter content is typically measured as total organic carbon (TOC) and dissolved organic carbon (DOC), which are fundamental components of the carbon cycle. Organic matter in water consists of thousands of components, including macroscopic particles, colloids, dissolved macromolecules and specific compounds. Total organic carbon has a major influence on both the chemical and biological processes that take place in sediments.

Organic material can be responsible for water taste, odor and color. Total organic carbon (TOC) content in sediments has been used as an indicator of pollution and eutrophication rate (Folger, 1972; EPA, 2002). The degradability of organic carbon is not only important for the "health" of the reservoir (Grøn et al., 1992), but also for the water supply systems (DEPA, 2002).

Organic compounds also lead to the formation of disinfection by- products (DBPs) after reacting with disinfectants (such as chlorine) during water treatment. Organic matter can be related to bacterial proliferation within distribution systems. Therefore, the control of organic matter has been recognized as an important part of the operation of drinking water plants and distribution systems.

Lakes are great in numbers (Downing et al., 2006) and hold a substantial amount of carbon in the water (Sobek et al., 2007) as well as in the sediment (Kortelainen et al., 2004). The carbon entering a lake with incoming water represents a size continuum of molecules, colloids and particles. Most of the organic carbon of natural waters consists of dissolved organic carbon (DOC) constituting 90 to 95% of the TOC (total organic carbon) (Wetzel, 2001; Kortelainen et al., 2006) and matter comprise the major part of DOC in lakes (Thurman, 1985; Münster and de Haan, 1998).

The objective of this research is to evaluate the total organic carbon (TOC) and dissolved organic carbon (DOC) in surface water and sediment of Moro reservoir, Ilorin, Nigeria in order to use them in assessing the water quality of the reservoir for domestic use.

MATERIALS AND METHODS

Description of the study area

Moro reservoir is a man-made reservoir constructed on Moro River in 1992. It is situated at Sobi Army Barracks, 10 km North of Ilorin township Kwara State, Nigeria on longitude 9°11'E and latitude 8°25N. The reservoir is the second largest in Kwara State, Nigeria with surface area of 296×10^6 m^2 and volume of 636×10^6 m^3. It has length of 80 m, breadth and depth of 26 and 6.5 m respectively. The reservoir was constructed primarily for supply of water to soldiers in the barracks to Shao township and some part of Ilorin metropolis. An estimated population of about 100,000 people uses the water and its resources for domestic water supply, fisheries production, irrigation, recreation and other municipal uses. The Moro reservoir is highly influenced by seasonal variation with high volume of water in wet season and low volume in dry season due to high evaporation rate (Mustapha, 2008). Figure 1 shows a sketch map of Moro reservoir.

Sampling

Surface water and sediment samples were taken twice monthly for seven months in spanning dry and rainy seasons between August 2015 and February, 2016. Sampling was done from three stations in the reservoir. The first station designated as station 1 is the upstream section of the dam about 50 m away from the dam site. The second station designated as station 2, is the dam site itself, while the third station designated as station 3 was downstream section of the dam about 25 m away from the dam site. Sediment samples were collected using Ekman grab sampler from the surface sediment while surface water samples were collected in sampling of 50 ml volume.

Methods

Water and sediment samples were collected from the subsurface with no air bubbles, directly to dark glass vessels. They were stored at +4°C. TOC and DOC determination in water and sediment samples were

