

David Publishing Company www.davidpublisher.com ISSN 2162-5263 (Print) ISSN 2162-5271 (Online) DOI:10.17265/2162-5263

## Journal of Environmental Science and Engineering B

Volume 7, Number 1, January 2018



From Knowledge to Wisdom

#### **Publication Information:**

*Journal of Environmental Science and Engineering B* (formerly parts of Journal of Environmental Science and Engineering ISSN 1934-8932, USA) is published monthly in hard copy (ISSN 2162-5263) and online (ISSN 2162-5271) by David Publishing Company located at 616 Corporate Way, Suite 2-4876, Valley Cottage, NY 10989, USA.

#### Aims and Scope:

*Journal of Environmental Science and Engineering B*, a monthly professional academic journal, covers all sorts of researches on environmental management and assessment, environmental monitoring, atmospheric environment, aquatic environment and municipal solid waste, etc..

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**Subscription Information:** 

Price (per year): Print \$600, Online \$480 Print and Online \$800

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Volume 7, Number 1, January 2018 (Serial Number 67)

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## Studying the Impact of Anions Pre-generated Iron Corrosion Products on the Efficiency of Contaminant Removal in Fe<sup>0</sup>/H<sub>2</sub>O Systems

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**Abstract:** The effects of  $Fe^0$  pre-corrosion by water, bicarbonate, chloride, phosphate and sulfate on the efficiency of  $Fe^0$  systems for water treatment were investigated. Batch experiments were conducted for a total duration of 72 days with MB (Methylene Blue) and MO (Methyl Orange). The efficiency of used  $Fe^0$  was assessed by characterizing the extent of MB and MO discoloration, pH variation and amount of iron released as a function of anion type. Before dye addition, used  $Fe^0$  in  $Fe^0$ /sand and 100%  $Fe^0$  systems was allowed to equilibrate with H<sub>2</sub>O or the anionic solution for 0 to 44 days. Pre-corrosion has low impact on MB discoloration but has negative impact on MO discoloration. Relative to the reference system (anion free system, H<sub>2</sub>O), all the tested anions enhanced MB discoloration but decreased that of MO.  $HPO_4^{2-}$  and  $HCO_3^-$  severely affects MO discoloration. The pH of the medium governs the discoloration with MB performing better at higher pH and MO doing same at lower pH. For MB,  $Fe^0$ /sand system shows higher efficiency than 100%  $Fe^0$  systems and other water treatment designs using  $Fe^0$ .

Key words: Corrosion products, dye discoloration, major anions, pre-corrosion, zero-valent iron.

#### **1. Introduction**

The contamination of the environment and particularly water sources is on the rise around the world. This is due principally to the continuous increase in world population with the corresponding increase in different activities that are aimed at sustaining life on earth. These activities which include principally industrial, agricultural and domestic pollute the already scarce water resources with different contaminants. This contamination modifies the properties of the water body, making it responsible for a number of environmentally related problems and particularly health related ones.

According to WHO (World Health Organization) estimates, up to 80% of all diseases and sicknesses in the world result from inadequate sanitation, polluted

water or unavailability of water [1]. It also estimated that approximately 1.6 million people are forced to use contaminated water globally and are at risk of exposure to diseases. This situation is even more alarming in developing countries where there is lack of appropriate water treatment technologies due to economic and technological constrains. In most rural areas of developing countries, water infrastructure is poorly developed or doesn't existent at all [2, 3]. Therefore, innovative, efficient but affordable technologies that are cheap and applicable without electricity are needed [2].

PRB (Permeable Reactive Barriers) based metallic iron (Fe<sup>0</sup>) has been demonstrated as a promising medium for environmental remediation and water treatment [2-4]. The use of PRB is advantageous over the other treatment methods due to its low energy input, continued productive use of installation, and cleans up on only the area of contamination [3]. The use of Fe<sup>0</sup>

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is particularly advantageous because it is easily available at low cost and can efficiently remove organic and inorganic chemicals and pathogens [5]. The main mechanisms of contaminant removal are degradation, precipitation and sorption of contaminants [3, 6]. Contaminant removal in Fe<sup>0</sup> system occurs on the surface of different iron corrosion products produced in a cycle of aqueous iron corrosion processes [7]. But the major limitation of Fe<sup>0</sup> system is that it undergoes volumetric expansion due to iron corrosion [8, 9], indicating the non-sustainable nature of pure Fe<sup>0</sup> systems [8]. In  $Fe^0$  system there is the need for free space to quantitatively undergo corrosion. In the absence of free space, corrosion stops due to clogging [8]. This implies the filter based Fe<sup>0</sup> system cannot more be used. Thus, for Fe<sup>0</sup> filter to be more sustainable, the amount of Fe<sup>0</sup> in the filtration system is reduced by mixing it with a non-expansive material. The most tested and used non-expansive material is sand [10], because it is cheap, non-reactive and porous [7].

Despite the fact that there are over 200 Fe<sup>0</sup> reactive walls working satisfactorily throughout the world [11], the mechanism of operation of Fe<sup>0</sup>/H<sub>2</sub>O system is far from been established [8]. There is still much controversy on almost all aspects of contaminant removal in these systems resulting from the fact that there are many factors determining the reactivity of Fe<sup>0</sup> under realistic conditions [12]. One of the most widely recognized and thoroughly studied being solution chemistry, especially the coexisting anions as summarized in Table 1. These studies evaluate the influence of major anions on the corrosion behaviour

of metallic iron.

While the Cl<sup>-</sup> and  $SO_4^{2-}$  enhance iron corrosion, bicarbonate ions passivate iron surface, but the role of phosphate ions is not very clear. Nonetheless, the contradictions may be due to experimental conditions.

Though the influence of these majors anions on iron corrosion has been widely studied as evident from Table 1, available literature on the role of iron corrosion products (FeCPs) pre-generated by these anions on the functioning of Fe<sup>0</sup>/H<sub>2</sub>O systems is scarce. The present study deals with the impact of anions pre-generated iron corrosion products on the efficiency of Fe<sup>0</sup>/H<sub>2</sub>O systems in removing MB (Methylene Blue) and MO (Methyl Orange) from aqueous solution for 28 days. Prior to the introduction of dyes (MB and MO), Fe<sup>0</sup> is pre-corroded for 0 to 44 days in the presence of 0.0464 M of a major anion. Tested anions include: Cl<sup>-</sup>, HCO<sub>3</sub><sup>-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup> and SO<sub>4</sub><sup>-2-</sup>. The reference system used is deionised water (anion free). 100% pure Fe<sup>0</sup> and Fe<sup>0</sup>/sand systems were investigated. Results of this study will help improve the understanding and functioning of  $Fe^{0}/H_{2}O$  systems for contaminant removal.

#### 2. Materials

Working solutions of anions were prepared with demineralized water. 0.0464 M of each anion (Cl<sup>-</sup>,  $SO_4^{2-}$ ,  $HPO_4^{2-}$  and  $HCO_3^{-}$ ) was prepared by dissolving the corresponding mass of salt in 1 L of demineralized water: 1.647 g NaCl, 4.45 g Na<sub>2</sub>SO<sub>4</sub>, 4.45 g NaHPO<sub>4</sub> and 2.27 g NaHCO<sub>3</sub>. Used salts were of analytical grade.

 Table 1
 Influence of anions on the corrosive behaviour of zero valent iron.

Decreasing order of ZVI corrosion (or reactivity)	Reference	
$HSiO_3^- > HCO_3^- > H_2PO_4^- > CIO_4^- \approx NO_3^- > CI^- > SO_4^{-2}$	[13]	
$PO_4^{3-} > HSiO_3^{-} > NO_3^{-} > CO_3^{2-} > SO_4^{2-}$	[14]	
$HCO_3^{-} > SO_4^{-} > Cl^{-} > NO_3^{-}$	[15]	
$Na_2SiO_3 > H_2O > NaHCO_3 > NaCl > Na_2SO_4 > NaH_2PO_4 > NH_4Cl$	[16]	
Chloride > nitrate > sulphate > phosphate	[17]	
Nitrate > iodide > perchlorate > bromide > chloride > sulfate	[18]	
$CO_3^{2-} > CI^-$	[19]	
$Pb(NO_3)_2 > NaHCO_3 > KI > CaCO_3 > KBr > NaNO_3 > MnSO_4 > MgSO_4 > NaCl > KCl > Na_2SO_4$	[20]	

MB and MO are widely used as model contaminants to characterize the suitability of various systems for water treatment [21, 22]. Both dyes were of analytical grade. They are selected due to (i) similitude in their molecular size (molar mass: 319.85 g·mol<sup>-1</sup> for MB and 327.33 g·mol<sup>-1</sup> for MO) and (ii) differences in their chemical character (MB cationic and MO anionic). Used initial dye concentration was 10  $\text{mg}\cdot\text{L}^{-1}$  for each dye. The working solutions were prepared by diluting a 50 times more concentrated stock solution (1,000 mg·L<sup>-1</sup>) of each dye using the demineralized water. The pH value of the initial solution was  $7.6 \pm 0.1$ . The used initial concentration  $(10 \text{ mg} \cdot \text{L}^{-1})$  was selected to approach the concentration range of natural waters (MB and MO as model micro-pollutants) [23, 24].

A standard iron solution  $(1,000 \text{ mg} \cdot \text{L}^{-1})$  from Aldrich Chemical Company, Inc., was used to calibrate the spectrophotometer used for analysis. All other chemicals used were of analytical grade. In preparation for spectrophotometric analysis, ascorbic acid was used to reduce Fe<sup>3+</sup> in solution to Fe<sup>2+</sup>. 1.10 orthophenanthroline was used as reagent for Fe<sup>2+</sup> complexation. Other chemicals used in this study included L(+)-ascorbic acid and L-ascorbic acid sodium salt. Ascorbic acid also degrades dyes (in particular MO) and eliminates interference during iron determination [24].

The used Fe<sup>0</sup> material was purchased from iPutech (Rheinfelden, Germany). The material is available as fillings with a particle size < 630  $\mu$ m. The fraction 0.3 to 0.5 mm was used in the experiments. The elemental composition of the material as analysed by X-ray fluorescence was: Mn: 0.62%; Si: 0.52%; Cu: 0.23%; Cr: 0.2%; Ni: 0.1%. The material was used without any pre-treatment.

The used sand was a natural material from the Maroua (Cameroon). Maroua sand was used as received without any further pre-treatment or characterization. The particle size between 0.3 to 0.5 mm was used. Sand was used because of its

worldwide availability and its use as admixing agent in  $Fe^{0}/H_{2}O$  systems [7, 10].

#### 3. Methods

Fe<sup>0</sup> pre-corrosion was realized in essay tubes containing 10 mL of demineralized water (H<sub>2</sub>O) or individual anions (Cl<sup>-</sup>, HCO<sub>3</sub><sup>-</sup>, HPO<sub>4</sub><sup>2-</sup> and SO<sub>4</sub><sup>2-</sup>). The anion initial concentration was 0.0464 M. The 10 mL solution was equilibrated with Fe<sup>0</sup> alone and Fe<sup>0</sup>/sand mixtures for 0 to 44 days in order to in-situ generate iron corrosion products (FeCPs). Each essay tube contained 0.1 g of  $Fe^0$  (Fe<sup>0</sup> alone or 100% Fe<sup>0</sup>) or 0.1 g of  $Fe^0$  and 0.2 g sand ( $Fe^0$ /sand system). The ensemble was placed in a closed cupboard, protected from day light. During the pre-equilibration period, essay tubes already containing materials (Fe<sup>0</sup> and/or sand) were gently turned end-over-end once per week. This operation intended to avoid compaction of the material by gelatinous FeCPs (cementation) [24]. At the end of the pre-corrosion period, prior to dye addition the pH value of all investigated systems was recorded.

