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Full Length Research Paper

Modelling dynamics of organic carbon in water hyacinth Eichhornia Crassipes (Mart.) Solms artificial wetlands

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The role of water hyacinth on removal of organic carbon was investigated in free water constructed wetlands. A model incorporating the activities of suspended and biofilm biomasses was developed in order to simulate the various processes involved in the transformation and removal organic matter in the water hyacinths constructed wetland. The results show that the major processes governing the organic carbon transformation and removal in a water hyacinth constructed wetlands system are sedimentation of solids (56.5%), regeneration of organic carbon (25.5%), oxidation of organic carbon to carbon dioxide (6.4%), plant decay (4.4%) and uptake of organic carbon by heterotrophic bacteria (4.2%). The total permanent removal of organic material was 26.7% of the total influent chemical oxygen demand (COD). The COD removal efficiency of the model when the effect of biofilm was considered was 40.5%. However, in absence of biofilm activities, only 34.0% of COD was removed. This confirms the significance of the water hyacinth roots as an attachment media, which is extremely biologically active in assisting the organic carbon removal in the water hyacinth constructed wetland.

Key words: Water hyacinth, artificial wetlands, modelling, organic carbon.

INTRODUCTION

Water hyacinths have demonstrated a great potential for purification of wastewater through physical, chemical and biological mechanisms (Mayo and Kalibbala, 2007). Artificial wetlands have been used for secondary treatment (Gersberg et al., 1985; Vymazal, 2010) and for specific tertiary treatment such as removal of nitrogen (Senzia et al., 2004) and bacteria (Kalibbala et al., 2008; Mayo and Kalibbala, 2007; Vymazal, 2010). Successful case studies indicate that wetlands significantly reduce organic matter, suspended solids (SS), pathogens, heavy metals and excessive nutrients such as nitrogen, phosphorus and heavy metals from wastewater (Yi et al.,

2009; Mugasha, 1995; Mayo and Kalibbala, 2007; Mayo and Bigambo, 2005; Vymazal, 2010; Mayo et al., 2013). The deviation in chemical, biological, and physical characteristics among wetland ecosystems and complications in understanding and predicting the efficiency of such systems, have motivated the development of artificial wetland systems (Barrie, 2002). As a result, for over 50 years, natural and artificial wetlands have been engineered for wastewater treatment (Senzia, 2003) particularly for small and medium sized communities and isolated areas in Europe and the USA where over 700 artificial wetlands have been constructed

(Water 21, 2000).

Artificial wetland systems use floating or submerged aquatic plants in the treatment of industrial or domestic wastewater such as *Eichhornia crassipes* (Mayo and Kalibbala, 2007), *Phragmites mauritianus* (Senzia et al., 2004; Bigambo and Mayo, 2005) and *Typha domingensis* (Senzia, 2003; Nakibuule, 2013; Okurut, 2013). Until recently, most of the floating aquatic plant systems for wastewater treatment have been water hyacinth systems (USEPA, 1988). *E. crassipes* have been used in a variety of experimental and full-scale systems either for removing algae from oxidation pond effluents or for nutrient removal following secondary treatment in tropical regions (USEPA, 1988; Polprasert and Khatiwada, 1997). Other beneficial functions of wetlands include supplementary wildlife and human use benefits resulting from treatment wetlands. However, some researchers have also pointed potential problems of wastewater treatment in wetlands such as bioaccumulation of toxins and transmission of diseases (Knight et al., 2000; Muyodi, 2000).

Numerous studies have verified the usefulness of constructed wetlands (Barrie, 2002), and have provided a database for the development of design manuals for wastewater treatment with artificial wetlands (Reed et al., 1995). In spite of these advances on removal mechanisms of organic matter in constructed wetlands, models have failed to adequately predict performance of wetland systems. Organic carbon removal variability has tended to be influenced by a variety of factors resulting in its irregular removal pattern, which has complicated the optimization of organic carbon removal in artificial wetlands. The objectives of this paper are to determine and quantify the role of water hyacinth *E. crassipes* (Mart.) Solm for removal of organic carbon and to develop a mathematical model incorporating the activities of suspended biomass and bio-film on plant roots on removal rate of organic carbon in artificial water hyacinths wetland.

METHODOLOGY

Layout of plant and data collection

Two pilot wetland units of dimensions 7.5 m long, 3.5 m wide and 0.85 m deep were constructed adjacent to primary facultative pond at the University of Dar es Salaam (Figure 1). The location of the wetland units was at latitude 6°48'S and 39°13'E, 30 m to the north where the mean monthly air temperature of the site varies between 23 and 28°C with a mean value of 26°C (Mayo, 1989). The wetland units, which were planted with *E. crassipes,* were supplied with wastewater from the primary facultative pond at an average flow rate of 1000 L/day.

Flow was measured at the inlet and outlet of the water hyacinth unit with the aid of graduated container and a stopwatch. Samples of examination of water quality parameters were collected at the inlet and outlet of the system at 10:00 a.m once every two days. Samples were also collected along the length and depth of the wetland unit from sampling ports installed at the sides of the wetland units. Collections were done in a clean 250 ml sampling

bottles and samples were immediately taken to the water quality laboratory at the University of Dar es Salaam for examination. Samples containing settleable solids were blended with a homogenizer and preliminary dilutions were made for wastes containing high chemical oxygen demand (COD) to reduce the error in measuring small sample volumes. All physical-chemical parameters were determined in accordance to Standard Methods for the Examination of Water and Wastewater (1996). Analyses of samples were conducted within 2 h of sampling. Measurement of temperature and pH were done *in-situ* using pH meter (Metrohm pH meter, model 704). Dissolved oxygen (DO) concentrations were determined *in-situ* using a digital DO meter (YSI DO meter, model 50B). Chemical oxygen demand was measured using closed reflux method in accordance with Standard Methods for the Examination of Water and Wastewater (2012). Surfer 7.0 software was used to produce contour variation of the physical and chemical parameters with time, along the length and across the depth in the wetland unit.

RESULTS

Variation of physical chemical parameters

Concentration of dissolved oxygen (DO) in the wetland decreased from an average of 2.16 mg/l in the influent to 0.51 mg/l in the effluent. Dissolved oxygen decreased because the rate of its consumption by microorganisms for biodegradation of organic carbon was higher than its rate of production in the system. It is worth mentioning that water hyacinth plant roots generate only a small portion of the oxygen required for oxidation of organic carbon (Senzia, 2003). Unfortunately, interfacial diffusion of oxygen from the atmosphere and the production of oxygen by algae photosynthesis were suppressed by the dense plant cover, which reduced the surface gas-exchange and wind-induced turbulence.

For similar reasons, the average pH in a water hyacinth wetland decreased from 7.87 to 7.26 because of complete cover provided by the plants on the water surface resulting in prevention light penetration, consequently inhibiting algae photosynthesis activities in the wetland. Consumption of CO_2 decreased as a result of inhibition of growth of algae resulting in shift of Equation (1) towards the right. This has resulted in reduction of hydroxyl ions, thus lowering the pH of wastewater.

$$CO_2 + OH^- \Leftrightarrow HCO_3^-$$

(1)

The wetland system was 0.8°C colder at the effluent compared to the influent because of plant biomass mat, which prevented the direct solar energy from increasing the temperature of the wetland unit. This has a negative effect on the system as temperature has a significant influence on the rate of uptake of organic carbon, the interfacial gas transfer and settling rate of biological solids (Metcalf and Eddy, 1995).