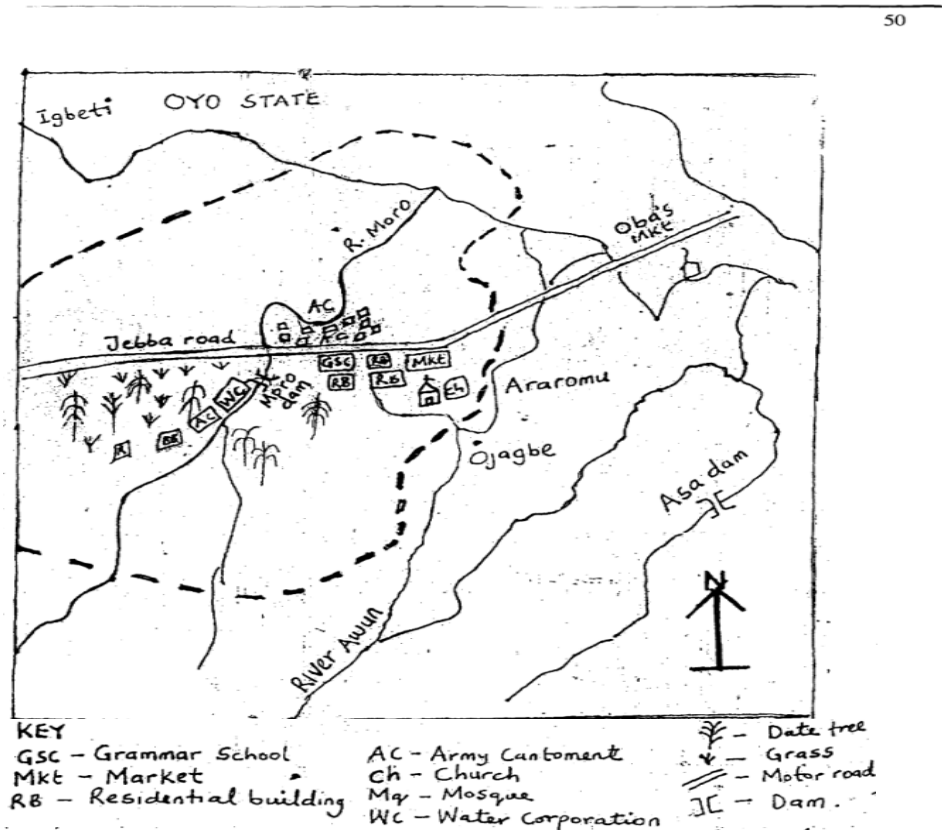


Figure 1: A sketch map of Moro reservoir. Scale: 1: 100,000.

performed using the Shimadzu TOC-VCSH with ASI-V auto analyzer. TOC and DOC content in water samples were determined according to the Polish Standard (PN-C, 1994).

Treatment for water samples

Oxidation of organic carbon in water to carbon dioxide by combustion through the addition of an appropriate oxidant and by UV-radiation was carried out. The carbon dioxide formed was determined by infrared detector. Inorganic carbon was removed by acidification and purging.

Procedure to determine DOC and TOC in water samples

A filtered and acidified water sample was sparged with oxygen to remove inorganic carbon. The water was then injected onto a combustion column packed with platinum-coated alumina beads held at 680°C. Non-purgeable organic carbon compounds were combusted and converted to CO_2, which was detected by a non- dispersive infrared detector (NDIR). DOC was determined after filtrating water samples through a filter paper with pore diameter of 0.45 µm.

For TOC in water sample, 10 ml of the water sample was measured into a 250 ml volume conical flask and 10 ml of 1N $K_2Cr_2O_7$ (1 normal Pottasium dichromate solution) was added to it and gently 20 ml of concentrated H_2SO_4 was also added.

The mixture was allowed to stay for about an hour for the temperature to cool down and further made up to 100 ml using distilled water. 3 drops of ferroin indicator (1,10-phenanthroline mono-hydrate solution) was added and the mixture titrated against Fe_2SO_4 (Ferrous sulphate solution). A change of colour from yellow/Orange through green to maroon brown which is the end point was observed. Titre value was recorded and a blank prepared in the same way for the samples to serve as standard. From the titre value, % T.O.C was calculated.

Treatment for sediment samples

The total organic carbon (TOC) was obtained by the difference between the results of the measurements of total carbon (TC) and total inorganic carbon (TIC). TC was converted to carbon dioxide by combustion in an oxygen-containing gas flow free of carbon dioxide. The released amount of carbon dioxide was measured by infrared detector. High temperature combustion method utilizing a Wheatstone bridge current differential was used. TOC and DOC content in sediments was determined in accordance

Table 1: Organic carbon concentration in surface water across stations In Moro reservior.