Dye discoloration was initiated by adding 10 mL of the dye solution (20 mg $\cdot$ L<sup>-1</sup>) to the 10 mL of pre-equilibrated systems (Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, H<sub>2</sub>O, HPO<sub>4</sub><sup>2-</sup> and  $HCO_3$ ). The resulting working dye concentration was 10 mg·L<sup>-1</sup>. Investigated systems were: (i)  $Fe^0$  alone and (ii) Fe<sup>0</sup>/sand. The reaction vessels were kept static (no agitation) in a laboratory cupboard to avoid any photo-catalytic interferences. The efficiency of individual systems for dye discoloration was characterized at laboratory temperature (about 25  $\pm$ 5 °C) for 28 days. The initial pH value was  $\approx$  7.6. After equilibration, up to 3.0 mL of the supernatant solutions were carefully retrieved (no filtration) for dye determinations (no dilution) and the pH value was recorded. The Fe<sup>0</sup> system characterizes the extent of dye discoloration by Fe<sup>0</sup>. The Fe<sup>0</sup>/sand system characterizes the impact of sand on the availability of 'free' corrosion products and thus their impact on dye discoloration [23].

Aqueous dye and iron concentrations were UV-Vis determined Spectro 23**R**S by а spectrophotometer (Labomed. Inc.). The working wavelengths for the dyes are 664 nm for MB and 464 nm for MO. Fe was determined at 510 nm. Cuvettes with 1 cm light path were used. The iron determination followed the 1.10 orthophenanthroline method [25]. The spectrophotometer was calibrated for dye concentrations  $\leq 10.0 \text{ mg} \cdot \text{L}^{-1}$  and iron concentrations  $\leq 10.0 \text{ mg} \cdot \text{L}^{-1}$ . The pH value was measured by a Mettler Toledo Education line pH meter.

After the determination of the residual dye concentration (C), the discoloration efficiency (E) was calculated (Eq. (1)) in order to characterize the magnitude of tested systems for dye discoloration:

$$E = \left(1 - \frac{c}{co}\right) * 100 \tag{1}$$

Where C<sub>0</sub> is the aqueous dye initial concentration (10 mg·L<sup>-1</sup>), while C is the dye concentration at any date (t > 0).

#### 4. Results

Fig. 1 shows the MB discoloration efficiency (E value) plotted as a function of the pre-corrosion time for the five investigated systems. The results of the  $Fe^{0}$ /sand system are presented in Fig. 1a while those for the pure  $Fe^{0}$  system are summarized in Fig. 1b.

It is seen that larger discoloration efficiencies were

achieved in the  $Fe^{0}$ /sand (70 to 95%) compared to the pure Fe<sup>0</sup> system (25 to 80%). It is also seen that varying the pre-corrosion time from 0 to 44 days mostly has low impact on the MB discoloration efficiency for individual anions. This observation suggests that, under tested experimental conditions. similar amount of reactive site for MB discoloration by adsorption and co-precipitation were present in individual systems despite prolonged pre-corrosion time. interpretation This appears to be counter-intuitive given that increasing amounts of FeCPs were generated with increasing pre-corrosion time [24].

Fig. 1b shows that the MB discoloration efficiency decreased from 60% (H<sub>2</sub>O-reference) to 30% in the HPO<sub>4</sub><sup>2-</sup> system. For all other systems, a slight increase of the E value was observed (60 to 80%) in the order: HPO<sub>4</sub><sup>2-</sup> < H<sub>2</sub>O < SO<sub>4</sub><sup>2-</sup> < Cl<sup>-</sup> < HCO<sub>3</sub><sup>-</sup>. In other words, in the 100% Fe<sup>0</sup> system, MB discoloration substantially increased when bicarbonate was present.

Meanwhile, Fig. 1a shows that the MB discoloration efficiency increased from 70% in the reference system (H<sub>2</sub>O) to up to 95% in all other systems. In other words, in the Fe<sup>0</sup>/sand system, the presence of tested anions enhanced MB discoloration. Overall, the impact of tested anions on MB discoloration by the Fe<sup>0</sup>/sand system followed the order:  $H_2O < SO_4^{2-} < CI^- < HPO_4^{2-} < HCO_3^-$ . The main

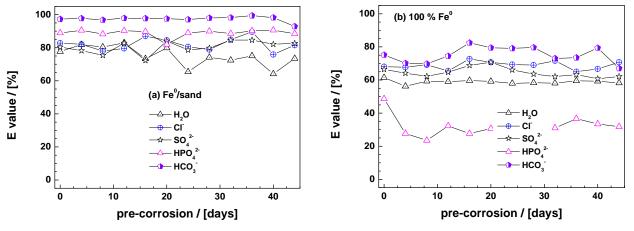


Fig. 1 Discoloration of MB using (a) Fe<sup>0</sup>/sand system and (b) 100 % Fe<sup>0</sup> system.

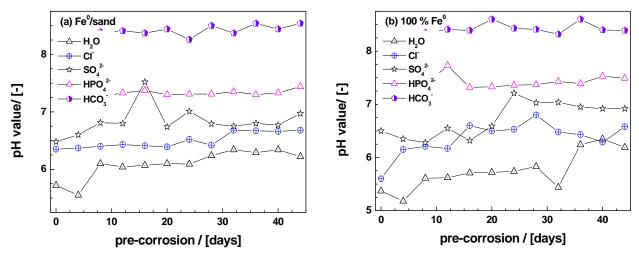


Fig. 2 Variation in pH for MB discoloration (a) Fe<sup>o</sup>/sand system and (b) 100% Fe<sup>o</sup> system.

difference to the 100%  $\text{Fe}^0$  system is that  $\text{HPO}_4^{2-}$  enhances MB discoloration.

Results of the variation of pH for the two systems are presented in Figs. 2a and b.

For the Fe<sup>0</sup>/sand system (Fig. 2a), the order of pH was:  $H_2O < Cl^- < SO_4^{2-} < HPO_4^{2-} < HCO_3^{-}$  (MB discoloration order:  $H_2O < SO_4^{2-} < Cl^- < HPO_4^{2-} <$  $HCO_3$ ). The same order is observed for pH in the 100% Fe<sup>0</sup> system (Fig. 2b) but the order of MB discoloration is different (MB discoloration order:  $HPO_4^{2-} < H_2O < SO_4^{2-} < Cl^- < HCO_3^-$ ). This analysis demonstrates that the pH (determined by products of corrosion) controlled the discoloration of MB. Thus, the discoloration was principally controlled by the electrostatic attractions between the cationic MB and charged anions iron solutions. This is why HCO<sub>3</sub> (pH almost 9) significantly enhanced discoloration in the two systems. In the case of the 100% Fe<sup>0</sup> system Fig. 2b, the same trend is observed but only for  $HPO_4^{2-}$ containing solution with very low MB discoloration despite its negative solution pH. During the pre-corrosion period (0-44 days) no change in colour or production of corrosion products (indicated by brown colouration) was observed in HPO<sub>4</sub><sup>2-</sup> containing solutions for both systems. However, a white precipitate was deposited on the walls of the reaction tube (due to the reaction:  $Fe^{3+} + HPO_4^{2-} \rightarrow$  $FePO_4 \downarrow + H^+$ ). This precipitate which is easily formed

(high enthalpy of formation) with Fe, is insoluble in water (Table 2). It then deposit and block the surface of iron thus giving low discoloration of MB in 100% Fe<sup>0</sup> system. The higher MB discoloration in Fe<sup>0</sup>/sand system compared 100% Fe<sup>0</sup> system is therefore probably due to the presence of sand which acted as a dispersant and limited clogging of iron corrosion products; creating more space for MB to react and also forming weak hydrogen bond with MB improving its discoloration [26]. Particularly, for solution containing HPO<sub>4</sub><sup>2-</sup> in Fe<sup>0</sup>/sand system, discoloration was enhanced by sand through formation of weak hydrogen bonds between MB and OH- groups on sand surface. The similarity in behaviour of SO<sub>4</sub><sup>2-</sup> and Cl<sup>-</sup> can also be seen from Table 2 where they easily react with iron but their complexes are easily soluble in water (Cl<sup>-</sup> more soluble), liberating the iron surface for further reaction.

The enthalpy of formation values, Table 2 shows that the formation of complexes with iron is of the order: phosphate > sulfate > carbonate > chloride. However, the order of solubility in aqueous media is chloride > sulfate > carbonate > phosphate. This indicates that soluble iron chloride dissolves on formation thus liberating the surface of the iron for more reaction and this tendency is followed by sulphate, carbonate and lastly phosphate where the formed precipitates block the iron surface.

#### Studying the Impact of Anions Pre-generated Iron Corrosion Products on the Efficiency of Contaminant Removal in Fe<sup>0</sup>/H<sub>2</sub>O Systems

Table 2 Thermodynamic properties of some re-amons compounds [27].						
Compound	Solubility in water at 298 K	$\Delta_f G_m^{e}_{298}/kJ/mol$	$\Delta_{\rm f} H^{\circ}_{298}  {\rm kJ/mol}$			
FeCl <sub>3</sub>	912 g/L	-415.7	-399.4			
Fe-sulfate	29.51 g/100 mL	-848.651	-991.235			
Fe-carbonate	0.0067 g/L	-648.68	-750.6			
Fe-phosphate	anhydrous: insoluble dihydrate: 0.642 g/100 mL (373 K)		-1,888			

 Table 2
 Thermodynamic properties of some Fe-anions compounds [27].

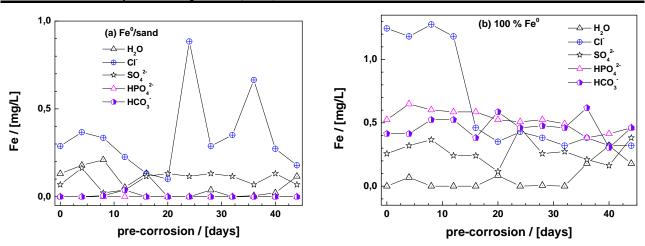


Fig. 3 Quantity of Fe released during MB discoloration in (a) Fe<sup>0</sup>/sand system and (b) 100% Fe<sup>0</sup> system.

The influence of the anions pre-generated iron corrosion products on the ability of the  $Fe^{0}$ /sand and 100%  $Fe^{0}$  systems to release iron in to solution during discoloration of MB is shown in Figs. 3a and b.

For the Fe<sup>0</sup>/sand system, Fig. 3a, the order of release is:  $CI^- > H_2O = SO_4^{-2-} > HCO_3^- (0.00 \text{ mg/L}) = HPO_4^{-2-}$  and for 100% Fe<sup>0</sup> system, the order is:  $CI^- > HPO_4^{-2-} > HCO_3^- > SO_4^{-2-} > H_2O$ .

The high iron released in the presence of the chloride for the two systems is due to its ability to easily corrode iron. Also, the FeCl<sub>3</sub> precipitate formed between chloride and Fe surface is very soluble in water, thus releasing charged iron species in to solution continuously. The high release of iron in 100%  $Fe^{0}$  system by  $HPO_{4}^{2-}$  and  $HCO_{3}^{-}$  (with low iron corroding potentials) is due to the solubility of the precipitates formed with iron surface in the reagents used for iron determination (evidenced by the disappearance of white precipitate initially present). The amount of iron released in the two systems is basically identical especially for chloride and the values are moderate despite the pre-generation of iron

corrosion products.

Fig. 4 shows the MO discoloration efficiency (E value) plotted as a function of the pre-corrosion time for the five investigated systems. The results of the Fe<sup>0</sup>/sand system are presented in Fig. 4a while those for the pure Fe<sup>0</sup> system are summarized in Fig. 4b.