Table 1 shows that COD concentration in the wetland
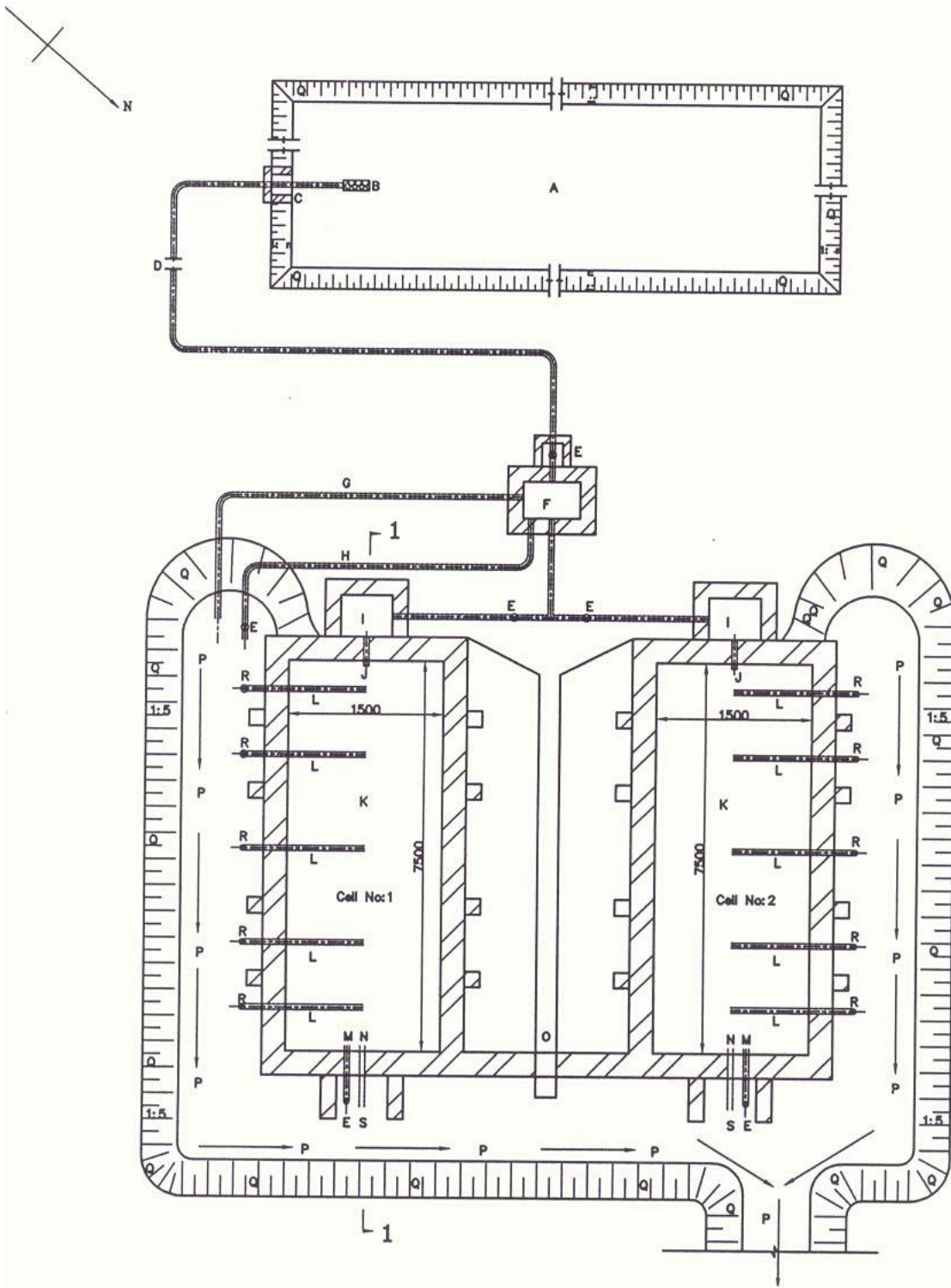
Figure 1. Layouts of the experimental wetland system.

decreased from an average of 210 mg/l in the influent to 121 mg/l in the effluent, which is equivalent to 42% removal efficiency. The variation of COD along the length and depth of the wetland unit shows that COD decreased from 215 mg l^{-1} near the influent to about 95 mg l^{-1} near the effluent (Figure 2). COD concentration decreased gradually along the length and appears to increase towards the bottom of the wetland unit. There was

Table 1. Variation of physical-chemical parameters in water hyacinth wetland.

No	Parameter	Influent		Effluent	
		Range	Mean	Range	Mean
1.	pH	7.75~8.14	7.87	7.10~7.48	7.26
2.	Dissolved oxygen (mg/l)	1.65~2.78	2.16	0.36~0.68	0.51
3.	Temperature (°C)	26.5~27.7	26.9	25.6~26.5	26.1
4.	Chemical oxygen demand (mg/l)	184~228	210	75~135	121
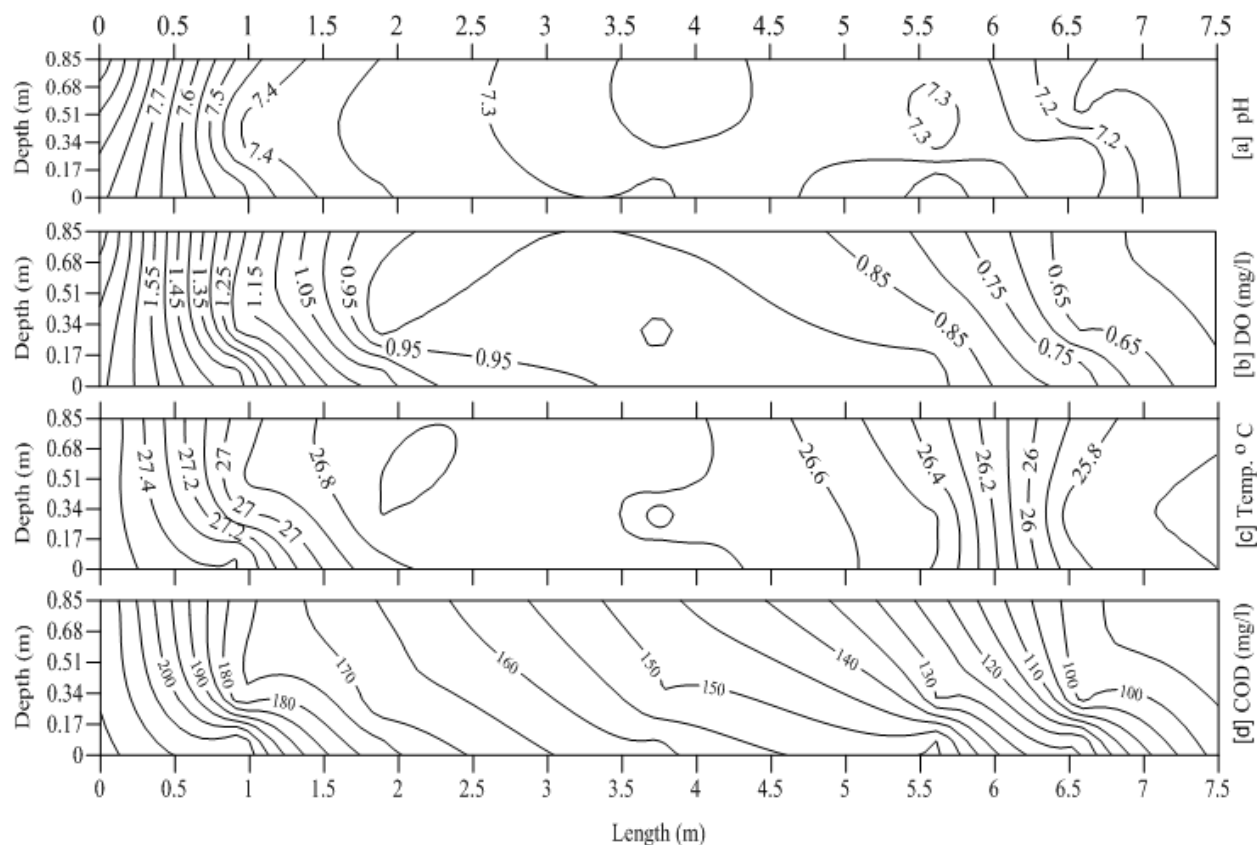
Figure 2. Variation of (a) pH (b) Dissolved oxygen (c) Temperature and (d) COD with the length and depth of the wetland.

evidence that COD was increasing with the depth of wetland unit, which is an indication of settling of organic particles to the benthic layer.

Model development

Conceptual model and organic carbon mass balance

The developed model incorporated activities of biofilm and suspended biomass on the transformation and removal mechanisms of organic carbon in the wetland unit. The model took into consideration the state variables substrate COD, COD in benthic layer and plant organic carbon as the major forms of organic carbon in the wetland unit. The transformation mechanisms that were considered in the model include oxidation of COD to carbon dioxide (CO_2), uptake of organic carbon by heterotrophic bacteria, regeneration of organic carbon, sedimentation of organic carbon, plant decay, generation of methane (CH_4) and release of carbon dioxide from the sediment. The transformation and removal mechanisms were conducted by attached root biofilm and suspended bacteria biomass.