S/N (gC/L)	Date	S1		S2		S3	
		TO0043	DOC	TOC	DOC	TOC	DOC
1	3rd August	1.459	1.190	0.640	0.410	0.570	0.360
2	17th August	2.470	1.997	1.171	0.954	1.019	0.848
3	31st August	2.947	2.529	1.587	1.124	1.315	0.789
4	14th September	5.981	4.772	3.091	2.011	2.051	1.471
5	28th September	4.966	3.170	2.674	1.710	1.910	1.220
6	12th October	8.219	6.989	5.121	3.099	2.010	1.951
7	26th October	6.599	6.010	7.579	6.909	1.477	0.989
8	10th November	5.070	3.640	9.980	6.370	1.780	1.140
9	24th November	4.610	3.951	10.414	8.968	1.219	1.019
10	7th December	4.090	3.581	9.789	7.988	0.887	0.615
11	21st December	2.813	1.799	11.768	10.898	0.721	0.463
12	7th January	2.149	1.854	11.013	10.415	0.561	0.411
13	21st January	1.717	1.012	6.481	5.321	0.321	0.256
14	6th February	0.952	0.466	3.101	2.902	0.159	0.088

TOC: Total organic carbon, **DOC:** Dissolved organic carbon, **S1:** Station 1- upstream, **S2:** Station 2- mid stream and **S3:** Station 3- downstream.

with the instruction for the Shimadzu TOC-VCSH analyzer.

Procedure to determine DOC and TOC in sediment samples

Samples were received in the frozen state and allowed to thaw at room temperature. Source samples were gently stirred and sub-samples removed with a stainless steel spatula and placed in labeled 20 ml polyethylene scintillation vials. Approximately, 5 g equivalent dry weight of the wet sample was sub-sampled.

Sub-samples were treated with two, 5 ml additions of 0.5 N reagent grade HCl to remove inorganic carbon (CO^{-3}), agitated and centrifuged to a clear supernate. Some samples were retreated with HCl to remove residual inorganic carbon. After HCl treatment and decanting, samples were washed with approximately 15 ml of deionized-distilled water, agitated, centrifuged to a clear supernate and decanted. Prepared samples were placed in a 60°C convection oven and allowed to come to complete dryness (approximately 48 h). Visual inspection of the dried sample before homogenization was used to ensure complete removal of carbonate containing materials (shell fragments). Two 61 mm (1/4") stainless steel solid balls were added to the dried sample, capped and agitated in a commercially available ball mill for three minutes to homogenize the dried sample.

Statistical data analysis

The TOC and DOC data obtained was correlated for sediment and water samples in order for Moro to determine significant correlation ($p<0.05$). SPSS v17 Pearson linear correlation test was used for the statistical analysis.

RESULTS

Table 1 shows the organic carbon concentration in surface water across the three stations in Moro reservoir. Highest TOC concentrations recorded were 8.219, 11.768 and 1.78 gCl^{-1} in S1, S2 and S3 on the following dates 12th October, 2015; 21st December, 2015 and 10th November, 2015 respectively. It was same for DOC as 6.989, 10.898 and 1.95 gCl^{-1} except for S3 in which 1.95 gCl^{-1} was recorded on 12th October, 2015. Lowest TOC concentrations of 0.952, 0.64 and 0.159 gCl^{-1} were recorded for S1, S2 and S3 on the following dates 6th February, 2016; 3rd August, 2015 and 6th February, 2016. It was the same for DOC which had 0.466, 0.41 and 0.088 $gC1^{-1}$ for S1, S2 and S3 respectively. Overall range for TOC across stations was 0.159 to 11.768 gCl^{-1}. This also corresponds with DOC across station which range from 0.088 to 10.898 gCl^{-1}

Figure 2 shows the fortnight variation in TOC concentration in water for each station. The highest TOC concentration was 11.768 gCl^{-1} obtained 21st December, 2015 at station 2 and lowest concentration was 0.159 gCl^{-1} obtained 6th February, 2016 at station 3.

Figure 3 shows the fortnight variation in DOC concentration in water for each station. The highest DOC concentration was 10.898 gCl^{-1} obtained 21st December, 2015 at station 2 and lowest concentration was 0.088 gCl^{-1} obtained 6th February, 2016 at station 3.

Table 2 shows the organic carbon concentration in surface sediment across the three stations in Moro