It is seen that larger discoloration efficiencies were achieved in the two systems (0.00 to 96%). Contrary to MB, varying the pre-corrosion time from 0 to 44 days mostly has an impact on the MO discoloration efficiency for individual anions. Figs. 4a and b show that the MO discoloration efficiency decreased from 96% (H<sub>2</sub>O-reference) to 0.00% in the HPO<sub>4</sub><sup>2-</sup> systems, 4% for HCO<sub>3</sub><sup>-</sup> in pure Fe<sup>0</sup> system and 32% in Fe<sup>0</sup>/sand system. Fig. 4a, for all other systems, a decrease of the E value was observed. The decrease is in the order: HPO<sub>4</sub><sup>2-</sup> > HCO<sub>3</sub><sup>-</sup> > SO<sub>4</sub><sup>2-</sup> > Cl<sup>-</sup> = H<sub>2</sub>O. In other words, in the Fe<sup>0</sup>/sand system, MO discoloration substantially increased when water and Cl<sup>-</sup> were present or the HPO<sub>4</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2</sup> presence reduce MO discoloration, with HPO<sub>4</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup> attaining 0.00% and 32% respectively. From Fig. 4b, the same trend is observed for the 100% Fe<sup>0</sup> system (HPO<sub>4</sub><sup>2-</sup> > HCO<sub>3</sub><sup>-</sup> > SO<sub>4</sub><sup>2-</sup> > Cl<sup>-</sup> = H<sub>2</sub>O) with reduction in MO discoloration attaining 0.00% and 4% respectively for HPO<sub>4</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup>.

The variation of pH for the two systems are presented in Figs. 5a and b.

For the Fe<sup>0</sup>/sand system (Fig. 5a), the order of final solution pH was:  $HCO_3^- > HPO_4^{2-} > SO_4^{2-} > CI^- > H_2O$  (MO discoloration order:  $HPO_4^{2-} < HCO_3^- < SO_4^{2-} < CI^- = H_2O$ ). The same order is observed for pH variation in the 100% Fe<sup>0</sup> system (Fig. 5b) with same order of MO discoloration. Like for MB, the discoloration of MO was controlled by electrostatic attractions between the negatively charged anionic dye, methyl orange and the charged anions-iron solutions.  $HPO_4^{2-}$  and  $HCO_3^-$  significantly reduced MO

discoloration with increase pre-corrosion time due to increase in pH; for Fe<sup>0</sup>/sand system, pH decreased from 9.06 to 8.24 for HPO<sub>4</sub><sup>2-</sup> and increased from 9.06 to 9.44 for HCO<sub>3</sub><sup>-</sup> from 0-44 days of pre-corrosion while for 100% Fe<sup>0</sup> system, pH decreased from 8.58 to 8.23 for HPO<sub>4</sub><sup>2-</sup> and increased from 9.20 to 9.45 for HCO<sub>3</sub><sup>-</sup> from 0-44 days of pre-corrosion. Thus, there was strong repulsion between negative charges of MO and those from solution containing these anions resulting in zero discoloration with solutions pre-corroded from the 12th day for HPO<sub>4</sub><sup>2-</sup>.

According to Sejie, F. P., [28], for MO as pH is increased to more basic conditions, the double bond conjugation is lost and a proton is lost, and the molecule rearranges to form a negatively charged. Due to excess anions in the solution, there will be repulsion of the dye by the negatively charged

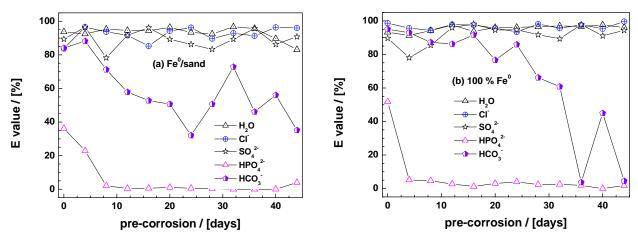


Fig. 4 Discoloration of MO using (a) Fe<sup>0</sup>/sand system and (b) 100% Fe<sup>0</sup> system.

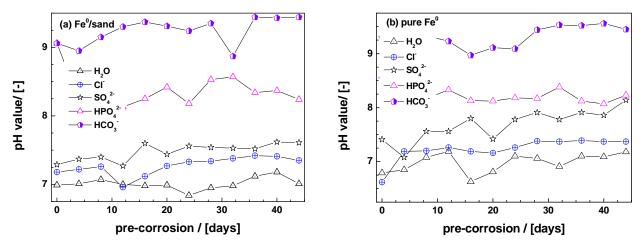


Fig. 5 Variation in pH for MO discoloration (a) Fe<sup>0</sup>/sand system and (b) 100% Fe<sup>0</sup> system.

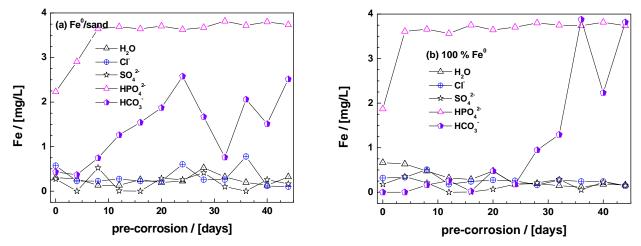


Fig. 6 Quantity of Fe released during MO discoloration in (a) Fe<sup>0</sup>/sand system and (b) 100% Fe<sup>0</sup> system.

surfaces of the adsorbents, also an increase in pH leads to the modification of the pi (II) system delocalization pattern. They concluded that, the uptake of methyl orange on several adsorbents was similarly found to be favoured at lower pH. This confirms why MO discoloration was best in water and chloride medium with pH turning towards neutral region.

The concentration of iron released in to solution in the  $Fe^0$ /sand and 100%  $Fe^0$  during discoloration of MO over the pre-corrosion period is shown in Figs. 6a and b.

For the two systems, the trend in iron release is the same with  $HPO_4^{2-}$  and  $HCO_3^{-}$  containing solutions highest amounts of iron. While this amount is constant from the second day of pre-corrosion for  $HPO_4^{2-}$ , it increases steadily with time of pre-corrosion for  $HCO_3^{-}$ . The amounts released are much higher than in the case of MB. This is probably due to the fact under strong basic conditions created by MO,  $HPO_4^{2-}$  and  $HCO_3^{-}$  easily form precipitates with Fe surface (they do not corrode the iron as their solutions were very clear during experiments) which are easily dissolved by reagents used in iron determination. Conversely, the iron released in the other anion containing solutions was negligible for the two systems as most of the iron charged species (corrosion products) produced were consumed by MO.

#### 5. Conclusions

The impact of  $HPO_4^{2-}$ ,  $HCO_3^{-}$ ,  $SO_4^{2-}$ ,  $Cl^{-}$  and  $H_2O$ pre-generated iron corrosion products on the functioning of Fe<sup>0</sup>/H<sub>2</sub>O systems for contaminant removal was investigated. The tested contaminants were methylene blue and methyl orange using Fe<sup>0</sup>/sand mixture and 100% Fe<sup>0</sup> systems. The discolorations of the dyes, the variation of pH of the different systems as well as iron released in to solution were used to characterize each system. Water was used as the reference system. Results show that larger discoloration efficiencies were achieved in the Fe<sup>0</sup>/sand compared to the pure Fe<sup>0</sup> system for MB. It is also seen that varying the pre-corrosion time from 0 to 44 days mostly has low impact on the MB discoloration efficiency for individual anions. MO also showed that larger discoloration efficiencies in the two systems. Contrary to MB, varying the pre-corrosion time from 0 to 44 days has an impact on the MO discoloration efficiency for individual anions. MO discoloration efficiency with all tested anions was all lower than that of the H<sub>2</sub>O-reference but higher for MB. The pH of each system was the controlling factor in discoloration. MB discoloration was favoured at higher pH while MO discoloration was favoured at low pH (almost neutral). The presence of  $HPO_4^{2-}$  and  $HCO_3^{-}$  showed a significant negative impact on the discoloration of MO than MB

by  $Fe^{0}/H_{2}O$  systems releasing much iron in to solution.

This work is very useful for design of Fe<sup>0</sup> based Permeable Reactive Barriers, particularly filters for small homes and communities.

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#### 10

## Studying the Impact of Anions Pre-generated Iron Corrosion Products on the Efficiency of Contaminant Removal in Fe<sup>0</sup>/H<sub>2</sub>O Systems

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## **Utilization Plan of Underground River in Dry Area**

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**Abstract:** Groundwater from underground rivers is one of the potential raw water sources in the karst area. Research to exploit the potential sources of water from underground rivers in karst areas is very important. Utilization of water resources should be based on technique, environmental and social conditions. The problems are to find the groundwater river flows, to design a well installation, to determine the feasibility, and to manage the water use. Analysis of the results of geological mapping, topography, geophysical measurements, drilling, pipeline and electrical survey, and pumping tests produce the feasibility of the water utilization. Geoelectric data indicates there is a saturated zone at a depth of about 70-90 m from the surface. Well construction is implemented by using a 83 m PVC (Polyvinyl Chloride) pipe and a 15 m screen length. The groundwater level remains stable even though it has been pumped with a maximum discharge of 5 liters/sec. Based on the elevation difference from topographic mapping results, the number of booster pumps can be calculated. Utilization of water from underground rivers can overcome the problem of water shortage in dry area.

Key words: Geological mapping, underground river, dry area, karst, water quality.

#### 1. Introduction

Geological research is mostly done in dry areas, such as karstic geomorphology [1-5], and studies on the development and utilization of karst areas [6, 7]. Other studies are models of conservation of the karst area [8, 9]. In the dry season, people living in arid regions need clean water supplies. Doline ponds have an important role as one of water resources in karst areas, especially during dry seasons [10, 11]. Many studies in the karst area of anticipatory action are providing permanent water supplies [12]. Groundwater from underground rivers is one of the potential raw water sources in the karst area. Research is often conducted to identify hydrogeological conditions as a reference in preparing water source utilization plans in a dry prone area [13-15]. Research on ground water potential through hydrogeological surveys is used to determine groundwater sources by evaluating geoelectric data to determine the location of production wells [16, 17]. Utilization of groundwater potential is based on groundwater quality analysis and environmental sustainability functions.

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Pumping test on hydrogeological research is conducted to analyze the potency of groundwater as raw water source [18].

Research to exploit the potential sources of water from underground rivers in karst areas is very important. Utilization of water resources should be based on social and environmental conditions. This case study was conducted in Central Java Province of Indonesia (Fig. 1). The primacy of research in this area is the potential of natural disasters related to geological hazards include: (a) landslides of rock and erosion that potentially occur on the slopes of limestone hill; (b) drought hazard potentially occurs in the southern research area. An interesting water potential for this steep coastal area is the emergence of an underground river stream that mixes with seawater (Fig. 2), but there is no cave in the area. The difference in elevation is quite large that is about 90 m, it makes a problem on the utilization of clean water potential.

#### 2. Objective

The objectives of the study were (a) to analyze hydrogeological conditions, and to plan the utilization of potential water sources to meet the community's



Fig. 1 Research location in Central Java Province of Indonesia to exploit potential water source from underground river in karst area.



Fig. 2 Underground river stream that mixes with seawater.

water needs in dry prone areas; (b) to design the utilization of water source of underground river in accordance with hydrogeological condition of study area.

#### 3. Methods and Material

Based on the survey, the population in the study

area is 2,711 people. During the dry season, this area is always lack of clean water. The research methodology includes: (a) topographic mapping, surface geology and underground geology; (b) pipe and electricity network and distribution survey; (c) geoelectric survey; (d) drilling and logging; (e) construction of well; (f) pumping test; (g) analysis of water samples; (h) social and community environmental surveys. Geological mapping is intended to collect various data, surface and subsurface geological information covering the distribution and physical properties of soil or rocks, groundwater conditions, morphology and geological Geoelectric method hazards. for analyzing groundwater potential using resistivity meter with configuration of Wenner-Schlumberger. And the determination of drilling location is based on the interpretation of field geology data and geoelectric measurement data. The purpose of logging is to determine the physical quantities of the rock based on the physical properties of the rock.