The conceptual model that includes suspended and biofilm biomass activities influencing the organic carbon transformations and removal were developed (Figure 3). The model illustrates the material flow in and out of the
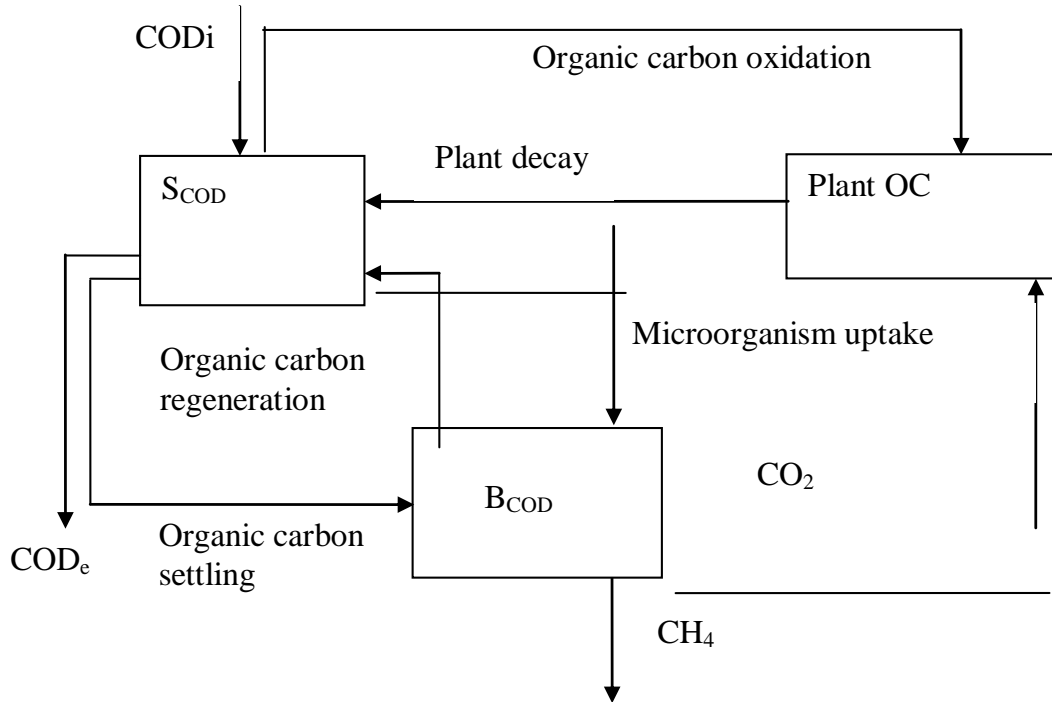
Figure 3. Conceptual model for organic matter transformation in wetland.

state variables substrate COD (S_{COD}), plant organic carbon (plant OC) and COD in benthic layer (B_{COD}), respectively.

The system was considered as a continuous plug flow hydraulic regime. The rate of change of COD concentration with time $\dfrac{dC}{dt}$ in wetland was based on the design assumption of the plug flow hydrodynamics and the first-order organic matter removal kinetics (USEPA, 1988) as shown in Equation (2).

$$\frac{dC}{dt} = -k_T t \tag{2}$$

In which t = hydraulic retention time (day^{-1}); and k_T is temperature-dependent first-order reaction rate constant at wastewater temperature of T°C, which is given as

$$k_T = k_{20} \theta^{(T-20)}$$

Where k_{20}= Reaction rate constant at 20°C and θ = Temperature coefficient. Equation (3) is obtained on integrating Equation (2).

$$C_{eff} = C_{inf} e^{-k_T t} \tag{3}$$

Where C_{eff} and C_{inf} are concentrations of COD in effluent in mg l^{-1} and influent in mg l^{-1}, respectively.

In analyzing the main influential mathematical expressions, mass balance equations of all organic materials were developed. The entire material balance that encompasses all forms of substances produced and consumed in biochemical processes, accumulations, inflows and outflows were considered. In this model, a steady state system was assumed. Equation (4) defines the overall mass balance equation for transformation and removal of organic carbon within the boundary of the water hyacinth constructed wetlands.

$$\left(\frac{dOC}{dt} = COD_{inf} - K_{ox} + K_{reg\,COD} + K_{dec} - K_{up} - K_{sd} - COD_{eff} \right) \tag{4}$$

Where dOC/dt = Rate of change of organic carbon concentration (g m^{-2} day^{-1}); K_{up} = Uptake rate of organic carbon by heterotrophic bacteria (g m^{-2} day^{-1}); K_{ox} = Organic carbon oxidized to carbon dioxide (g m^{-2} day^{-1}); $K_{reg\,COD}$ = Organic carbon regenerated from the sediment (g m^{-2} day^{-1}); K_{sd} = Sedimentation rate of particulate organic carbon settling (g m^{-2} day^{-1}); K_{dec} = Plant decay rate (g m^{-2} day^{-1}); COD_{inf} = Chemical oxygen demand load in influent (g m^{-2} day^{-1}); COD_{eff} = Chemical oxygen demand load in the effluent (g m^{-2} day^{-1}).

The oxidation term (K_{ox}) in Equation (4) is the amount of organic carbon oxidized to CO_2 (day^{-1}) by heterotrophic bacteria and is influenced by the concentration of dissolved oxygen and temperature in accordance with Equation (5).

$$K_{ox} = \left[(k_{20} + k_b) \left(\theta^{(T-20)} \cdot \left(\frac{DO}{K_{DO} + DO} \right) \right) \right] S_{COD} \tag{5}$$

Where K_{ox} = Oxidation term (g m^{-2} day^{-1}); k_{20} = First order reaction rate constant (day^{-1}); k_b = Biofilm constant (day^{-1}); θ = temperature coefficient; DO = Dissolved oxygen concentration (g m^{-3}); K_{DO} = Half saturation rate constant for dissolved oxygen concentration (g m^{-3}); B_{COD}= COD concentration (g m^{-2}).

The substrate consumption rate by the biofilm bacteria K_{sb} is defined by Equation (6).

$$K_{sb} = k_b C_t \tag{6}$$

Where C_t = Substrate concentration at time t (g m^{-2}). Biofilm constant k_b was modelled using Equation (7) in accordance with Polprasert and Agarwalla (1994).

$$k_b = a_s \left(\frac{\alpha \lambda}{\alpha + \lambda} \right) \tag{7}$$

a_s is specific area for biofilm activity (m^2 m^{-3}) which is calculated from the sum of the surface area of the bottom, sidewalls of the wetland and the roots of the plants in accordance with Equation (8).

$$a_s = \frac{1}{h} + \frac{2}{W} + \frac{2}{l} + \frac{R_S}{h} \tag{8}$$

The term α (m day^{-1}) in Equation (7) is defined by Equation (9).

$$\alpha = \frac{D_s}{L_S} \tag{9}$$

Where D_s = Diffusivity of the substrate through the liquid (m^2 day^{-1}); L_s = the liquid sub-layer thickness (m). The liquid sub-layer thickness L_s was considered by Williamson and McCarty (1976) to consist of two layers, namely: L_o the outer liquid sub-layer and L_b the inner layer. The inner layer is considered constant with a dimension of 56 μm. Experiments on column reactor conducted by Rittmann and McCarty (1980) revealed that the liquid sub-layer thickness (L_s) ranged from 1.198×10^{-4} to 2.26×10^{-4} m for superficial flow velocities between 3.22 and 43 m day^{-1}.

Coefficient λ in Equation (7) is mathematically defined by Equation (10).

$$\lambda = \tanh(\phi) K_{fa} \frac{L_f}{\phi} \tag{10}$$

Where K_{fa} = First order biofilm rate constant (day^{-1}); L_f = Biofilm thickness (m) which range from 1.462×10^{-4} to 1.615×10^{-4} in water hyacinth wetlands (Polprasert and Agarwalla, 1994). The characteristic biofilm parameter (ϕ) is defined by Equation (11).

$$\phi = \sqrt{\left(\frac{k_{fa} L_f^{\,2}}{D_f} \right)} \tag{11}$$

The uptake rate of organic carbon by heterotrophic bacteria in Equation (4) is influenced by forcing functions such as dissolved oxygen, quality of substrate, temperature and pH within the system of growth. The uptake rate of organic carbon by heterotrophic bacteria in g m^{-2}day^{-1} is given by Equation (12).

$$K_{up} = \frac{S_{COD}}{Y_{max}} \left[\mu_{max} \left(\frac{S_{COD}}{K_{SCOD} + S_{COD}} \right) \left(\frac{DO}{K_{DO} + DO} \right) \left(\frac{K_{pH}}{K_{pH} - \left[10^{(pH_{opt} - pH)} - 1 \right]} \right) \theta^{(T-20)} \right] \cdot \tag{12}$$

Where μ_{max}= Maximum growth rate of heterotrophic bacteria (day^{-1}); Y_{max} = Maximum substrate utilization rate (mg biomass/mg COD); K_{pH} = Limiting value for pH; pH_{opt} = Optimum pH; K_{SCOD} = Half rate saturation constant for COD concentration (g m^{-2}); S_{COD} = COD concentration (g m^{-2}).

The decay of plants K_{dec} depends on the uptake of inorganic carbon and mortality of the plants. Plant decaying rate is modeled using first-order kinetics in accordance with Equation (13).

$$K_{dec} = P_{OC} D_{rate} \tag{13}$$

Where K_{dec} = Plants decay rate (g m^{-2}day^{-1}); P_{OC} = Uptake of organic carbon by plants (g m^{-2}); D_{rate} = Plant decay constant (day^{-1}).