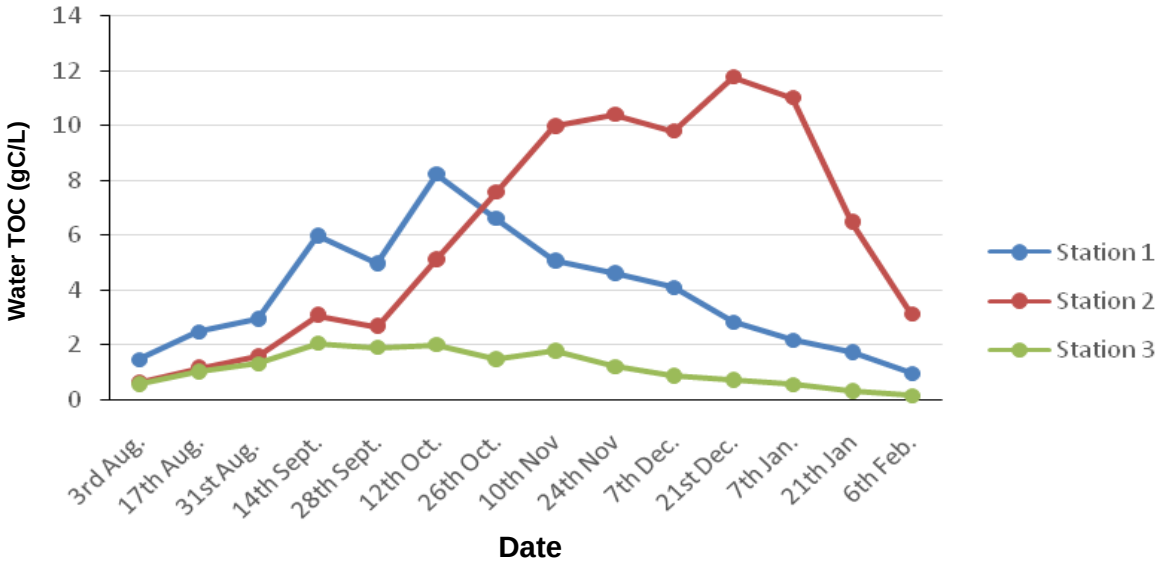


Figure 2: Fortnight variations in TOC concentration in water of each station.

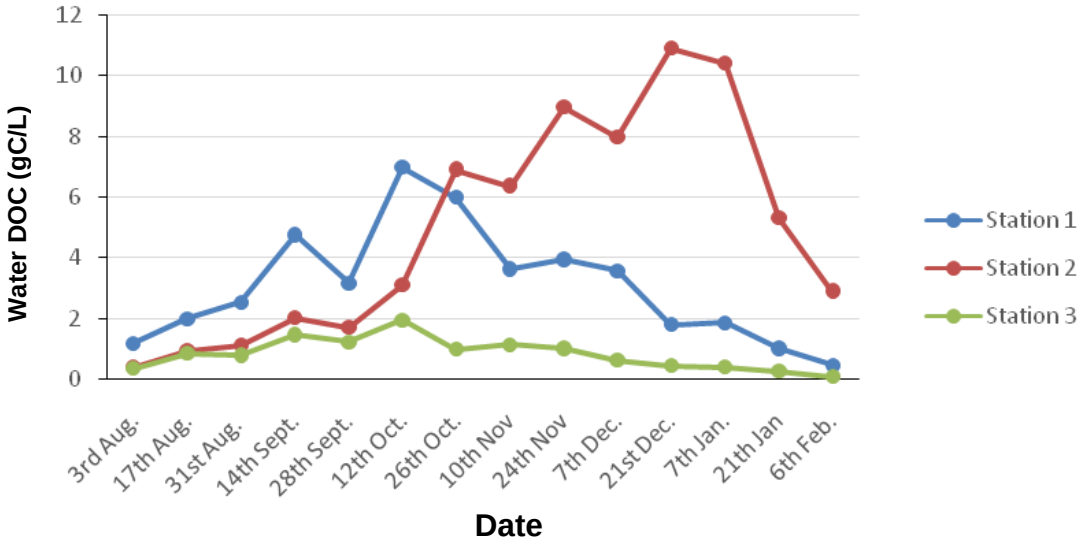


Figure 3: Fortnight variations in DOC concentration in water of each station.

Table 2: Organic carbon concentration in surface sediment across stations in Moro reservoir.

S/N (gC/kg)	Date	S1		S2		S3	
		TOC	DOC	TOC	DOC	TOC	DOC
1	3rd August	30.29	19.33	13.17	8.41	27.66	17.65
2	17th August	37.01	22.86	16.77	11.56	32.99	23.07
3	31st August	41.69	28.51	19.86	15.44	38.16	27.56
4	14th September	43.90	30.22	24.29	18.85	25.81	17.63
5	28th September	31.324	19.99	30.942	19.75	15.28	9.75
6	12th October	25.449	14.09	31.02	17.11	19.69	12.88

TOC: total organic carbon, **DOC:** dissolved organic carbon, **S1:** station 1- upstream, **S2:** station 2- mid stream and **S3:** station 3- downstream.