Well construction includes the installation of casing and screen pipe in accordance with the design of the production well construction. Well construction planning is carried out to a depth of 90 m. The water from the well flows into the tubs and then flows to the surrounding community. The purpose of this pumping test is to examine the condition of underground river flow and deep well type capacity, so that it can be determined the type and capacity of the pump to be quality installed. Groundwater tests include temperature, pH and electrical conductivity, while laboratory tests include physical, chemical and metal content to ensure that water quality is safely consumed by the community. Important aspect in this research is calculation of diameter and length of pipe, flow velocity, selection and calculation of pump. The pump is expected to generate optimum debit with maximum efficiency.

Pipe diameter and flow velocity are important factors in the pumping system. The discussion follows the equation given by Ref. [19, 20]. Calculation of two parameters using Eq. (1):

$$D_i = 3.9 \times Q^{0.45} \times \rho^{0.13} \tag{1}$$

where  $D_i$ : pipe inner diameter, mm or inch; Q: capacity/debit, m<sup>3</sup>/hr. or liter/min;  $\rho$ : density of fluid, kg/m<sup>3</sup>.

Calculation of fluid flow velocity:

$$V = \frac{Q}{A} \tag{2}$$

where V: fluid flow velocity, m/sec; Q: debit /capacity,  $m^3/hr$ . or liter/min; A: surface area,  $m^2$ .

Other aspects considered are (a) the total head includes the pump's static head, the head loss on the pipe, the friction loss, and the shock loss; (b) the velocity head arising from the speed of the water flow in the pipe, both suction and discharge. Calculation of high-pressure static head using Eq. (3):

$$h_s = t_2 - t_1 \tag{3}$$

where  $h_s$ : high press static pump;  $t_2$ : water elevation in the outlet;  $t_1$ : water elevation in the suction pipe. The velocity head formula is Eq. (4):

$$h_v = \frac{v^2}{2g} \tag{4}$$

where hv: velocity head, m; v: the water velocity in the pipe, m/sec; g: the force of gravity. Head loss consists of friction loss and sock loss. Generally, the pipe-producing factory publishes the pipe friction handbook, whereas for the calculation of shock loss using Eqs. (5, 6) [21, 22]:

$$HF = HL \times L_{pipe}$$
 (5)

$$HL = \left[\frac{3.35 \times 10^6 \times Q}{d^{2.63} \times C}\right]^{1.852}$$
(6)

where  $HF_{pipe}$ : pipe friction loss, m;  $L_{pipe}$ : pipe length, m; *HL*: pipe head loss, m; *Q*: pump debit, liter/sec; *d*: pipe inner diameter, mm or inch; *C*: Hazen William's constant. The total pump head is the sum of all head loss and is expressed in Eq. (7):

$$H_t = h_s + h_v + H_f + H_{fs}$$
 (7)

Calculation of pump power using Eq. (8):

$$P_p = 1.02 \times Q \times H_t \times SG \times E_f \tag{8}$$

where Pp: power pump, kW; Q: pump discharge, m/sec; Ht: total head, m; SG: density of water; Ef: pump efficiency, %. The pump used in the well is a submersible pump. Electricity network and distribution surveys are needed to determine the potential state of power distribution that is useful to assist the design process of utilizing the underground water source.

Social and community environmental surveys are needed to identify demographic data of research area

such as population, occupation, culture and community environment. Social and environmental surveys to support the sustainability of underground river water use are contextually adapted to the conditions of the communities in the study area. Development of drinking water from water sources, raw water drainage, drinking water treatment, distribution network to home connections is implemented taking into account the rules and norms of environmental sustainability. Based on studies conducted by Kevany, K., and Huisingh, D. [23] involving women in the development process from planning, implementing and managing water supply and sanitation facilities proved to improve the sustainability of water and sanitation infrastructure.

#### 4. Results

Based on the results of geological mapping, the research area is included in the geological unit of karst hillside environment. This unit forms a coarse rough morphology, and a steep slope. Limestone in this morphology is formed of karst natural phenomena. The process of dissolving limestone causes the cavity within the limestone. The formation of cavities is the initial process of forming the underground river basin. The underground river stream eventually emerges as a spring and empties into the Indian Ocean. Geoelectric data indicates there is a saturated zone (aqueous cavity) at a depth of about 70-90 m from the surface. Implementation of drilling activities with a depth of 90 m is based on the geoelectric data. In drilling activities, the water indicated to rise at a depth of 68 m and the estimated depth of the base of the underground river is 83 m. Based on underground river research, water flows from north to south. Water enters karst fracture directly, flows up into a basin, and becomes an underground river. Water continues to flow down and has no phreatic level which is homogeneous as in non-karst aquifers.

Well construction is implemented by using a 83 m PVC pipe and a 15 m screen length. Based on the test results, groundwater table was found at depth of 68 m (28 m a.s.l). Based on drilling results, the saturation zone thickness is 15 m, and the lowest saturation zone is at 83 m (13 m a.s.l). The pumping test results show a 3 m groundwater level decrease, then the submersible pump installation is carried out at a depth of 74 m (22 m a.s.l). The data recorded in the pumping test are (a) preliminary groundwater level (pizometric baseline); (b) pumping flow; (c) groundwater advance during draw-down; (d) time of pumping start; (e) time after the pumping test, the groundwater level remains stable even though it has been pumped with a maximum discharge of 5 liters/sec.

The total population in the research area is 2,711 people. If the water debit is 5 liters/sec, while the assumption of the pump's working time is 10 hr/day, the water produced is 180,000 liters/day. If the water requirement is assumed to be 60 liters/day/person (Regulation of the Minister of Home Affairs No. 23 of 2006), then about 3,000 people can use clean water. Utilization of water from underground rivers can overcome the problem of water shortage in arid area such as in research area. Based on the elevation difference from topographic mapping results, the number of booster pumps can be calculated. The total length of the pipeline is 5,544 m. This pipe network is divided into 12 segments that require 4 booster pumps; in other areas, the water flow uses the force of gravity. Based on the results of the lane survey, and field data analysis for the water source utilization plan, requires the addition of new power lines. Planning for distribution of electricity network is MVN (Medium Voltage Network) and LVN (Low Voltage Network). The total length of the medium voltage network is 2,080 m and the total length of the low-voltage network is 210 m.

Water quality testing from underground river is based on Regulation of Minister of Health Republic of Indonesia No. 492 of 2010. Test results on water from the underground river classified on drinking water through the processing. Parameters that require special attention for the initial treatment are organic and inorganic chemicals. The organic material contained in water is a detergent content that shows a value above the maximum allowable level of 329.7 mg/liter (more than 0.05 mg/liter). An-organic chemical parameters such as cadmium need to be treated. Actually, in the research area, there is a lokva (the small karts lake situated in limestone area), but the water quality is very bad. Infrastructure and drinking water facilities cannot be utilized optimally. The lack of community involvement in planning, construction, operation and maintenance activities resulted in non-optimal water utilization. In addition, the non-contextual choice of technology makes it difficult for people to determine the infrastructure and facilities according to the needs, local culture, the ability of communities to manage infrastructure and local physical conditions. Lack of community involvement also makes the infrastructure and facilities of drinking water unsustainable, unable to function properly, as well as the lack of public attention to maintain the sustainability of infrastructure and facilities.

Investments in infrastructure and facilities for drinking water and environmental sanitation which have been supply-driven oriented, have had an impact on the low effectiveness of existing infrastructure and facilities. The change of management paradigm in this research is focused on the management of facilities and infrastructure. This management involves the whole society of users. Involvement in decision making results in greater community participation in implementation and maintenance. The development of drinking water services by engaging the community contextually has better effectiveness and sustainability. Making the community as a decision maker means positioning the community as the main responsibility in the service of drinking water and environmental sanitation. Community involvement at each stage is an effort to increase community ownership of drinking

water infrastructure and facilities. This is an effort to change society behavior gradually. The sense of belonging from the community generates awareness in maintaining the sustainability of water resources. This study encourages community participation in financing the development of water supply and sanitation infrastructure and develops community empowerment systems to manage, control and direct financial resources.

Contextual management is the highest decision making of all aspects related to drinking water and or environmental sanitation. The water management is from early stages of identification of drinking water needs. technical planning, and development implementation. In the research area, the role of women is very dominant to meet the needs of drinking water and environmental sanitation. As a party related to the utilization of drinking water and sanitation infrastructure, women are more aware of what they need in terms of access to water and ease of use of infrastructure and facilities. In this study, women are the main roles in the development of drinking water and environmental sanitation. Placing women as the main roles is defined as their active participation in identifying basic issues of drinking water and sanitation.

The following is the cost of water utilization of underground river: the cost of drilling activities for groundwater use is US\$ 11,264.00; construction of pipe network and pump installation at production wells US\$ 34,545.00; plans for adding new electricity network US\$ 28,788.00. Total cost of utilizing water source is US\$ 74,597.00. Success indicators are appropriate technology, acceptable projects, facility maintenance, encouraging active participation in finances, women are involved in every stage of the project. The fulfillment of success indicators can ensure the sustainability.

#### 5. Conclusion

Based on the discussion above, some conclusions

can be noted: (a) Based on geoelectric measurement, saturated zone is at depth of 70-90 m. Groundwater is found at a depth of 68-83 m, therefore the installation of a submersible pump at a depth of 74 m. The construction of wells is implemented by using a pipe of 83 m PVC and 15 m long screen; (b) Based on the pumping test resulting in a maximum debit of 5 liters/sec, it provides a source of clean water for 2,711 inhabitants living in the arid region; (c) detergent and cadmium content require a special attention. The treatment of the water is required before consumption in order to safeguard human health.

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## Quantity and Trends in Streamflows of the Malewa River Basin, Kenya

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**Abstract:** Freshwater availability in sufficient quantity and quality is necessary for both people and nature. Environmental flow data is useful in the management and allocation of water resources. This study aimed at quantifying stream flows and their trends in the Malewa Basin rivers in central rift valley, Kenya. Daily stream flow data (1960-2013) in four gauges (2GB01, 2GB05, 2GB0708 and 2GC04) were subjected to exploratory data analysis, fixed interval method of baseflow separation and Mann Kendall trend test. The results shows that on average, the Malewa river at Gauge 2GB01 discharge (excluding abstractions) about 191.2 million cubic metres of water annually, equivalent to a discharge of  $6.06 \text{ m}^3$ /s. While discharges had not experienced a step change, huge annual fluctuations were noted suggesting periodicity with changes in climatic conditions. No trend was noted in annual stream data for the four gauges assessed. However, extreme low and high flows, median flows and baseflows for daily data showed either positive or negative trends. The baseflow index for daily flows showed trends: 2GB01 (Z = 4.519), 2GB05 (Z = -6.861), 2GB0708 (Z = -16.326) and 2GC04 (Z = 5.593). The findings suggest that Malewa rivers are likely experiencing effects of extreme climatic conditions and land cover changes. Land cover degradation seems to create conditions of increased flow, although the intensity varies from sub-catchment to another. The data also seems to suggest that stream discharge is much dependent on baseflows. There is need to regulate water use, improve soil cover and manage or adapt to the adverse effects of climate change.

Key words: Streamflow, baseflow, trend, discharge.

#### 1. Introduction

Freshwater availability in sufficient quantity and quality is necessary for both people and nature. The concept of environmental flows has been the subject of study and consideration [1-5]. Environmental flow information guides on how water is managed and allocated to different competing uses. The need for improved water efficiency in the allocation has led to increasing focus on environmental flows or environmental water allocations [6], although national and international policies have not yet accounted for them [7]. Streamflow volumes and trends are important for decision making on water allocation. As reported by Kundzewicz, W. Z., et al. [8], changes in streamflow may occur gradually (a trend) or abruptly (a step change), and this may affect any aspect of the data in question [9].

Environmental flow assessments are conducted using different methods. According to Dyson, M., et al. [2], this may conveniently be grouped into four categories, namely hydrological rules, hydraulic rating methods, habitat simulation methods and holistic methodologies [10]. The Service Provision Index is an example of an environmental assessment approach that links environmental flows, ecosystem services and economic values [11]. This study aimed at quantifying stream flows and trends of the Malewa Rivers in central rift valley, Kenya. Such information was deemed useful in informing the allocation and management of competing water uses and also in the planning for restoration and or management of the water deficit.