The sedimentation term K_{sd} (g m^{-2}day^{-1}) is considered to be the sum of sedimentation in the root zone (S_{root}) and plain sedimentation in the liquid zone (S_w) and is represented by Equation (14).

$$K_{sd} = S_{root} + S_w \tag{14}$$

Sedimentation in the root zone (S_{root}) is defined by Equation (15). The reaction rate coefficient is based on the cylindrical collector (Logan et al., 1993) because the root of the water hyacinth plants is assumed cylindrical.

$$S_{root} = \frac{4}{\pi} \eta \frac{\alpha u_f (1-p)}{d_c} \tag{15}$$

The parameter η is a single collector removal efficiency calculated from Stokes' law in accordance with O'Melia (1985) and is defined by Equation (16).

$$\eta = \frac{\left(\rho_p - \rho_w\right)gd^2{}_p}{18\mu_T}$$

(16)

Where g = Acceleration due to gravity (m s^{-2}); ρ_p = Density of particle (kg m^{-3}); ρ_w = Density of water (kg m^{-3}); d_p = Diameter of settling particle (m) which ranges from 0.5 to 40 µm (Metcalf and Eddy, 1995); α = Sticking coefficient of the particle which ranges from 0.0008 to 0.012 (Khatiwada and Polprasert, 1999); u_f = Q/A = Flow velocity of the liquid (m s^{-2}), where Q and A are flow rate and surface area; P = Porosity of the media in percentage, which varies from 95 to 96.5% (Kim and Kim, 2000); D_{co} = Diameter of collector (m) which ranges from 0.0006 to 0.003 (Reddy, 1985).

For temperature above 20°C the viscosity of water (µ) varies with temperature in accordance with Equation (17) (Weast, 1981).

$$\log \frac{\mu_T}{\mu_{20}} = \left(\frac{1.3220\,(20-T) - 0.0010539\,(T-20)^2}{T+105}\right)$$

(17)

Where μ_T = Viscosity of water at T°C (kg m^{-1} s^{-1}); μ_{20} = Viscosity of water at 20°C = 1.002×10^{-3} (kg m^{-1} s^{-1})

Plain settling in the liquid zone follows Stoke's law in accordance with Equation (18).

$$S_w = \left(\frac{\rho_p - \rho_w}{18\mu}\right)gd^2{}_p$$

(18)

The total sedimentation term (K_{sd}) in the wetland unit is then defined by Equation (19).

$$K_{sd} = \left[\frac{4}{\pi}\left(\frac{\rho_p - \rho_w}{18*\mu}\right)gd^2{}_p u_f\left(\frac{1-P}{D_{CO}}\right) + \left(\frac{\rho_p - \rho_w}{18*\mu}\right)gd^2{}_p\right]S_{COD} - (19)$$

The mass balance for COD$_{sink}$ term (g m^{-2}) is represented by Equation (20).

$$\frac{dSink_{COD}}{dt} = K_{up} + K_{sd} - K_{reg_{COD}} - K_{CO_2} - K_{CH_4}$$

(20)

The rate of methane generation (K_{CH4}) is influenced by anaerobic condition in the COD sink. The generation rate of methane is modelled using first order kinetics in accordance with Equation (21).

$$K_{CH_4} = D_m Sink_{BOD}$$

(21)

Where K_{CH4} = Generation rate of methane (g m^{-2} day^{-1}); COD$_{sink}$= Sink COD term (g m^{-2}); D_m = Generation constant for methane (day^{-1}); K_{CO2} = Release rate of carbon (day^{-1}) from the sediment in Equation (20), and is defined by Equation (22).

$$K_{CO_2} = U_{r(20)}\beta^{(T-20)}S_{BOD} * 0.531S_b$$

(22)

Where $U_{r(20)}$ = Release rate (day^{-1}); β = Arrhenius temperature constant; COD$_{sink}$ = Active bacterial biomass (g m^{-2}); S_b = Fraction of bacteria settling.

The mass balance for plant uptake rate of inorganic is defined by Equation (23).

$$\frac{dP_{OC}}{dt} = K_{OX} + K_{CO_2} - K_{dec}$$

(23)

Calibration and optimization of model parameters

STELLA 6.0.1 software was used to run the developed conceptual model that incorporated equations of different processes involved in the wetland system. Mathematical processes were used to connect the various relationships among state variables and forcing function. Equations defining processes like sedimentation, biofilm activity and growth of microorganism, regeneration of organic carbon, decay of plant biomass and oxidation of organic carbon to carbon dioxide were included into the model. The data collected from the wetland units were used as inputs to the model for model calibration. The inputs were the influent concentration of COD, dissolved oxygen concentrations, pH and temperature values that were measured on daily basis. The simulation was done using Stella II software, which integrated the model using the in-built fourth-order Runge-Kutta approximation. The best values for unknown coefficient were obtained through calibration using observed data against simulated ones. The model efficiency R^2 was calculated from Nash and Sutcliffe (1970), which is given by Equation (24).

$$R^2 = \frac{F_o - F}{F}$$

(24)

Where F_o is the sum of the difference of squares between the observed and mean of observed values while F is the sum of the difference of squares between the observed and computed values.

The conceptual diagram shown by Figure 3 was used for modeling the transformation of organic carbon in wetlands. The sensitivity analysis of model results against model inputs indicated the sensitive parameters as the maximum growth rate of microorganism bacteria (μ_{max}), temperature coefficient (θ), specific area for biofilm

Table 2. Model calibration values.

No.	Parameter	Literature range	Reference	Calibration
1.	Temperature coefficient (Θ)	1.0 to 1.1	Metcalf and Eddy (1995)	1.02
2.	Maximum growth rate of heterotrophic bacteria at 20°C, μ_{max_20}	0.18	Ferrara and Hermann (1980)	0.16
3.	Optimum pH, pH_{opt}	4.0 ~ 9.5	Barnes et al. (1981)	7.5
4.	First order biofilm rate constant K_{fa} (day^{-1})	336.6	Polprasert and Agarwalla (1994)	336.6
5.	Half rate saturation constant for DO, K_{DO} (g m^{-3})	0.1 ~ 1.0	Okabe et al. (1995)	1.0
6.	Sticking coefficient, α	0.0008 ~ 0.012	Polprasert and Khatiwada (1999)	0.008
7.	Specific area for biofilm activity, a_s (m^2 m^{-3})	5.76 ~ 20.83	Polprasert and Agarwalla (1994)	6.76
8.	Diffusivity of a substrate through a liquid, D_f (m^2 day^{-1})	5.26×10^{-5}	Polprasert and Agarwalla (1991)	5.268×10^{-5}
9.	Liquid layer thickness, Ls (m)	1.19×10^{-4} ~ 2.26×10^{-4}	Ritmann and McCarty (1980)	2.26×10^{-4}
10.	Biofilm thickness, L_f (m)	1.462×10^{-4} ~ 1.615×10^{-4}	Polprasert and Agarwalla (1994)	1.615×10^{-3}
11.	Half rate saturation constant for COD, K_{SCOD} (g m^{-3})	15 to 75	Okabe et al. (1995)	18
12.	Density of settling particle, ρ_p (kg m^{-3})	1050 to 1500	Metcalf and Eddy (1995)	1300
13.	Fraction of bacteria settling, S_b	0.05	Canale (1976)	0.05
14.	Maximum substrate utilization, Y_{max} (mg biomass/mg COD)	0.5 to 1.0	Metcalf and Eddy (1995)	1.0
15.	Limiting value for pH, K_{pH}	199 ~ 288	Mashauri and Kayombo (2002)	288
16.	First order reaction rate constant, k_{20} (day^{-1})	0.1 ~ 1.2	Reed et al. (1995)	0.1
17.	Viscosity of water, μ_{20} (kg m^{-1} s^{-1})	1.002×10^{-3}	Metcalf and Eddy (1995)	1.002×10^{-3}
18.	Diffusivity of a substrate in biofilm layer, D_f (m^2 day^{-1})	2.3×10^{-5}	Rittman and McCarty (1980)	2.38×10^{-5}
19.	Diameter of collector, D_{co} (m)	0.0006 ~ 0.003	Reddy (1985)	0.0007
20.	Regeneration rate for inorganic carbon, U_r (day^{-1})	0.09	Foree and Jewell (1970)	0.07
21.	Arrhenius temperature constant at 20°C, B	1.02 ~ 1.09	Fritz et al. (1979)	1.04
22.	Porosity, P (%)	95~ 96.5	Kim and Kim (2000)	96
23.	Generation constant for Methane, D_m (day^{-1})	-	-	0.006
24.	Settling particle diameter, d_p (μm)	0.5 ~ 40	Metcalf and Eddy (1995)	5.6 μm

activity (a_s), settling particle diameter (d_p), first order reaction rate constant (k_{20}), half rate saturation constant for COD concentration (K_{COD}), density of settling particle (ρ_p) and maximum substrate utilization (Y_{max}).