Table 2 Contd: Organic carbon concentration in surface sediment across stations in Moro reservoir.

S/N (gC/kg)	Date	S1		S2		S3	
		TOC	DOC	TOC	DOC	TOC	DOC
7	26th October	21.67	9.89	30.99	19.68	17.59	11.17
8	10th November	7.84	5.03	32.07	20.47	24.94	15.92
9	24th November	5.97	4.01	35.61	20.11	27.02	21.90
10	7th December	5.02	3.95	34.28	19.62	25.28	19.59
11	21st December	7.99	4.89	33.01	26.55	18.28	9.63
12	7th January	4.68	2.79	30.66	21.82	23.97	14.79
13	21st January	3.78	2.56	29.68	26.17	15.39	9.41
14	6th February	4.41	2.99	21.17	18.89	11.61	8.64

TOC: total organic carbon, **DOC:** dissolved organic carbon, **S1:** station 1- upstream, **S2:** station 2- mid stream and **S3:** station 3- downstream.

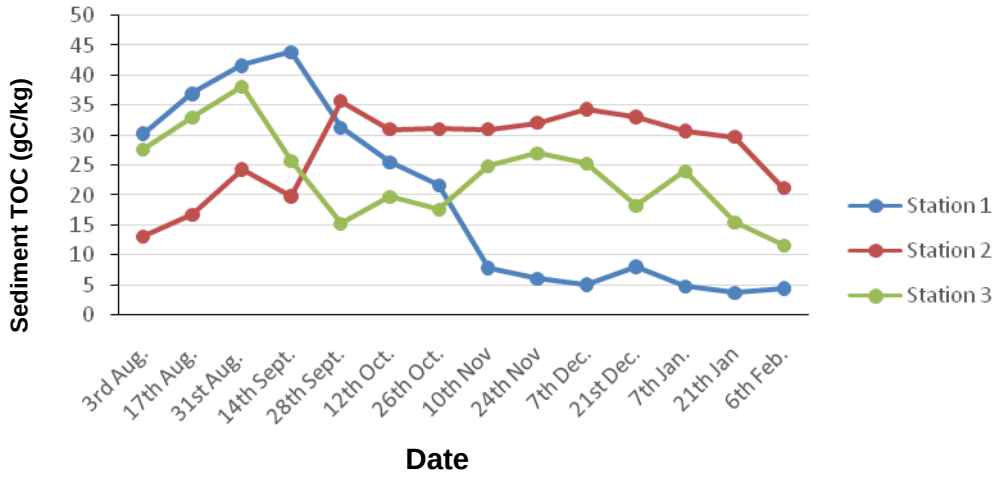


Figure 4: Fortnight variations in TOC concentration in sediment of each station.

reservoir. Highest TOC concentrations of 43.9, 35.61 and 38.16 gCKg^{-1} were recorded S1, S2 and S3 on the following dates14th September, 2015; 24th November, 2015 and 31st August, 2015. It is same for DOC which as 30.22, 26.55 and 27.56 gCKg^{-1} was recorded in S1, S2 and S3 on same dates as earlier mentioned except for S2 in which 26.55 gCKg^{-1} was recorded on 12th December, 2015. Lowest TOC of 3.78, 1317 and 11.61 gCKg^{-1} were measured for S1, S2 and S3 on the following dates 21st January, 2016; 3rd August, 2015 and 6th February, 2016 respectively. It was same for DOC which had 2.56, 8.41 and 8.64 gCkg^{-1} measured in S1, S2 and S3. Overall range for TOC across stations was 3.78 to 43.9 gCKg^{-1} while DOC ranged between 2.56 to 30.22 gCKg^{-1}.

Figure 4 shows the fortnight variation in TOC concentration in sediment for each station. The highest TOC concentration was 43.90 gCKg^{-1} obtained 14th September, 2015 at station 1 and lowest concentration was 3.78 gCKg^{-1} obtained 21st January, 2016 at station 1.

Figure 5 shows the fortnight variation in DOC concentration in sediment for each station. The highest DOC concentration was 30.22 gCKg^{-1} obtained 14th September, 2015 at station 1 and lowest concentration was 2.56 gCKg^{-1} obtained 21st January, 2016 at station 1.