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#### 2. Material and Methods

#### 2.1 Study Area

The Malewa river basin  $(1,760 \text{ km}^2)$  (Fig. 1) is located in the larger Naivasha basin within Nakuru and Nvandarua counties of the eastern Africa (Gregory) Rift valley, Kenya. Located at 36°05' E-36°42' E longitudes and 00°07' S-00°45' S latitude, it is administratively bordered by Nyeri and Muranga counties on the east. East of the study area is the Aberdares Mountains and Kinangop plateau. The topography of the study area ranges from about 1,900-3,990 m above mean sea level [12]. Soil types have been influenced by the topographical variation, volcanicity and geology [13]. The soils are predominantly of lacustrine, volcanic and lacustrine-volcanic origins [14, 15].

The area is positioned within a semi-arid type of climate, with a bimodal rainfall distribution. It is characterized by longer rainy season (March-May) and short rainy season (October-November), with February, July and December being the driest months [16]. Annual rainfall ranges between 600-1,700 mm, with the Kinangop plateau experiencing 1,000-1,300 mm [17]. Rainfall in the upper catchment exceeds potential evaporation in most parts of the year [18]. The mean annual temperature ranges from 16 °C to 25 °C and daily range from 5 °C to 25 °C [19].

Lake Naivasha (145 km<sup>2</sup>) is drained by two main rivers: Malewa and Gilgil. The Malewa river with a dendritic drainage system has four streams, namely the Turasha, Kitiri, Mugutyu and Makungi. Its annual flow is estimated at 153 MCM (Million Cubic Metres) [20].

Agriculture, grassland, bush/scrub land and forest are the major land cover types [21]. The upper catchment (the Nyandarua range) is dominated by forests and cropland, the lower end by livestock grazing [22].

#### 2.2 Data

Using ArcGIS 10.3.1, a 30 m by 30 m resolution

Digital Elevation Model for Kenya projected into UTM (Universal Traverse Mercator) Zone 37 was used to delineate the drainage basin and stream network. After basin delineation, the study area was sub-divided into three sub-catchments, namely Turasha (Sub-catchment I), Upper Malewa (Sub-catchment II) and Lower Malewa (Sub-catchment III). Daily stream discharge data for the years 1960-2013 in four gauge stations i.e. 2GB01, 2GB05, 2GB0708 and 2GC04 (Fig. 2) was sourced from the Water Resources Management Authority.

#### 2.3 Exploratory Data Analysis

Stream data for the four gauge stations were analyzed for volumes and trends in daily and annual flows. Using Microsoft Excel®, EDA (Exploratory Data Analysis) was done to estimate stream volumes and visualize trends in data. Using EDA, annual total flow, median flow (50th percentile) and daily flow (90th, 95th, 25th, 10th and 5th percentiles) were generated [9].

#### 2.4 Baseflow Separation

Baseflows were established using the fixed interval method of baseflow separation. In this method, the lowest discharge in each interval (N) was assigned to all days in that interval by starting with the day of the period of record. After this, the bar is moved one interval (2N\* days) horizontally and thereafter the process is repeated. Assigned values were connected to define the base-flow hydrograph [23]. This method was applied using BFI+3.0 program (a base-flow index calculation programme) developed based on Tallaksen, L. M. and van Lanen, H. A. J. [24] among others [25].

#### 2.5 Mann Kendall Trend Tests

Using Microsoft Excel® based add-in XLSTAT statistical analytical software, MK (Mann Kendall) tests [26-28] were performed on annual and daily streamflow data to detect trends. Baseflow and baseflow index for the four gauge stations was also subjected to MK test to establish trends.

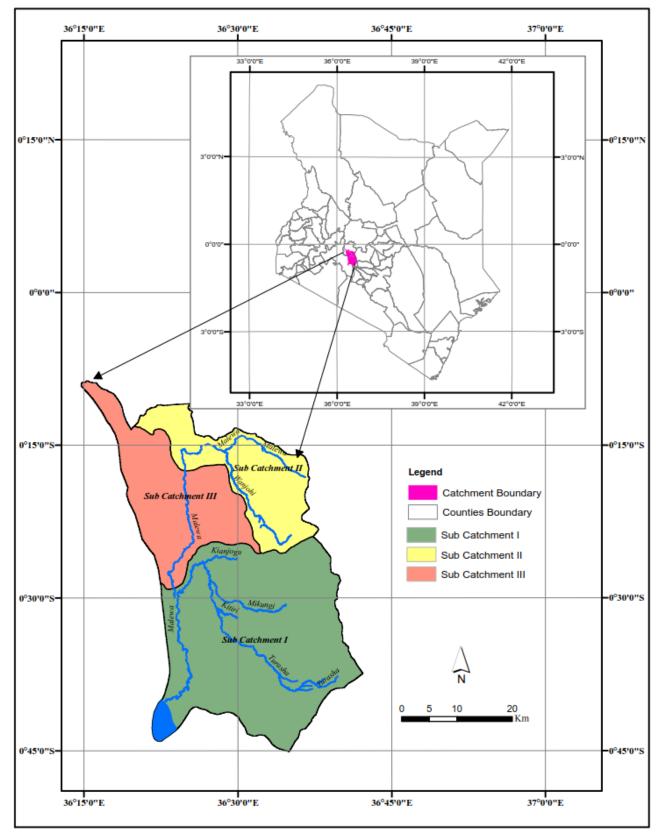


Fig. 1 Area of study.

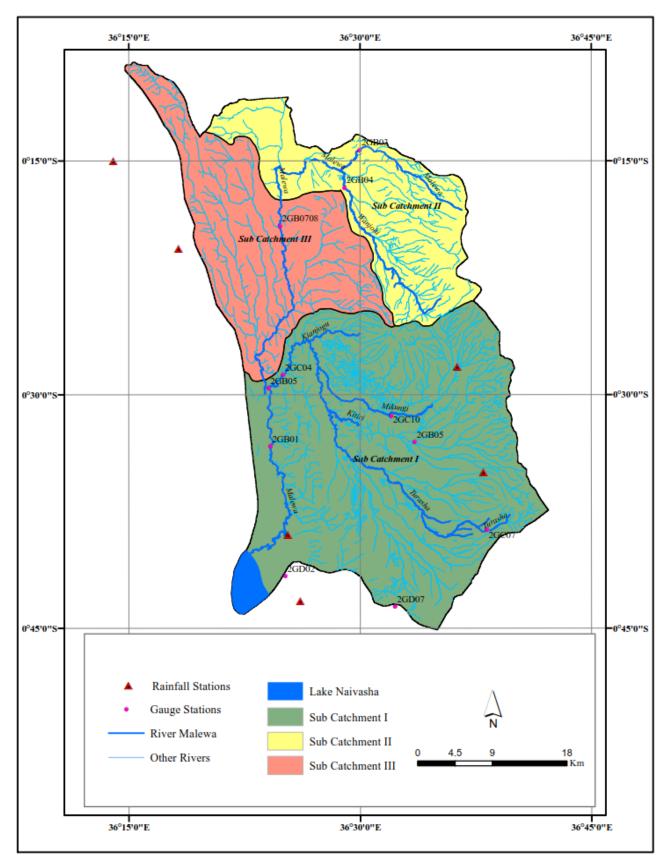


Fig. 2 Location of gauge stations.

#### 3. Results

#### 3.1 Trends in Daily and Annual Stream Discharges

The results show that on average the Malewa river at gauge 2GB01 discharges (excluding abstractions) about 191 MCM of water annually. This is equivalent to a discharge of  $6.06 \text{ m}^3$ /s. There were wide variations in minimum and maximum diurnal and annual flows recorded in all the four gauges. The daily and annual stream volumes and trends for the four gauges stations (1960-2013) are shown below (Table 1). The fluctuations in annual total flows for the four gauges are shown in Fig. 3.

Trends in streamflow (Q) level of the four gauge stations are shown in Table 2. The MK tests on annual streamflows (annual totals) for all the four gauge stations indicates no trend. All the four gauges except 2GB01 indicated trends in daily stream discharge. At 2GB01, the Z scores showed an increasing trend in streamflow at Q5, Q10, Q25, Q50, Q75, Q90 and Q95 levels. At Gauge 2GB05, trend was observed for daily discharge for all levels of flow examined. Increasing trend was observed for daily discharge values at Q10, Q25, Q75, Q90 and Q95. However, decreasing trends were observed at Q5 and Q50. At Gauge 2GB0708, trends was noted for all levels of daily flows except Q90. In this station, except for daily values, Q5 and Q95 indicating decreasing trends, all other levels showed increasing trends. No trend was observed for Q5, Q10, Q25 and Q75 at Gauge 2GC04. All the remaining levels (daily values, Q50, Q90 and Q95) showed increasing trends in streamflows.

Table 1 Daily (m<sup>3</sup>/s) and annual (MCM) discharges at four gauge stations of Malewa rivers.

Cauca		Mean	-	Minimum	Ν	/laximum	SD	
Gauge	Daily	Annual	Daily	Annual	Daily	Annual	Daily	Annual
2GB01	6.06	191.25	0.34	53.11	139.17	358.64	7.12	74.7
2GB05	3.37	106.37	0.25	28.63	115.42	235.68	5.58	47.04
2GB0708	2.25	70.89	0.00	7.55	144.35	186.06	6.10	45.62
2GC04	4.77	150.41	0.00	38.94	136.72	352.98	8.04	67.17

Daily data in m<sup>3</sup>/s; Annual data in MCM.

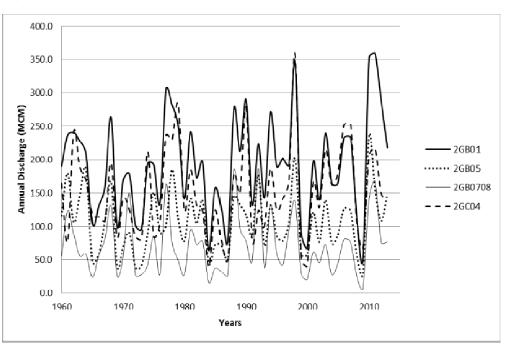


Fig. 3 Fluctuations in annual streamflows in four gauge stations of the Malewa rivers.

Q Metrics	2GB01	2GB05	2GB0708	2GC04
A 1 1	0.776	0.254	0.164	0.851
Annual totals	(0.438)	(0.800)	(0.870)	(0.395)
Datta dia da	-0.586	9.588	-18.903	2.318
Daily discharge	(0.558)	(< 0.0001)	(< 0.0001)	(0.02)
05	2.924	-2.518	-2.376	0.912
Q5	(0.003)	(0.012)	(0.017)	(0.362)
010	3.781	7.465	2.064	1.176
Q10	(< 0.0001)	(< 0.0001)	(0.039)	(0.239)
0.05	5.978	7.465	6.619	0.896
Q25	(< 0.0001)	(< 0.0001)	(< 0.0001)	(0.37)
050	8.394	-3.57	7.831	2.35
Q50	(< 0.0001)	(< 0.0001)	(< 0.0001)	(0.019)
075	5.467	4.636	11.616	0.342
Q75	(< 0.0001)	(< 0.0001)	(< 0.0001)	(0.732)
000	4.234	4.382	0.188	2.116
Q90	(< 0.0001)	(< 0.0001)	(0.851)	(0.034)
005	4.166	6.683	-7.623	2.495
Q95	(< 0.0001)	(< 0.0001)	(< 0.0001)	(0.013)

 Table 2
 Trends in streamflow characteristics of the gauge stations.

Z-scores and *p*-values (brackets) in bold are significant at 0.05 level.