The main objective of the simulation was to predict the effect of the activities of suspended biomass and attached plant root biofilm, on transformation and removal mechanisms of organic carbon in water hyacinths constructed wetlands. The efficiency of the model was found to be 73%, which indicates that the observed data fits well with the simulated values. The values of the optimized constants and coefficients used in the model during calibration are shown in Table 2.

The system performance showed the mean observed COD effluent was 110.5 g m^{-2} while the computed effluent was 104.4 g m^{-2}. The Mean Absolute Deviations (MAD), which is the average deviations between each data value and the mean, was determined from 25 data sets collected over a two month period. MAD of the observed and the computed effluent were 16.4 and 19.4 g m^{-2}, respectively and the observed and simulated removal percentages of COD in the unit were 38.3 and 40.5%, respectively. The closeness of these values suggests that the model predicted well the organic carbon transformation mechanisms in water hyacinth constructed wetlands. Table 3 shows the COD mass balance for state variables simulated by the model. The state variables

were substrate COD, plant organic carbon and sink COD. The processes involved in transformation mechanisms were oxidation of organic carbon to carbon dioxide, plant decay, regeneration of organic carbon, uptake of organic carbon by heterotrophic bacteria, settling of organic carbon and generation of methane.

The overall mass balance was 69.2 g m^{-2} day^{-1} which is close to 67.1 g m^{-2} day^{-1}, which is the total sum of the accumulation in plant OC, sink$_{COD}$, and S$_{COD}$ in the system. This shows that the system obey the law of mass conservation. About 7.5 g m^{-2}day^{-1} of carbon dioxide was consumed by plants in the photosynthesis process (the oxidation process contributed 6.4%) while the decay process returned 6.7 gm^{-2} day^{-1} to the water body (contribution to the transformation process was 4.4%) Thus, an accumulation of 0.95 g m^{-2} day^{-1} organic carbon in the plant biomass was observed which is completely removed from the system. About 17.9 g m^{-2} day^{-1} of organic carbon was consumed by microorganism in the formation of new cellular material (contribution to the transformation was 4.2%). The uptake of organic carbon by microorganism resulted to the regeneration of 53.1 g m^{-2} day^{-1} of organic carbon back to water column (this transformation process accounted only 25.5%). About 106.4 g m^{-2} day^{-1} of organic carbon was settled down to the sediment leading to high removal of 56.5% from the system. Therefore, due to sludge accumulation anaerobic

Table 3. Transformation mechanisms of organic material in Water hyacinth wetland.

No.	Transformation process	Mass load of organic material (g m^{-2} day^{-1})
1.	Influent organic material	175.5
2.	Effluent organic material	104.4
3.	Organic material settled in the benthic layer	106.4
4.	Organic material regenerated from the benthic layer	53.1
5.	Methane released from the benthic layer	3.8
6.	Water hyacinth decay rate	6.7
7.	Organic material oxidized by heterotrophic bacteria	7.4
8.	Uptake of organic material by microorganisms	17.9
9.	Oxidative catabolism of organic material to CO_2	2.7

decomposition in the sediment released 2.7 g m^{-2} day^{-1} of CO_2 to the system and 3.8 g m^{-2} day^{-1} of CH_4 was completely removed from the system (CO_2 and CH_4 contributed 1.2 and 1.8% to the transformation process). The permanent COD removal was 26.7% and largely contributed by sedimentation, biofilm activity and to smaller extent by generation of methane.

The effects of biofilm biomass activities were studied by setting the biofilm parameter to zero in the calibrated model and re-run. The output produced the removal percentage of COD was 34.0% when the model was simulated without considering the effect of biofilm, which is lower than 40.5% when biofilm effect was taken into consideration. The mean absolute deviation (MAD) of simulated effluents with and without biofilm effect was 10.0 and 34.5 g m^{-2}, respectively. This high divergence showed the significance of the biofilm effect in transformation and removal of organic carbon through bio-oxidation mechanism as studied by Sooknar (2000). These results confirm the results of Stowell et al. (1981) who reported that water hyacinth roots provide physical support for a thick bacteria biofilm that actively degrades the organic matter.

Model applications and limitations

This mathematical model can be used to predict transformation and removal of organic material in artificial wetlands implanted with *E. crassipes*. Its applications require knowledge of influent concentration of organic material, effective surface area of *E. crassipes* roots, flow rates of domestic wastewater, density and size of settling particle, porosity of the media and biofilm activities. Other environmental and physical-chemical parameters required include pH, temperature and dissolved oxygen. Stella 6.0.1 software or any other software may be used to simulate any state variable or process provided all inputs are known.

Conclusions

From the results of this study the following conclusions

are made:

(1) Transformation of organic material in *E. crassipes* artificial wetland was governed by settling of organic solids to benthic layer (104.4 g $m^{-2}day^{-1}$), regeneration of soluble organic matter from particulate matter (53.1 g $m^{-2}day^{-1}$) and uptake of organic matter by microorganisms (17.9 g $m^{-2}day^{-1}$) and uptake by organic material by biofilm growth on *E. crassipes* (7.4 g $m^{-2}day^{-1}$). Other transformation route such as decay of *E. crassipes* (6.7 g $m^{-2}day^{-1}$) and release of gases such as methane (3.8 g $m^{-2}day^{-1}$) and carbon-dioxide (2.7 g $m^{-2}day^{-1}$) from benthic layer were relatively ineffective.
(2) Organic material was largely removed through net loss to sediments (64.7 g $m^{-2}day^{-1}$), production of methane from benthic layer (3.8 g $m^{-2}day^{-1}$) and net carbon removed through uptake by plants and microorganisms (3.4 g $m^{-2}day^{-1}$). The total mass of removed carbon amounted to 71.9 g $m^{-2}day^{-1}$, which is equivalent to 41% efficiency of organic carbon removal in this wetland.

Conflict of Interests

The author(s) have not declared any conflict of interests.

REFERENCES

Barnes D, Bliss PJ, Gould BW, Valentine HR (1981). Water and Wastewater Engineering Systems. Pitman Books Limited London.

Barrie A (2002). Modelling COD removal in water hyacinths constructed wetland. MSc Dissertation, Department Water Resources Engineering, University of Dar es Salaam, Tanzania.

Bigambo T, Mayo AW (2005). Nitrogen transformation in horizontal subsurface flow constructed wetlands II: Effect of biofilm. J. Phys. Chem. Earth 30:668-672.

Canale RP (1976). Modelling biochemical processes in aquatic ecosystems. Ann Arbor Science Pub. Co, Ann Arbor, Michigan.

Ferrara RA, Hermann DPF (1980). Dynamic Nutrient Cycle Model for Waste Stabilization Ponds. J. Environ. Eng. Div. Am. Soc. Civ. Eng. 106(1):37-55.

Foree EG, Jewell WJ (1970). The extent of nitrogen and phosphorus regeneration from decomposing algae. In: Advances in Water Pollution Research. Proceedings of the 5th International Conference on Water Research. Pergamon Press Ltd., London. New Zealand J.

Mar. Freshw. Res. 14(2):121-128.

Fritz JJ, Middleton AC, Meredith DD (1979). Dynamic Process Modelling of Wastewater Stabilization Ponds. J. Water Pollut. Control Fed. 51(11):2724-2742.

Gersberg RM, Elkins SR, Lyons A, Godman CR (1985). Role of aquatic plants in wastewater treatment by artificial wetlands. Water Res. 20:363-368.

Kalibbala M, Mayo AW, Asaeda T, Shilla DA (2008). Modelling faecal *streptococci* mortality in constructed wetlands implanted with *Eichhornia crassipes*. Wetland Ecol. Manage. 16:499-510.

Khatiwada NR, Polprasert C (1999). Kinetics of fecal coliform removal in constructed wetlands. Water Sci. Technol. 40(3):109-116.

Kim Y, Kim WJ (2000). Roles of water hyacinth and their roots for reducing algal concentration in the effluent for waste stabilization ponds. Water Res. 34(13):3285-3294.

Knight LR, Clarke AR, Bastian KR (2000). Treatment Wetlands as Habitat for Wildlife and Humans. 7th International Conference on Wetland Systems for Water Pollut. Control (1):37.

Logan BE, Hilbert TAA, Anold RG (1993). Removal of bacteria in laboratory filters: Models and experiments. Water Res. 27(6):955-962.

Mashauri DA, Kayombo S (2002). Application of the two Coupled Models for Water Quality Management: Facultative pond cum Constructed Wetland Models. J. Phys. Chem. Earth 27:773-781.

Mayo AW (1989). Effect of the pond depth on bacteria mortality rate, J. Environ. Eng. Div. Am. Soc. Civ. Eng. 115(5):964-977.