Figure 6 shows a cross plot for DOC and TOC sediment samples collected in all stations. The range of values is much smaller but also the two parameters are much more closely correlated (R^2=0.9085). Figure 7 shows a cross plot for DOC and TOC water samples collected in all stations. Table 3 shows the correlation matrix across TOC and DOC in both sediment and water.

DISCUSSION

TOC and DOC concentration in Moro reservoir surface water

The location of S1 in the reservoir is prone to run-off which makes high TOC and DOC concentrations to be recorded in the wet season. Highest concentrations of 11.768 and

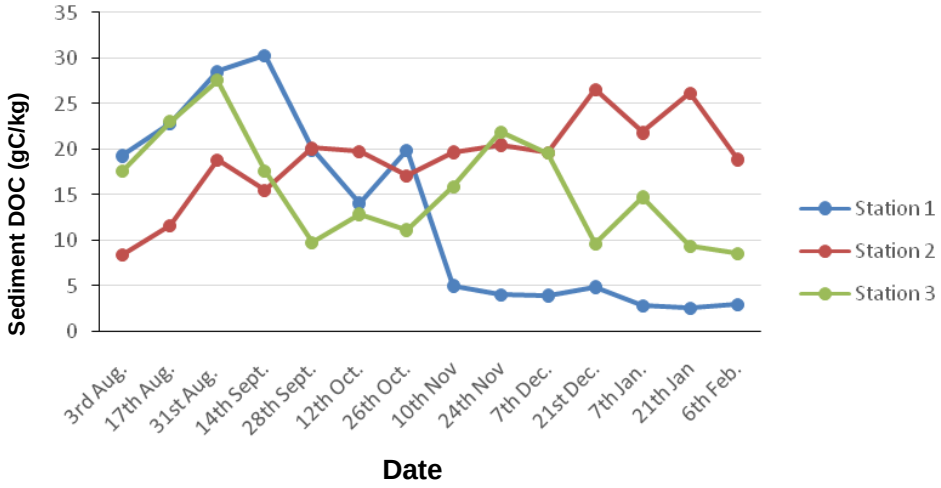


Figure 5: Fortnight variations in DOC concentration in sediment of each station.

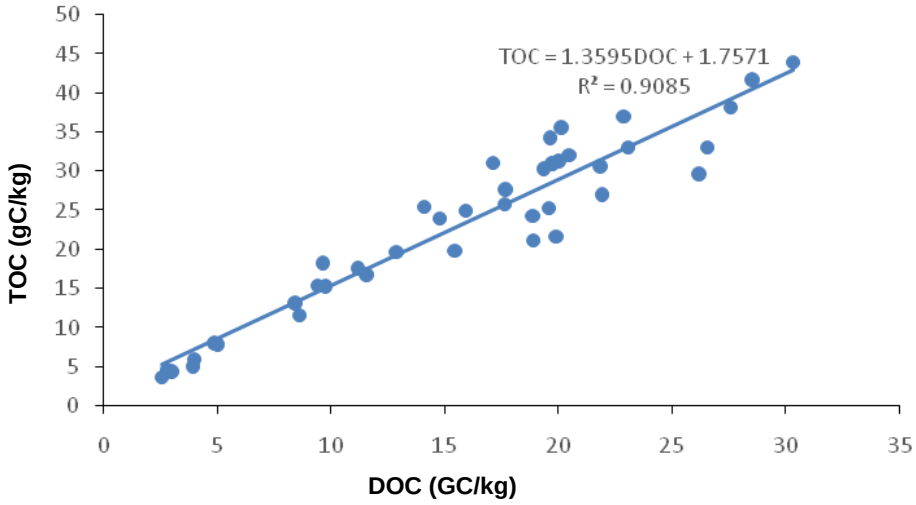


Figure 6: Cross plot TOC and DOC in sediment samples from all stations.