#### 3.2 Trends in Daily and Annual Baseflows

The mean annual baseflows (MCM) of the four stations (1960-2013) were: 149.67 (2GB01), 72.38 (2GB05), 43.07 (2GB0708) and 100.47 (2GC04). The data also show wide fluctuations in diurnal and annual streamflows. The mean daily and annual baseflows are shown in Table 3.

As shown in Fig. 4, annual baseflows in the four gauge stations examined highly fluctuated over the last 43 years. There were no trends on daily baseflows for Gauge 2GB01 (Z = 1.113, p = 0.266). However, Gauges 2GB05 (Z = 13.903), 2GB0708 (Z = -16.326) and 2GC04 (Z = 6.368) showed increasing trends. Fig. 5 shows the BFI (Baseflow Index) fluctuations in the four gauge stations. The BFI for Gauge 2GB01 ranged between 0.76 and 0.90 (Mean = 0.85, SD = 0.03); 0.74 and 0.99 (Mean = 0.86, SD = 0.05) in Gauge 2GB05; and 0.74 to 0.92 (Mean = 0.82, SD = 0.04) in 2GB0708. Gauge 2GC04 had a BFI range of 0.68 to 0.84 (Mean = 0.79, SD = 0.03). All the four gauge stations show trends in BFI: 2GB01 (Z = 4.519), 2GB05 (Z = -6.861), 2GB0708 (Z = -16.326) and 2GC04 (Z = 5.593).

#### 4. Discussions

It is evident that there have been huge annual

fluctuations in streamflow. The fluctuations seem to suggest periodicity: a decrease in annual flows coincide with dry periods recorded such as that of 1965, 1969, 1973, 1984, 2000 and 2009. It is also indicative of extreme flows during the wet years of 1961, 1968, 1977, 1988, 1990, 1994, 1998 and 2010-2011. As such climatic variability seems to play an important role in the annual discharges. These fluctuations likely impacted decreased flow regime and increased scarcity of water during dry conditions; and intense rains and subsequent floods particularly in the absence of adequate vegetation cover.

Table 2 showed diversity in trends reflected as positive or negative changes. Overall, as shown in Gauge 2GB01, there seems to be no major changes in streamflow regarding both annual and daily total discharges. However, the data seems to suggest an overall increase in streamflow at low (Q75-Q95), median (Q50) and high flow (Q5-Q25) metrics of the watershed. The fewer the number of days in a year with greater flows recorded, the lesser the magnitude of positive stream flow trends. In the contrary, the more the number of days in a year with greater flows, the greater the magnitude of streamflow trends. However, median flows demonstrated higher magnitude of streamflow changes. Gauges 2GB05 and 2GB0708

Cauga	Mean		]	Minimum		Maximum		SD	
Gauge	Daily	Annual	Daily	Annual	Daily	Annual	Daily	Annual	
2GB01	4.75	149.67	1.37	43.32	8.68	273.81	1.80	56.88	
2GB05	2.30	72.38	0.82	25.85	4.91	154.90	0.94	29.53	
2GB0708	1.37	43.07	0.18	5.69	4.69	147.76	0.85	26.80	
2GC04	3.19	100.47	0.94	29.56	8.03	253.22	1.43	45.24	

 Table 3
 Daily and annual baseflows in the four gauge stations.

Daily data in m<sup>3</sup>/s; Annual data in MCM.

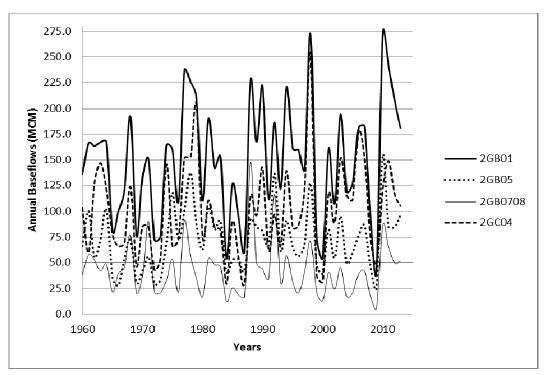


Fig. 4 Fluctuation in annual baseflows in four gauges of the Malewa rivers.

demonstrated a lot of diversity in either increasing or decreasing trend, while 2GC04 were either increasing or no trend at all. While 2GB05 and 2GC04 generally had an increase in daily streamflow, 2GB0708 had fluctuated changes in streamflow, with a positive change in Q10 to Q75. While no evidence exists to suggest a step change in discharge, the trends observed in all the four gauge stations but at different Q levels suggest that the Malewa rivers are experiencing effects of extreme climatic conditions and land cover change. These findings seem to suggest that degradation in land cover appears to create conditions of increased flow, although the intensity varies from sub-catchment to another. A big change in flow at 2GB0708 is difficult to interpret, although this may be due to inter-basin water transfer.

The contribution of annual baseflows to streamflow: 2GB01 (78%), 2GB05 (68%), 2GB0708 (61%) and 2GC04 (67%) seems to suggest that stream discharge for this area is much dependent on baseflows. The evidence that about 78% of the discharges are attributed to baseflows in 2GB01 shows that the hydrological regime is much dependent on ground water systems. Baseflow matched very well with stream flows as the results shows that no changes are happening at 2GB01 yet increases were observed at 2GB05 and 2GC04, while a decline was noted in 2GB0708. It is likely that water abstraction is a key factor experienced at the lower catchment where 2GB01 situates. Inter-basin water transfer could be

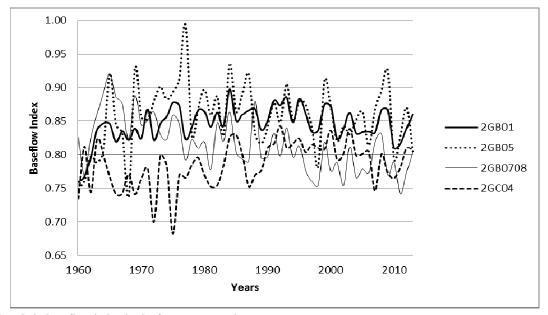


Fig. 5 Trends in baseflow index in the four gauge stations.

influencing reporting of decline at 2GB0708. Increased infiltration at 2GB05 and 2GC04 due to improved ground cover are likely factors driving enhanced baseflows. This is supported by BFI data showing increasing trends (2GB01 and 2GC04) and decreasing trends (2GB05 and 2GB0708).

As reported by Becht, R., et al. [29], the surface water inflow for the entire Malewa basin was 217 MCM over the period 1932-1997. The authors suggest that permits for river abstraction may have influenced the reported inflow. This is because the total permitted abstraction was then about 17% of the estimated surface inflows into the lake. As such, without abstraction, the Malewa inflow is much higher than reported. The findings from this study slightly differs from that reported by Everard, M., et al. [30] of an annual (153 MCM/year) and daily (4.84  $m^3/s$ ). However, as indicated by Åse, L. E., [31] and Becht, R., et al. [29], this varies from one study to another depending on the time period considered [32]. As regards trends, Kyambia, M. M., et al. [12] have reported significant increase in annual maxima at Gauges 2GB01, 2GB05, 2GB04 and 2GC04. The annual O95 at 2GB01 and 2GB05 had increasing flows while a decrease was observed for annual Q90

and Q97 at 2GB04 and 2GC04 respectively. As such, this variation points to climate change realities in terms of increased intensity and frequency of flows and the need to respond through different adaptation actions. These findings are similar to one reported by this study, although the unit of analysis differs.

An increase in streamflow is usually attributed to rainfall. In the Mississippi river, an increase (1940 to 2003) in flow was caused by increased baseflow attributed to land use change driven by soybean cultivation. A conversion of perennial vegetation to seasonal row crops and accompanying agricultural activities decreased evapotranspiration and surface runoff, and increased groundwater recharge, baseflow, and thus streamflow [33]. Increase in winter baseflows in the Tahe River and Duobukuer River watersheds of north-eastern China may be due to enhanced groundwater storage and winter groundwater discharge caused by permafrost thaw. It could also be due to an increase in the wet season rainfall [34].

#### **5.** Conclusions

This study has established that the Malewa rivers are experiencing fluctuations in streamflows over the years. While no step change was detected, nor trend at the outlet, there are significant fluctuations in annual streamflows and baseflows suggesting periodicity. Daily discharge and baseflow index have shown trends, both positive and negative in flows. It is suggested that the Malewa rivers are likely experiencing effects of extreme climatic conditions and land cover changes. Land cover degradation seems to create conditions of increased flow, with varied intensities per locality. In addition to the effects of climate and land cover change, water abstraction, inter-basin water transfer and increased infiltration are likely reasons for fluctuating flows in discharge and baseflow. Stream discharge is much dependent on baseflows suggesting the influence of infiltration. These fluctuations likely impacted on decreased flow regime and increased scarcity of water during dry conditions; and intense rains and subsequent floods in the absence of adequate vegetation cover. This study has provided evidence of increasing and decreasing trends in extreme and median flow metrics. There is thus need to regulate water use, improve soil cover and manage or adapt to the adverse effects of climate change.

#### Acknowledgements

Authors would like to sincerely thank the Water Resources Management Authority for providing secondary streamflow data. Many thanks go to Messrs. Joseph Munyao and Dominic Wambua of the Water Resource Management Authority, and also Zachary Maritim and Reuben Soy for their help in the map production. Authors are also much grateful to Messrs. Daniel Koros and Peter Muigai for their logistical assistance in the field.

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## Relationship between Land Cover Changes with Water Quantity in Lake Victoria—A Case Study of Mara River Basin in Tanzania

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**Abstract:** LV (Lake Victoria) is valuable to the East African sub region and Africa in general, sources of water for LV are from its catchment areas and tributaries e.g. Kagera and Mara Rivers on Tanzania part. Apparently, catchment areas in proximities of LV and on MR (Mara River), indeed on MRB (Mara River Basin) in particular, are experiencing increased anthropogenic activities such as mining, fishing, settlements, agriculture etc., which lead to increased water usage, land degradation and environmental pollution. Such activities threaten the sustainability of the environment surrounding MRB and impliedly LV and its ecosystem. The level of water in LV is reported to be declining threatening its extinction. This paper is reporting on a study undertaken to establish the relationship between land cover changes with ground water discharge from specifically MRB into LV over the period of 24 years, i.e. 1986 to 2010. Methodology used is assessment of vegetation changes by using remote sensing through analysis of TM (Thematic Mapper) Landsat Images of 1986, 1994, 2002 and 2010 ETM (Enhanced Thematic Mapper) Landsat images, from which respective land cover change maps were generated and compared with ground water levels from MRB. Results indicates that there is a significant decline of land cover and ground water flowing into LV from MRB, and that there is positive correlation between land cover changes and the quantity of ground water flowing from MRB to LV. This phenomenon is common to all tributaries of LV, thus leading to decline of water in LV. It is recommended that relevant government institutions should endeavor formulating policies to control excessive use of wetlands and drylands in the proximity of LV and MRB in particular, such that the flow of water to LV may be sustained.

Key words: Land Cover Changes, Ground Water, Remote Sensing, LV (Lake Victoria), MRB (Mara River Basin)

#### 1. Introduction

MRB (Mara River Basin) is composed of wetlands and drylands. Whereas the wetlands are used as water catchment areas for LV (Lake Victoria), drylands are used by surrounding communities for socio-economic activities such as settlements, mining, agriculture and so on.