Mayo AW, Muraza M, Norbert J (2013). The Role of Mara River Basin Wetland in Reduction of Nitrogen Load to Lake Victoria. Int. J. Water Resour. Environ. Eng. 5(12):659-669.

Mayo AW, Bigambo T (2005). Nitrogen transformation in horizontal subsurface flow constructed wetlands I: Model development. J. Phys. Chem. Earth 30:658-667.

Mayo AW, Kalibbala M (2007). Modelling faecal coliform mortality in water hyacinths ponds. J. Phys. Chem. Earth 32:1212-1220.

Metcalf and Eddy Inc. (1995). Wastewater Engineering: Treatment, Disposal and Reuse. 3rd McGraw-Hill Ltd. New Delhi, pp. 82-1204.

Mugasha AL (1995). A study of the potential use of water hyacinth, *Eichhornia crassipes* (Mart.) Solms., in the control of chromium and lead pollution in fresh waters. MSc. Thesis, University of Dar es Salaam.

Muyodi FJ (2000). Microbiological analysis of the waters of Lake Victoria in relation to the invasion of the water hyacinth *Eichhornia crassipes* (Mart.) Solms.: A case study of the lakeshores of Mwanza Municipality. Ph.D Thesis, University of Dar es Salaam.

Nakibuule J (2013). The transformation and removal of nitrogen in horizontal sub-surface flow constructed wetlands. Final Year Project, Department of Water Resources Engineering, University of Dar es Salaam.

Nash JE, Sutcliffe JV (1970). River flow forecasting through conceptual models. J. Hydrol., 10:282-290.

Okabe S, Hirata K, Watanabe Y (1995). Dynamic changes in spatial microbial distribution in mixed population biofilm, experimental and model simulation. Water Sci. Technol. 32(8):67-74.

Okurut D (2013). Biofilm Effects on Nitrogen Transformation and Removal in Subsurface Flow Constructed Wetlands planted with *Typha Domingensis*. MSc Dissertation, Department of Water Resources Engineering, University of Dar es Salaam.

O'Melia CR (1985). Particles, pretreatment and performance in water filtration. J. Environ. Eng. Div. Am. Soc. Civ. Eng. 116(6):874-905.

Polprasert C, Agarwalla BK (1994). A Facultative Pond Incorporating Biofilm activity. Water Environ. Res. 66(5):725-732.

Polprasert C, Khatiwada NR (1997). Role of Biofilm Activity in Water Hyacinths Pond Design and Operation. Proceedings of Asian Water Quality 97, 6th IAWQ Asian-Pacific Regional Conference, Int. Association on Water Quality and Korean SOC of Water Quality. Seoul, Korea.

Reddy KR (1985). Nutrient transformations in aquatic macrophyte filters used for water purification. Purification Water Reuse 111, American Water Works Association, Denver, Colorado, pp. 660-678.

Reed SC, Crites RW, Middlebrooks EJ (1995). Natural systems for waste Management and Treatment. McGraw-Hill Book Co., New York, NY, pp. 225-262.

Rittmann BE, McCarty PL (1980). Evaluation of Steady State Biofilm Kinetics. Biotechnol. Bioeng. 22:2343-2359.

Senzia MA (2003). Modelling of nitrogen transformation and removal in subsurface flow constructed wetlands during treatment of domestic wastewater. PhD Thesis, Department Water Resources Engineering, University of Dar es Salaam, Tanzania.

Senzia AM, Mashauri DA, Mayo AW (2004). Modelling Nitrogen Transformation in Horizontal Subsurface flow Constructed Wetlands Planted with *Phragmites mauritianus*. J. Civ. Eng. Res. Pract. 1(2):1-15.

Sooknar R (2000). A review of the mechanisms of pollutant removal in water hyacinth systems. Sci. Technol. Res. J. Univ. Mauritius, Reduit, Mauritius 6:50-56.

Standard Methods for the Examination of Water and Wastewater (2012). American Public Health Association, American Water Works Associations, Water Pollution Control Federal - 22nd Edition, Washington, DC.

Stowell R, Ludwig R, Colt J, Tchobanoglous T (1981). Concepts in aquatic treatment design. J. Environ. Eng. Div. Am. Soc. Civ. Eng. 112:885-894.

U.S Environmental Protection Agency (1988). Design Manual. Constructed Wetlands and Aquatic plant Systems for Municipal Waste Treatment. EPA/625/1-88/002, Cincinnati, OH 45268, pp. 2-53.

Vymazal J (2010). Constructed wetlands for wastewater treatment. Water 2:503-549.

Water 21 (2000). Constructed wetlands: A global technology. Magazines of International Water Association, June, pp. 57-58.

Weast RC (1981). Handbook of Chemistry and Physics 61st Ed. CRC Press, Boca Raton, Florida.

Williamson KJ, McCarty PL (1976). A Model of Substrate Utilization by Bacteria Films. J. Water Pollut. Control Fed. 48(1):9-24.

Yi Q, Hur C, Kim Y (2009). Modelling nitrogen removal in water hyacinth ponds receiving effluent from waste stabilization ponds. Ecol. Eng. 35(1):75-84.

Review

Prospective techniques for *in-situ* treatment and protection of aquifers: A sustainable hydrology review

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Most water table aquifers are polluted, yet they are the primary sources of urban and rural water supply. Sustainable hydrology in this millennium will capture *in-situ* treatment and protection of shallow aquifers particularly in developing countries. Permeable reactive barrier (PRB), biological and electrochemical methods with air and steam injection techniques will advance. *Ex-situ* pump and treat method is slow, costly and unsustainable. Many private treatment plants for pump-treat-use have been abandoned due to unsatisfactory output and operational problems. *In-situ* treatment of polluted aquifer starts with mapping pollution source(s), identifying stressors and migration pathway, estimating quantum of stress, and terminating release of stressors from the source. Sustainable hydrology shall also include developing hydrologic models code that can predict pollution, treatment method; amount and period of treatment. This shall be based on the characteristics of the aquifers; the pollution stress and the subsurface.

Key words: Aquifer cleanup, permeable reactive barrier (PRB), biological, chemical, hydrodynamic model, sustainability

INTRODUCTION

An aquifer may be polluted by a number of pollution stressors from one or more sources in a continuous or discontinuous manner. The most active stressor(s) produce the *pollution stress* that characterizes the aquifer. Pollution occurs only when the accumulated stress exceed the aquifer containment level. Sustainability of water resources is not only for the purpose of fulfilling needs for water usage but also for bringing people into harmony with their ambient natural environment. To achieve this, Melloul and Collin (2002) made two important suggestions: (1) develop a global understanding of an aquifer's hydrological and environmental properties in order to delineate appropriate eco-hydrological scenarios and recommend corresponding operational management activities; and (2) emphasize the importance of educating and increasing the awareness of citizens involved as to the need for and viability of socially acceptable measures for sustainable management of groundwater and other resources. Nandakumar (2012) reported that groundwater resources in Kerala–India have come under increasing stress from rising levels of exploitation and pollution. Nwachukwu et al. (2013) reported the water table aquifer of the lower Imo River basin as being increasingly polluted due surface pollutants arising from poor waste management.

International and national action at all levels will be needed to improve water access in those regions lacking water such as North Africa and West Asia and to improve

the efficiency of water use in the regions that have water. This is the aspect of sustainable hydrology that challenges hydrologist in this 21st century. The goal is to achieve sustainable development of groundwater so that water supply could be sustained for future generations. Though the aspect of sustainable hydrology is of global concern, it is yet to be properly recognized with respect to groundwater management in Africa. Key to sustainable management of water resources is having the knowledge needed to make the right decisions towards preservation of the accessible aquifer systems worldwide. Melloul and Collin (2000) described migration and accumulation of contaminants into groundwater, rate of water abstraction and land use as the three major aquifer stress vehicles. This paper focuses on how a polluted aquifer can be cleaned up, recovered, and preserved for future use, while considering safety of public health.

Accumulation of pollutants following improvement of urban and rural infrastructure such as road construction in particular in many developing countries has increased pollution stress on water table aquifers, affecting water quality. For example, borrow pits from where materials were collected for road projects are usually abandoned instead of reclaimed. Soon after, these abandoned borrow pits become urban waste disposal pits. Emissions from these pits accumulate to pollution stress until the underlying water aquifer becomes polluted (Nwachukwu and Osoro, 2013). Again, lack of storm water management during road construction and other open engineering sites such as mechanic villages causes continuous enrichment of pollutants to surface water. This in turn, causes groundwater pollution. As a result, near surface aquifers in many regions of the world are highly polluted and most shallow wells in these regions produce water of poor quality. The consequence is endemic water related diseases, poverty, and poor quality of life (Nwachukwu et al., 2010).