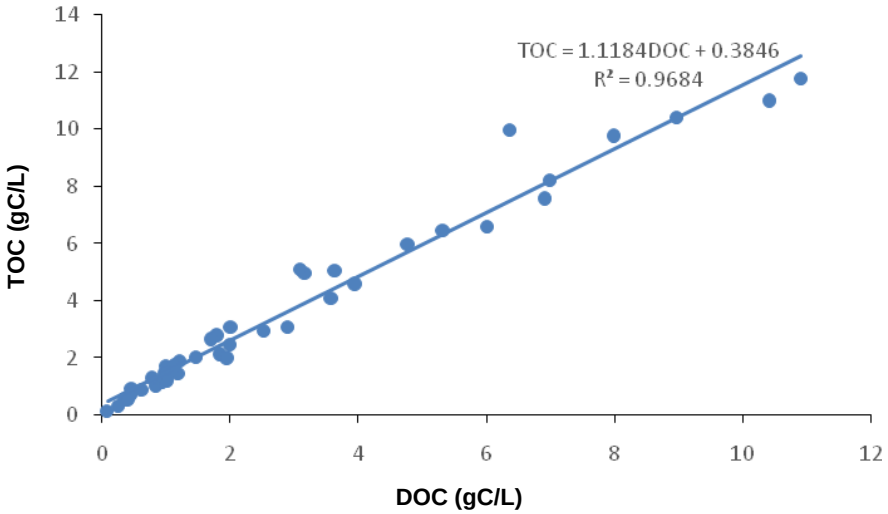


Figure 7: Cross plot TOC and DOC in water samples from all stations.

Table 3: Correlation matrix of TOC and DOC in surface water and sediment of Moro reservoir.

Variable	sedTOC	sedDOC	watTOC	watDOC
SedTOC	1			
sedDOC	0.909**	1		
watTOC	0.357*	0.350*	1	
watDOC	0.344*	0.353*	0.968**	1

Correlation is significant at the 0.01 level (2-tailed) and *Correlation is significant at the 0.05 level (2-tailed). **sedTOC: Sediment TOC concentration, **sedDOC:** Sediment DOC concentration, **watTOC:** Water TOC concentration and **watDOC:** Water DOC concentration.

10.898 gCl^{-1} recorded for TOC and DOC at S2 which is the impoundment sites was due to the impoundment accumulations of carbon in sediment through its trapping of particles. This occurs in the dry season when factors that facilitate current were prominent such as wind. S3 has the lowest TOC and DOC concentrations of 0.159 and 0.088 gCl^{-1} because the location was not prone to organic carbon loading through run-off and current. The little organic carbon (OC) from impoundment spills was due to mineralization for degradable OC while recalcitrant OC were for sedimentation making the S3 reservoir floor rocky. S3 TOC and DOC concentrations increased in the wet season and decreased in the dry season.

TOC and DOC concentration in Moro reservoir surface sediment

Highest TOC and DOC concentration was recorded for S1 as 43.9 and 30.22 $gCKg^{-1}$ in September, 2015. The sharp drop of TOC and DOC in dry season was due to low precipitation leading to low organic carbon loading at S1. TOC and DOC concentration in S2 was regular and steady throughout the study period. Little alteration observed at S2 sediment was due to absence of factors that could cause significant changes. S2 location was not prone to run-offs like S1, therefore, sedimentation, flocculation, coagulation, mineralization, bioturbation, current and bioaccumulation that aids the OC in sediment was therefore stable. There was no much discrepancy in sediment OC at S2 across seasons. TOC and DOC concentration in S3 was stable and regular across the season. Sediment in the station was not prone to organic carbon loading due to its location. Settling of particles for sedimentation and diagenesis occurs at high rate in the station due to little or no disturbance except for bioturbation which are always insignificant.

Figure 3 shows a direct comparison made between DOC and TOC sediment samples collected in the Moro reservoir indicating a very strong positive correlation between the two parameters (R^2=0.909) with TOC generally higher in concentration than DOC, suggesting little POC. Therefore, flocculation and coagulation of DOC from water column to particles would occur and will be due for sedimentation and digenesis. Complexes of contaminants and toxic metals such as aluminum, zinc, copper and mercury soon will be formed due to high content of DOC in the sediment with a reactive complexing agent.

The range of values is much smaller but also the two parameters are much more closely correlated and a very strong positive correlation was observed between the two parameter (R^2=0.968) with TOC generally higher in concentration than DOC, suggesting little POC in the surface water. DOC constituted over 80% of TOC in surface water from data obtained in the study, therefore, flocculation of DOC to POC would take place increasing sedimentation of particles allowing microbes prolification. Correlation of water TOC and sediment TOC; water TOC and sediment DOC; water DOC and sediment TOC and water DOC and sediment DOC in Table 3 are fairly weak and positively correlated between the two parameters.