Sustenance of LV water and its environment is critical, as it supports the Great Lakes countries in several ways such as provision of water for domestic use, agriculture, irrigation, fishing, transportation and others. As such, concerted efforts are required to ensure its sustainability. Sustainability of the LV entails sustaining its water, which in turn depends on water flowing into it from its respective tributaries

It is a well known fact that vegetation is related to ground water discharge [1-4]. This is because of its direct and indirect influence on soil type which together with that vegetation roots structure has the capacity of withholding ground water. However, as observed by Mutie, S. M. [5], ground water is directly related to vegetation species on the ground surface. This means that there is interaction between vegetation and groundwater discharge; there is evidence that changes in vegetation alter both recharge rates and water-table depths [6]. The effects

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of vegetation dynamics on ground water can either be positive or negative. Vegetation also intercept rainfall and leaks out water obtained from the rooted profile (including soil, regolith, saprolite and rock fractures), and also facilitates infiltration (by improving soil condition and creating surface storage opportunities) whereas plant root systems increase percolation rates by creating macropores. It is noteworthy that, tilled ground surface tends to retain more water than bare soil and improves conditions of water infiltration into the soil. Roots provide channels for the preferential flow of water through the unsaturated zone to the water table, particularly in low-permeability soils, thereby increasing recharge rate. Therefore holding of water in wetland depends on the vegetation and soil structure, which implies that there is relationship between vegetation and ground water. In general, vegetation cover holds ground water quantity. However, the capacity and the trend of vegetation holding water is dependent on soil and vegetation roots structure. This capacity and trend of withholding water for MRB is unknown.

The liberazation of the Tanzania economy has resulted into proliferation of various small, medium and large scale mining activities within the MRB, such as the North Mara Gold Mines and others which subsequently have attracted into population increase in the basin. For example, in the past 10 years, the population of over 800,000 people in the MRB is reported by Maro, P. S. [7]. The growing population relies on respective wetland and dry lands for their livelihood activities; all of which of have direct impacts on vegetation cover changes resulting into vegetation dynamics which subsequently alter ground water flowing into LV.

LV Water level is reported to be declining threatening communities relying on it for various socio-economic activities [8]. Water for LV emanates from both ground and surface water from its catchment areas and tributaries. Surface water is largely dependent on rainfall, which also has been declining due to global factors particularly climate changes [9].

Owing to the fact that land cover has ability of withholding ground water, it is logical relating the decline of water in LV partly due to changes in vegetation cover within its surrounding environments (including its tributaries and water catchment areas e.g. MR and MRB). However, the relationship of land cover and ground water quantity varies from one place to another, and the exact relationship between land cover changes with groundwater in the MRB is not known. This is the problem which this work was set to establish so that authorities responsible for overseeing the LVB e.g. LVBC (Lake Victoria Basin Commission), WWF (World Wildlife Foundation) and others may formulate strategies for effective sustainable management of MRB, implicitly for the LV water. The problem of vegetation changes and its effect on LV water quantity was conceived from a research study recommendation by Makalle, A. M. P. [10], which insisted that all concepts such as the biodiversity management, streams flow, water reduction activities, and the interrelationships between land cover and all water resources must to be further studied for developing sustainable protection mechanism for LV.

#### 2. Research Design

Due the fact that different vegetation types have varying capabilities of withholding ground water, it was logical directly relating the decline of water in LV with vegetation cover changes. Thus, in this regard, parameters of this study were land cover changes and corresponding ground water quantity. As there were no means of directly quantifying ground water, it was indirectly inferred from observed water levels of MR and relating it with analysis of vegetation cover changes over the study period. Subsequently, the methodology of this study was largely based on assessment of vegetation cover changes vis as vis MR water levels.

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#### 3. Methodology

The involved of methodology assessment vegetation cover changes in the MRB and relating it with respective water quantity in MR. Assessment of vegetation cover changes was effected using Remote Sensing Techniques. Satellite Images used were Landsat TM of the years 1986, 1994, 2002, and due to lack of data covering the study area, the study was compelled to use a slightly different sensor i.e. Landsat TM (Thematic Mapper) and Landsat ETM (Enhanced Thematic Mapper) satellite images for 2010, all the images were processed and classified into thematic classes typical of MRB area [11-13]. The methodology, however, disregarded storm water flowing into LV from Mara River. In this respect, water emanating from the entire MRB was sorely based on measured water levels at a gauge located at Kirumi Bridge (a point where MR enters LV (Fig. 1)), on assumption that the source of water for MR is exclusively from ground water. Apart from Kirumi bridge gauge station, there were other water level measuring gauges at stations within LVB such as at Grumet, Mbarageti, Mori, Mara Mines, Suguti and Musoma port for monitoring ground water flowing from respective rivers into LV. Water levels data from Kirumi gauge was then related with vegetation dynamics data as computed from land cover changes.

## 4. Reliability of Water Level Data observed at Kirumi Recording Station

Regarding water levels data from Kirumi gauge, it was noted that the data had gaps due following anomalies:

a. Ineffective Data Management

This was due to following reasons:

(i) The Data was being recorded by casual gauge workers who were not aware of the importance of the data they were recording, as such; they were not adequately motivated to comprehend that the data collected needed to be continuous [14].

(ii) Non-accountability arising from the fact that

gauge readers are answerable to their respective Regional Water Authorities, while the main custodian of the data is the LVBC [15, 16]. This was perceived as a mere administrative problem which had an effect of reduction of enthusiasm towards data recording.

b. Inflow and Outflow Nature of LV Water

It was noted that MR water has outflow and inflow characteristics. During outflow phenomenon, which depends on the forces acting on the lake, water moves some distance either northwards or southwards or Eastwards or Westwards. This phenomenon seemed to have affected gauge readings possibly (refer to Fig. 1 for the opening which facilitates inflow and outflow phenomenon). This is believed to have adversely influenced subsequent interpretations from the data, which significantly deviated from theoretical known situations [17-19].

The above anomalies then rendered ground water level data recorded at Kirumi gauge to be discarded. Instead, LV water quantity was inferred from partial water spatial extents of the lake as drawn from classified satellite images as extracted from relevant epochs.

Spatial extents were used to infer water quantity under assumption that quantity of water is directly proportional to spatial water extent and that water depth variation is insignificant (See Fig. 2 for spatial shift of LV water boundary over the study epochs).



Fig. 1 The Kirumi water level measuring gauge.

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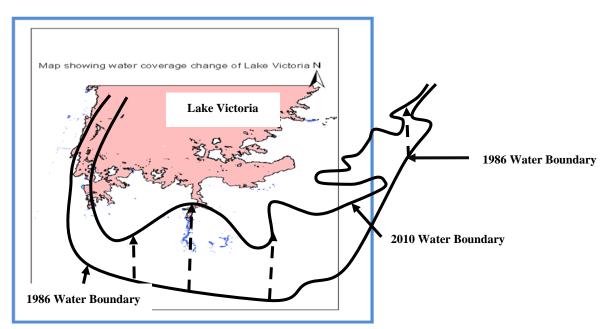


Fig. 2 Trend of spatial shifts of LV water extent (on Tanzania side) from 1986 to 2010.

#### 5. Data Processing and Analysis

This involved firstly adaptation of data for subsequent analysis and secondly quantification of land cover changes over the study period. With regard to satellite image data, they were first preprocessed for radiometric and geometric inconsistencies as well as restoration and secondly they were classified. Image classification was preceded by identification of potential thematic classes typical of MRB which are cultivated areas, bush land, grasses, water, bare land and swamps.

Training data were collected from field visit to the area and others were from existing data sources specifically topographic maps. Ground truth data was used in determination of class spectral signatures which was used in supervised classification of all images whose outputs are as presented in Figs. 3-6.

All the classification results were validated by accuracy assessment using the subset of the ground truth dataset as check points. Classification Accuracy obtained were over 80 percent, which was a testimony of the success of the classification exercise. This was followed by image differencing of classified images to determine land cover changes over time which inferred vegetation dynamics [20-24].

#### 6. Results

This involved a process of change detection of land cover in the MRB over the study period. As mentioned earlier on, land cover change detection was based on classified image differencing i.e. each classified image was differenced from its respective previous image. The results of image differencing are as shown in Table 1.

For purpose of simplifying subsequent analysis woodland and grass classes were combined formulating vegetation class; also water class was combined with swamps yielding water class; combination of classes was done to create manageable classes, in the course of this only four classes were left which were cultivated areas, vegetation, water and forests.

#### 7. Discussion of Results

The results demonstrated that water areas, forests and vegetation generally declined, while cultivated areas increased over the study period. This is testimony that there are excessive land use activities in the fringes of MR and MRB resulting from increased population in the area, which subsequently degrades

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Fig.3 Clasified Landsat TM of 1986.

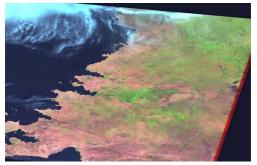


Fig.4 Clasified Landsat TM of 1994.

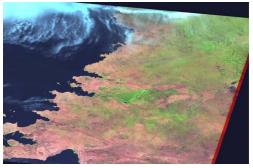


Fig. 5 Clasified Landsat TM of 2002.

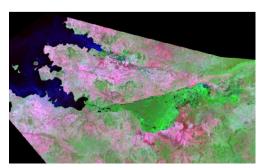


Fig.6 Clasified Landsat ETM of 2010.

Table 1Summary of vegetation changes.

	v	8	8	
Year	Cultivated	Water	Vegetation	Forests
1986	819	8,001	6,713	5,702
1994	1,229	8,324	5,980	4,262
2002	1,525	7,878	6,470	3,843
2010	4,820	6,566	1,484	2,929

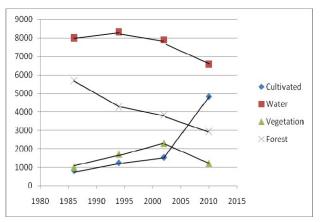


Fig. 7 Graphical plot of land covers dynamics.

the environment, specifically, the water catchment areas for LV. This has adverse effect on the sustainability of LV. Summary of land cover changes are as graphically presented as shown in Fig. 7.

Spatial water extents were directly linked with water quantity in relative terms, the results of which are shown in Fig. 7.

#### 8. Conclusions

In the light of the analysis above, it is being concluded that there is a notable decline of vegetation over the study period, which indirectly infers a similar decline of ground water flowing from MRB to LV over the same period. This phenomenon has a long term adverse effect of reducing the quantity of water in LV.

Additionally, more areas have been converted into cultivation particularly from 2002 onwards for increased socio-economic activities in the MRB leading to land degradation.

Land cover dynamics is prevalent in the environments of MRB threatening the ecosystem of the area. There is indication of a positive correlation between ground water and vegetation in MRB.

#### 9. Recommendations

Encourage effective land use management in the MRB area from either the local government level or institutional level so as to protect the area from environmental degradation. Effective land use

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management should be used to reduce further vegetation depletion in MRB and other catchment areas thereby indirectly protecting ground water flowing to LV from respective catchment rivers. As the water for LV is from both ground as well as surface water which is much dependent on availability of rainfall which in turn is affected by global climatic changes, it is recommended that a study be conducted to establish how climatic change have affected surface water quantity which flows from catchment rivers to LV.

#### Acknowledgement

The author thanks the LVBC for financial support which enabled the field work undertakings. LVBC offices in Mara region played a key role of providing pertinent literature which formed the knowledge base for undertaking this research. Special acknowledgements go to Ardhi University Directorate of Postgraduate Studies for logistical support.

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## General Principles on Environmental Policy in Industrial Units

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Abstract: Within the environmental policy framework, one could distinguish two categories, both of which aim at the protection of the environment. The first category is based on the concept of reducing the use of non-renewable resources and energy, as well as on the replacement of "poisonous elements" and "hazardous" types of energy. This second category includes different kind of actions which tackle the issue of unwanted by-products of production and consumption. More specifically, it includes measures that aim at: conversion of leftover substances or materials (e.g. elimination of poisonous gas), utilization of leftover substances or materials, waste avoidance, reduction of waste production, waste "dispersion" which includes "decentralization" (disposal) and "centralization" (collection). "Decentralization" describes the process of controlled diffusion (emission) of waste in water, air and soil. "Centralization" involves waste collection into designated storage premises, which of course need to comply with certain requirements and regulations.

Key words: Environmental policy, methodology framework, product, production.

#### **1. Introduction**

Within the framework set by the two basic categories regarding the protection of the environment, a series of measures will be examined that could apply to businesses and industrial units in particular. Those measures could be described as "Measures of Environmental Policy" and include for instance: the production process inside the industrial unit, the identity and composition of the products, their number and life-cycle, the choice of raw materials and by-products, the ways and methods of production and waste management [1].