Cases of water table aquifer under pollution stress have been discussed by many scholars. For example, Benaabidate and Cholli (2011) reported groundwater stress and vulnerability to pollution of Saiss basin shallow aquifer, Morocco. According to them, the vulnerability of this shallow aquifer to pollution diagnosed by DRASTIC method occurs in different degrees. Not all aquifers are equally vulnerable to pollution. Those where fractures or cavities permit rapid flow tend to be more vulnerable than those where water flows slowly through pore spaces and more opportunities exist for attenuation of pollutants. However, vulnerability to pollution has an inverse relationship to the difficulty of remediation. Once polluted, slow movement of groundwater through a porous aquifer generally makes cleanup difficult, expensive, and in some cases impossible. Three main sources of groundwater pollution are: agricultural, urban and industrial developments.

In-situ remediation is often the method of choice as it destroys contaminants in place, rather than merely transferring them to another environmental medium, as occurs with Pump and Treat method. Thus, industrialized nations like USA, different parts of Europe and Australia are investing on *in-situ* clean up of their polluted aquifers. Unlike most developing countries, they have continuously invoked various techniques in their efforts towards sustainable hydrology. The idea of sustainable hydrology this millennium shall be the primary concern of all hydrologists, NGOs and governments worldwide. Case examples of these applications are hereby reviewed. For example, Key et al. (2013) demonstrated how two pilot tests of an aerobic *in situ* bioreactor (ISBR) have been conducted at field sites contaminated with petroleum hydrocarbons. The two sites differed with respect to hydrocarbon concentrations. At one site, concentrations were low but persistent, and at the other site concentrations were high enough to be inhibitory to biodegradation. Brown et al. (2010) applied surfactant-enhanced aquifer remediation (SEAR) as alternatives to conventional pump-and-treat remediation for aquifers contaminated by dense non aqueous phase organic liquids.

Suthersan et al. (2010) reported a full-scale non–aqueous phase liquid (NAPL) remediation of Area A of the Northeast Site at the Young-Rainey STAR Center, Largo, Florida. Area A covered an area of 930 m^2 (10,000 ft^2) and extended to a depth of 10.7 m (35 ft), representing a total cleanup volume of 9930 m^3 (12,960 cubic yards). The site was contaminated with ~2500 kg (5500 lb) of NAPL constituents such as trichloroethylene, *cis*-1,2-dichloroethylene, methylene chloride, toluene, and petroleum hydrocarbons. The site consists of a fine-grained sand aquifer underlain by Hawthorn clay at 9 m (30 ft) depth. The upper 1.5 m (5 ft) of this clay formed part of the remediation volume, as dense non–aqueous phase liquid was present in this layer. The site was remediated using a combination of steam-enhanced extraction and electrical resistance heating. Operations lasted 4.5 months. The site was heated to the target temperatures within 6 weeks, at which time the mass removal rate increased more than 1000-fold. The post operational sampling showed that ~0.5 kg (1 pound) of VOCs remained in the remedial volume, and showed remedial efficiencies between 99.85% and 99.99% for the four chemicals of concern.

Piotrowski et al. (2006) presented the case of soil and two aquifers under an active lumber mill in Libby, Montana, which had been contaminated from 1946 to 1969 by uncontrolled releases of creosote and pentachlorophenol (PCP). In 1983, because the contaminated surface soil and the shallower aquifer posed immediate risks to human health and the natural environment, the U.S. Environmental Protection Agency placed the site on its National Priorities List. Feasibility studies in 1987 and 1988 determined that *in situ* bioremediation would help clean up this aquifer and that biological treatment would help clean up the

contaminated soils.

Rao et al. (2010) showed a comprehensive, field-scale evaluation of *in situ* co-solvent flushing for enhanced remediation of non aqueous phase liquid (NAPL) in a field site at Hill Air Force Base, Utah. This sand-gravel-cobble subsurface aquifer, underlain by a deep clay confining unit at about 6 m below ground surface, was contaminated with a multi component NAPL as a result of jet fuel and chlorinated solvent disposal during the 1940s and 1950s. The co- solvent flushing test consisted of pumping about 40,000 L (approximately nine pore volumes) of a ternary co-solvent mixture (70% ethanol, 12% *n*-pentanol, and 18% water) through the test cell over a period of 10 days, followed by flushing with water for another 20 days. Several methods for assessing site remediation yielded consistent results, indicating that on the average >85% mass of the several target contaminants was removed as a result of the co solvent flushing; NAPL constituent removal effectiveness was greater (90 to 99$^+$%) in the upper 1 m zone, in comparison to about 70 to 80% in the bottom 0.5 m zone near the clay confining unit.

A popular type of *in situ* remediation method currently used to clean up contaminated groundwater is the permeable reactive barrier (PRB). PRBs are treatment zones composed of materials that degrade or immobilize contaminants as the groundwater passes through the barrier. They can be installed as permanent, semi permanent or replaceable barriers within the flow path of a contaminant plume. The material chosen for the barrier is based on the contaminant(s) of concern (U.S. EPA 2001). Liu (2013) investigated the biodegradation of three selected benzo triazoles (BTs), namely benzotriazole (BT), 5-methyl-benzotriazole (5-TTri) and 5-chloro-benzotriazole (CBT), in aquifer materials. Under anaerobic conditions, CBT was found to be degraded better with its half-life of 21 days under nitrate reducing conditions than under aerobic conditions with its half-life of 47 days.

Nano-technology

Nano-remediation methods entail the application of reactive nano-materials for transformation and detoxification of pollutants. These nano particles have properties that enable both chemical reduction and catalysis to mitigate the pollutants of concern. For nano-remediation *in situ*, no groundwater is pumped out for above-ground treatment, and no soil is transported to other places for treatment and disposal (Otto et al., 2008). Nano-materials have highly desired properties for *in situ* applications. Because of their minute size and innovative surface coatings, nano-particles may be able to pervade very small spaces in the subsurface and remain suspended in groundwater, allowing the particles to travel farther than larger, macro-sized particles and achieve wider distribution. However, in practice, current

nano-materials used for remediation do not move very far from their injection point (Tratnyek and Johnson, 2006). For a comprehensive overview of the chemistry and engineering of various nanotechnology applications addressed in Supplemental Material, Table 1, and used for remediation, see Theron et al. (2008) and Zhang (2003). For a comprehensive overview of supplemental materials of nano-particles and their remediation applications adapted from Theron et al. (2008) and Zhang (2003), see Table 1.

Nano particles range from 10 to 100 nm in diameter, although some vendors sell micrometer-scale iron powders as "nano-particles." The second metal creates a catalytic synergy between itself and Fe and also aids in the nano-particles' distribution and mobility once injected into the ground (Saleh et al., 2007; Tratnyek and Johnson, 2006; U.S. EPA, 2008b). Some noble metals, particularly palladium, catalyze dechlorination and hydrogenation and can make the remediation more efficient (U.S. EPA, 2008b; Zhang and Elliott, 2006). The underlying chemistry of the reaction of Fe with environmental pollutants (particularly chlorinated solvents) has been extensively studied and applied in micrometer-scale zero-valent iron (ZVI) PRBs (Matheson and Tratnyek, 1994). There are two main degradation pathways for chlorinated solvents: beta elimination and reductive chlorination. Beta elimination occurs most frequently when the contaminant comes into direct contact with the Fe particle (Elliott and Zhang, 2001; Glazier et al., 2003). Zhang (2003) also showed that modifying Fe nano-particles could enhance the speed and efficiency of the remediation process. Some of the particles flow with the groundwater and remain in suspension for various amounts of time, whereas others are filtered out and bind to soil particles, providing an *in situ* treatment zone that could hold back emanating plumes (Henn and Waddill, 2006).