All water samples from the Moro reservoir can be qualified as those loaded with organic substances exceeding standards for Polish and German legislation. The waters can be classified as Class V of each of the legislations, which are in the ranges of (20 to 40) $mgCl^{-1}$. This makes the water unhygienic for drinking and some domestic use directly. Due to high organic carbon content of the water which ranged between 0.088 to 11.768 gCl^{-1}; there could be high microbial activity mineralizing the degradable organic carbon thus releasing green house gases GHG from the reservoir. There could be microbial bloom in the water and the water susceptible to depleted dissolved oxygen. Mustapha and Omotosho (2005) revealed dissolved oxygen of the reservoir to range between 3.2 to 5.2 mgl^{-1} which is low for normal fish life and carbon dioxide to range between 2.0 to 4.6 mgl^{-1} which is high indicating high organic carbon loading capable of releasing GHG. Mineralization will also be occurring in the surface water as a result of exposure to ultraviolet ray.

DOC concentrations in Moro reservoir water makes about over 70% of TOC. The DOC determines the reservoir water taste, odour and colour. The high DOC concentration in water will alter thermal structure, mixing depth and photic zone range and therefore, impedes photosynthesis (Fee et al., 1996; Del Giorgio, 1994). This high DOC increases attenuation of solar radiation, that is, increases attenuation of photosynthetically active radiation, which reduces primary productivity (Christensen et al., 1996). DOC reacts

with oxidizing disinfectants to reduce their effectiveness implying high cost in the purification of the reservoir water before use.

Sediment samples of Moro reservoir are mainly in the range 10 to 40 $gCKg^{-1}$ which falls in the intermediate and high impact according to United States Environment Protection Agency (EPA, 2002). They are above the threshold value >10 $gCKg^{-1}$. It was only at S1 in the dry season when TOC concentration in sediment was of low impact <10 $gCKg^{-1}$. This was due to low run-offs and high current re-establishing settled OC in sediment to column and surface water. The TOC high concentration in sediment will allow contaminant availability, environmental and physiological stress factors such as dissolved oxygen depletion, ammonia, sulphides and metal transport by organic matter. This kind of transport and molecular mass distribution of associated metals to organic matter are closely connected with the size of the organic material (Patel et al., 1999; Hyland et al., 2000). All of which will impact negatively on the water quality. The profundal sediments in S1 and S2 were black and muddy while S3 was brown with pebbles: therefore, TOC concentration in S3 was generally low compared to S1 and S3.

Measures to reduce high organic carbon content in surface sediment and water of Moro reservoir

An effective organic matter control relies upon a good understanding of the origin, occurrence and fluctuation of the organic matter in source water and sediment. Reductions in organic carbon content in sediment and water could be achieved through:

- By diluting sediment with clean sand (Clark et al., 1986; Clark et al., 1987; Tatem, 1986; Knezovich and Harrison, 1988). However, this can change sediment characteristics resulting in non-linear responses in toxicity (Nelson et al., 1993).
- Combustion has also been used to remove fractions of organic carbon (Adams et al., 1985; IJC, 1988). However, this method results in substantial modification of the sediment characteristics, including oxidization of some inorganic components.

A variety of treatment processes can be used to control organic matter in water. Removal of organic carbon varies widely and generally between 10 and 90% (Edzwald, 1994). In general, organic carbon levels are reduced after settling, adsorption, granular activated carbon (GAC) filtration or membrane processes.

The degree of organic carbon removal depends on several parameters such as the quality and quantity of organic materials in the source water, the treatment train design and operational conditions.

Reducing the level of organic carbon during treatment may be an effective approach to improving water aesthetic, controlling bacterial water quality without the use of excessive levels of disinfectants or the formation of disinfectant by-products and reducing cancer risk.

Conclusion

In accordance with polish and German legislation, all tested water samples from the Moro reservoir can be qualified as those loaded with organic substances exceeding the standards. While in accordance to United States Environmental Protection Agency over 80% of sediment TOC concentrations from Moro reservoir are above threshold. Higher TOC concentrations in the reservoir in comparison with other bigger European rivers indicate that the majority of pollutants are from run-offs and human activities. Dissolved Organic Carbon (DOC) constituted the main fraction 70% of TOC in analyzed water and sediment samples. Therefore, the order for the reservoir to meet up the water quality standards for its intended purpose, the high DOC and TOC in the reservoir should be reduced.

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