#### 2. Product and Production Process

Environmentally friendly product (eco-friendly) is the product that its production process minimizes the use of natural resources and energy and also inflicts reduced or zero waste.

Thus, the identity and composition of the product have immediate effect on the environment. Its identity

and composition involve the shape, material, size, color, scent, function and its impact (e.g. noise) and so on. Furthermore, the product packaging is of vital importance, as it can be harmful for the environment [2].

Consequently, one could say that the nature of a product includes all those characteristics that constitute "quality". Product quality is initially a technical term, which however has economic and ecological implications. To be more specific, from an ecological aspect, the identity and composition (quality) of the product directly affect the production process, use and waste processing.

The production of specific products defines to great extent the raw materials, the semi-finished materials and the energy that will be used during this process. The above statement however, allows some flexibility. As a result, in chemical technology, sulfuric acid can be formed using a series of raw materials such as gypsum and sulfate minerals etc., through various methods each time though. During the selection of raw materials and production process, one should take under consideration not only the cost, but how

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"friendly" the product is towards the environment too [3].

In the mechanical engineering and production technology field, the nature of the product specifies the raw materials and semi-finished materials necessary for its production. This rule, however, applies to the kind of the raw materials, not to the quantity needed.

Thus, it has been calculated that by changing the type of milk packaging could contribute to 18% less material use, while the bottling industry in Germany could reduce the weight of bottles by 49% if single-use bottles were used. In the metal products industry—besides the manufacturing or production process—the nature of the product plays a crucial role. Various technological systems (both software and hardware) are being employed and targeting to material decrease [4].

Additionally, in the cosmetics industry, the specification of ingredients and directions about function on the finished product are of great importance. Raw materials that have been used can be either natural or chemical or both. There is no much doubt that the nature of the product affects to great extent the nature and quantity of raw materials. There is some degree of freedom in the making process though. The correct choice of production process and product processing can generously contribute to environmental protection (e.g. reduce of dissipated energy).

Moreover, it should be mentioned that economic and ecological impact could significantly be reduced, if during the decision making process regarding the composition, factors that lead to recycling and avoidance of waste production are taken into account. Furthermore, waste processing and storage are costly procedures.

It is easy to understand that the negative impact on the environment is the result of both the quantity of the produced goods, having been produced in a certain time period and the overall time spent for production and consumption. In other words, it is the amount of products and the production process that contribute to the preservation of the environment [5].

#### **3. Production Methods**

Within the environmental policy framework, enterprises shouldn't only focus on the composition of the product. On the contrary, they should take into consideration all the individual stages through the final product passes. Environmental pollution is the result of the production of each individual product inside the industrial unit and it piles up either because of waste production, hazardous substances, emissions etc.. As a result, all the above create negative environmental impact caused by this one industrial unit.

The state or the industrial unit itself set (or have the ability to do so) specific limits on industrial emissions. These limits apply to all emissions per time unit. Consequently, as soon as it becomes obvious to the unit that it approaches or exceeds those limits, it can either reduce the production or intervene in the production process. In the second case, pollutants could be decreased if, for example, part of the necessary products were purchased from another unit which—at least geographically—belonged to another region [6].

It is necessary that the typical decision-making model about production methods, which most of the times is profit oriented, embrace additional regulations about the protection of the environment. Thus, starting with maximizing the production function, that is the contribution of all the factors in the time period, one should add beyond the classical constraints such as the potential or the availability of products, the following limitations too: the use of the necessary resources should not exceed the sum of the initial ones together with the reused (recycled) materials, substances harmful to the environment should not exceed the limits.

Assume that it start from a linear production function. After taking into account the variable cost of

production and waste processing, then the optimal production can be calculated with relative precision. The mathematical function can become particularly complex if all the substances harmful to the environment are taken into consideration. In this case, one must consider all pollution factors per unit of production and time. A common denominator should be created with the aid of simulation coefficients. This latter procedure is covered under the "Ecological Accounting". This thesis does not look in depth the presentation of the model of such a mathematical function. Its target is to present a production process that includes the ecological dimension without focusing on the theoretical approach of the problem [7].

#### 4. Selection of Product Life-cycle

Environmental damage is—among other reasons—the result of the product life-cycle. As a rule, the longer the life-cycle of a product, the lesser the damage of the environment, caused by the production and consumption of the product.

"Life-cycle" could be the time or duration of a product, which either as means of production or as a good for consumption, fits the purpose for which the product had been created, before it becomes useless (waste). The product lifespan depends on the product composition. The life-cycle of a product regarding its technology should guarantee a minimum service life, which can be achieved due to the characteristics and specifications which have been given to the product. Undoubtedly, product's lifespan is directly affected by the "intensity" of its use. Consequently, driving at continuous high speeds could ruin the engine of the car much sooner than driving at "regular" speeds [8].

The "Economic" life-cycle of a product is different from the technology life-cycle and depends to great extent on the values each individual sets. As a general rule, the sales department's strategy aims at shortening the "economic" lifetime of a product, which is quite often considerably shorter compared to its service lifetime. The fact that the entire industry uses "trends" as a motive, leads to withdrawal and destruction of products, which otherwise would function properly. The words once said by a member of the general motors board of directors were very interesting. He pointed out, in a speech he made years ago, that the pre-planned product aging is another expression of the word "progress". Without a doubt, from the sustainability standpoint, statements such as the one above are quite wrong.

Extending the life of products, in order to achieve some of the ecological and economic targets, requires change in the mentality of both the producer and the consumer.

Consumers shall gradually turn their attention to products with long lifespan, while industries, taking into account the economic and social consequences that may occur to the industrial unit due to wrong environmental policies, should gain power in the market by distributing products with long lifetime.

#### 5. Choosing the Right Production Method

The final product (its composition, properties etc.) largely depends on the method it was produced. Generally speaking, production of mechanical products, that is products coming from the modification of raw materials or semi-finished products usually are products of the same composition as the original ones.

The possibilities of choosing other materials and/or completely different methods of production are limited. The undesired negative effects on the environment can be controlled relatively easy. So, for instance, it is possible that remains of metal processing to be reused in production, noise can be reduced with noise-absorbing materials, temperature can be controlled with thermal insulation materials and so on. Contrary to the production of mechanical products. the choice of the method in chemical-technology production has immediate effect on the qualitative and quantitative composition of the final product. The potential environmental effects caused by those methods can be harmful or even disastrous. As a result, phenol trichloride can be produced—a product used in the cosmetics industry—in two different ways. The first way, which is relatively safe, is to use low temperature and high pressure [9].

The second method, which is definitely more dangerous, uses high temperature and low pressure. In this case, performance grades are higher compared to the first method, but it could lead to undesired results. A boiler overheating led to the tragic Seveso accident, when the extremely poisonous substance dioxin diffused into the atmosphere, causing catastrophic environmental damage. Moreover, it should be taken into consideration that dangerous materials used as raw materials and intermediate goods occurred during the production process must be transported and stored with the maximum care, so as environmental accidents be avoided.

Finally, comparing the composition of the product to the production method, one could claim that the production method defines the remains of the production process, while the composition of the product is responsible for the consumption waste, if it is about consumption goods.

While selecting the raw materials one must take into account the raw materials and semi-finished products as well as the types of energy necessary to the production process and function of the final products. Each business should be aiming at replacing materials and/or energy harmful to the environment with sustainable materials and eco-friendly forms of energy.

Generally, this replacement means to change the production methods. However, there are exceptions to the rule. As a result, without changing the production process, non-cyanide electrolytes can be preferred over cyanide ones. Similar replacements could happen not only in the chemical-technology production, but could relate to the composition of the product. Consequently, in the telecommunications industry, copper wires could be replaced by optical fibers [10].

#### 6. Recycling

A measure of vital importance, which nowadays is becoming more and more necessary, is recycling. The definition of the word describes the process of converting waste materials either from production or consumption into new materials and objects that can be used again in the production stream. There is a number of recycling variations such as: reuse: waste materials or remains are used again for the original purpose they had already been produced (bottles); repurpose: waste materials or remains are channeled with or without processing into the original process (e.g. scrap iron pieces for steel production); further use or exploitation: waste materials or remains are used with or without biological or/and chemical processing in a new production process to fulfill a new purpose (e.g. old car tires for new rubber flooring, hot air turbine waste for heating a household).

Depending on the origin and the place of recovery of the waste, there is: internal recycling: waste materials or remains from the industrial unit are used afresh in the production process in the same industrial unit; inter-industrial recycling: recycling as a result between industrial units, for instance semi-finished products used in an industrial unit are processed further by another unit. Waste materials produced during the last process are given back to the original unit to be used as raw materials. Interconnections such as the one above can become really complicated.

Examining recycling in relation to the environment, it can be noted that recycling protects the environment and reduces the use of the raw materials. As a result, in Germany, 70% of the need in antimony comes from recycling. At the same time, returning waste materials to the production stream, could contribute to less environmental impact. Negative impact as a result of waste caused by production and consumption can be highly hazardous. Scarcity in raw materials and their price rise are two basic reasons why recycling is so compelling. Leaving speculation aside, future price increase remains an indisputable fact.

Furthermore, an equally important reason why industries should examine the potential of introducing recycling within the industrial unit is the public opinion. Also, the unit has to deal with the regulatory framework about sustainability and all the strict measures—current and future ones—imposed by the law. In case the unit does not comply with those measures, it faces penalties, which vary from fines to license revocation.

The technological potentials of recycling are not without limits. Recycling performance and rates can vary. In iron and steel industry, recycling rates are, for instance, 32%, while in textile industry reach 5%. Nevertheless, today's technology allows waste exploitation of solid, liquid and gas waste materials. For example, recycled plastic can make thermal insulation materials and new plastic objects, while from soap industry waste glycerin can be produced and refineries exhaust gas can be used to produce sulfuric acid. Waste heat exploitation and regeneration of radioactive rods in designated premises are also significant. Overestimation, however, of the recycling advantages could lead to wrong conclusions.

Thus, waste treatment and purification could give drinking water and result to less environmental damage from liquid waste, but the remaining material are still a danger for the environment [10].

#### 7. Conclusion

As a conclusion, before deciding on adapting a particular recycling process, one should consider the environmental impact that the introduction of that specific method will bring in relation to how effectively that method protects the environment in practice.

The company's decision on which recycling method is the most effective relies upon the cost of the recycling method. Very briefly, the cost of recycling should be compared to the cost that would arise from waste disposal and the cost of raw materials needed in production process, provided that the raw materials were original materials and not fed back to production.

The overall recycling cost is the sum of collection, segregation, preparation and processing of waste. Special attention must be given to the usually high segregation and transportations cost. Cost is primarily based on the geographic and time dispersal of the waste. Problems, usually serious, appear in the consumption sector, and more specifically in the waste sorting. Efforts are already being made to ensure that waste sorting happens inside the households (e.g. glass and aluminium object are placed in special bins).

In the field of inter-industrial recycling, waste "stock markets" are of great interest. These stock markets play a mediating role between waste seller and buyer and provide with the assistance of "information banks" plenty of useful information. It should be marked, that the company which uses recycling faces some further risks. Recycling as a method turns useless material into financial goods. This means that whoever has undertaken this task could potentially affect—at least to some extent—the prices of those goods.

During the discussions about recycling, the company should take into account the fact that the technical requirements regarding waste disposal will keep becoming stricter by the law. To meet these requirements, it is very likely that advanced technology must be used, a fact that could contribute to further rise of the waste disposal cost. Moreover, it must be taken into consideration that recycling premises generally function with satisfactory economy, while experience shows that recycling results to significant amounts of energy savings and resource conservation.

Finally, it must be mentioned that it is about time to took recycling seriously in Greece and Cyprus. The efforts should start from the industrial units, already at the research and product development stages. The products must be made with as less non-recycling materials as possible.

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Volume 7, Number 1, January 2018

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