Laboratory tests have shown 99% removal of As using 12-nm-diameter Fe oxide nano-particles (Rickerby and Morrison, 2007). Kanel et al. (2006) concluded that nZVI can reduce As(V) to As(III) in a short period of time at neutral pH. Macé et al. (2006) found that nanoscale zero-valent iron (nZVI) moved with groundwater away from the injection site. Based on this, they hypothesized that nZVI could treat larger areas of the affected aquifers. They found dramatic but short-lived reductions of volatile organic compounds (VOCs) in fractured bedrock and a slower, steadier decrease of VOCs in primary porosity aquifers. The same study suggested that the degradation of VOCs and travel velocity are indirectly proportional to the hydraulic conductivity. In an extensive study, the Navy conducted field tests using nZVI to remediate two of its contaminated sites (Naval Air Engineering Station, Lakehurst, NJ, and Naval Air Station, Jacksonville, FL). In the Jacksonville study, TCE concentrations in a well approximately 20 ft from the source zone were reduced up to 99%, suggesting that some of the nZVI migrated

Table 1. List of manufactured nanoparticles and the pollutants potentially remediated

Number	Nano particle	Application
1	Nanocrystalline zeolites	Toluene, nitrogen dioxide
2	Carbon nanotubes (CNTs)	Benzene, toluene, xylene, ethylbenzene, heavy metal
3	Activated carbon fibers,	Benzene, toluene, xylene, ethylbenzene, heavy metal ions
4	CNTs functionalized with polymers and Fe	p-nitrophenol Benzene,toluene, dimethylbenzene, heavy metal ions
5	Multi-walled CNTs	Heavy metal ions, THMs, Chlorophenols, Herbicides, Microcystin toxins
6	Self-assembled monolayer on mesoporous supports	Inorganic ions, Heavy metal ions, Actinides, Lanthanides, Radionuclides TiO2
7	Zero-valent iron nanoparticles	Chlorinated methanes, Trihalomethanes, Chlorinated benzenes, Chlorinated ethenes, Pesticides, Polychlorinated hydrocarbons, Organic dyes, Heavy metal ions, Inorganic ions, Chlorinated organic compounds.
8	Photo catalysts	Heavy metal ions, Azo dyes, Phenol, Aromatic pollutants, toluene
9	Bimetallic: Pd/Fe nanoparticles	PCBs, Chlorinated ethane and methanes
10	Ni/Fe nanoparticles Pd/Au nanoparticles	TCE, PCBs, Dichlorophenol, Triclorobenzene, Chlorinated ethene, Brominated organic compounds

Adapted from Theron et al. (2008) and Zhang (2003)

outside of the treatment zone through preferential pathways (Gavaskar et al., 2005).

In addition to groundwater remediation, nanotechnology holds promise in reducing the presence of NAPLs.

Recently, a material using nano-sized oxides (mostly calcium) was used *in situ* to clean up heating oil spills from underground oil tanks. Preliminary results from this redox-based technology suggest faster, cheaper methods and, ultimately, lower overall contaminant levels compared with previous remediation methods. Most of these sites have been in New Jersey, with cleanup conducted in consultation with the New Jersey Department of Environmental Protection (Continental Remediation LLC, 2009). These fate processes depend on both characteristics of the particle and that of the environmental system (Boxall et al., 2007). The use of nano-particles in environmental remediation will inevitably lead to the release of nano-particles into the environment and subsequent ecosystems. To understand and quantify the potential risks, the mobility, bioavailability, toxicity, and persistence of manufactured nano-particles need to be studied (Nowack, 2008). The Royal Commission on Environmental Pollution (2008) summed up the current approach to potential implications from nano-material.

METHODS AND SPECIFIC ADVANCEMENTS

To accomplish this study, several journal articles, text books, technical reports and regulatory documents from different parts of the world concerning groundwater pollution and management have been reviewed. Recent opinions going by technological advancement are most considered. Pollution stress can be quantified and measured as pollution index and stress enrichment factor. These are the key elements that can be measured in order to determine the pollution level of aquifer and the quantum of treatment required. The challenge is to develop a hydrodynamic model code for polluted shallow aquifers. Such a model code should indicate shallow aquifer pollution stress (SAPS). The code shall predict pollution, treatment method; pathway, amount and period of treatment. Quantifying SAPS is important in the present day hydrology and hydro-geological studies. SAPS hydrodynamic model software can be adaptable in all cases to monitor shallow aquifer pollution even as the pollution stressors are being removed.

In designing aquifer treatment, a primary assignment is to determine the direction of groundwater flow. This involves the use of advanced numerical modeling software such as DRASTIC, RADMOD, and ZONEBUDGET, PHAST and SHARP etc. MODFLOW code (McDonald and Harbough, 1988) and MODDATH module Pollock (1994) of the GMS package are widely applicable. These model software codes will by graphical illustration explain the direction of groundwater flow along with contaminants migration pathway, fate and transport.

The understanding of this will enable effective design of treatment method, quantum of treatment and procedure. A case example is the study conducted by Nwachukwu et al. (2010b) on south-west end of the lower Imo River Basin. They used MODFOW and MODPATH codes to show Groundwater Flow Model and Particle Track Analysis across Owerri metropolis (Figure 1). Based on
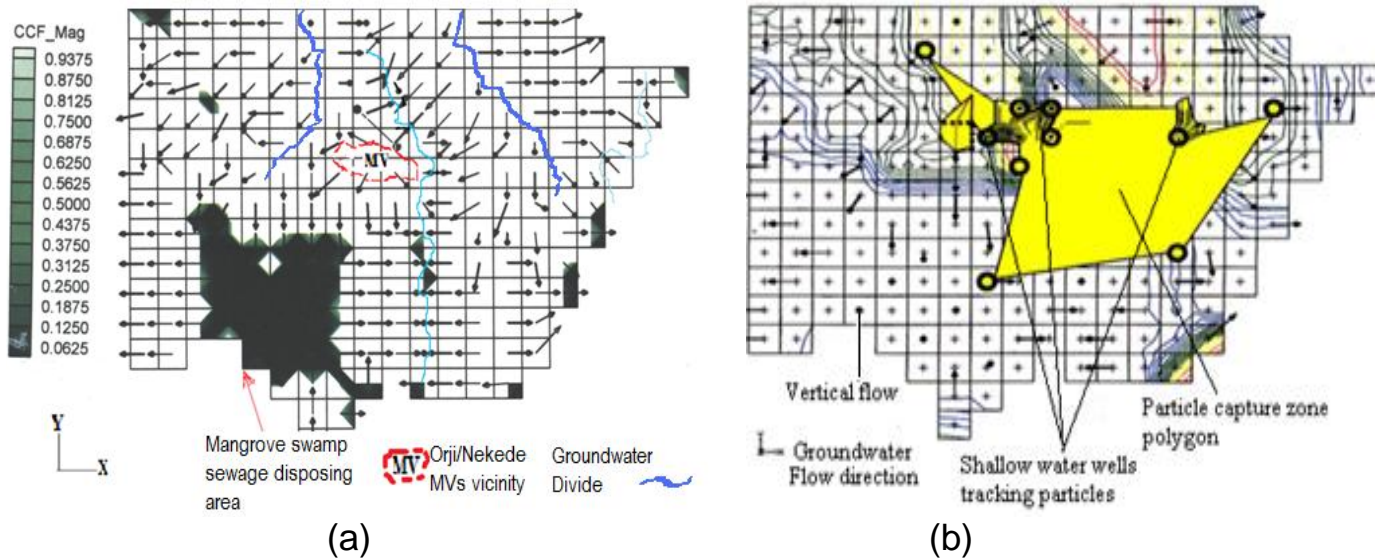
Figure 1. (a) Groundwater flow pattern based on model layer 5. In the SW portion is the highly contaminated sewage dump mangrove swamp area of Umuapu and Egbeda (b) Particle capture zone across Owerri metropolis (Source: Nwachukwu et al., 2010b).

the result of this study, the polluted water table aquifer which remains the very source of drinking water in the area could receive *in-situ* treatment as per result of monitoring wells. This aquifer is easily accessible at shallow depth, even with cheap manual drilling tools, making more than 95% of wells in the area to be shallow. Most of these wells terminate at depths from 34 to 49 m, and are private/commercial water wells. As a result, about 60% of wells in the area are producing water of poor quality (Nwachukwu et al., 2012).

Isotopes can be used to investigate groundwater sources of water to determine their source, how they are recharged, whether they are at risk of saltwater intrusion or pollution, and whether they can be used in a sustainable manner. The isotopes of pollutants, such as trace metals, or chemical compounds dissolved in water, also offer clues about its origin and applicable treatment. Jaisi (2013) conducted a study aimed at determining whether abiotic reactions of phosphate during its transport involve fractionation of oxygen isotopes in phosphate ($\delta18Op$). The results collectively suggest that abiotic reactive transport processes exert minimal influence on the $\delta18Op$ composition of groundwater systems.

New advances in geophysics have enabled characterization of sites based on time and cost. The hydrology and basic geochemistry at the sites are established, and used as input data to a hydrologic model code. Parameters required include average depth and thickness of aquifer, drainage area, and distance to pollution source. Others include aquifer pollution stress maximum containment limit (MCL), concentration of primary pollutant, hydraulic conductivity and porosity. These are obtainable from geophysical field study and

other hydro geological methods to improve the prospects of sustainable hydrology in this 21st century.

A baseline characterization of the microbiology is essential to establish that the right microorganisms are present for biological treatment of a polluted aquifer. It must be established that the micro-organisms can be stimulated, and that no undesirable reactions with the stimulants or daughter products from the stimulation will occur. This usually requires some treatability and soil compatibility studies and monitoring of microbial community structure and function to establish the base conditions prior to stimulation (Plaza et al., 2001). With new advances in geophysics, aquifer heterogeneity: hydraulic conductivity, aquifer depth, thickness and drainage area are easily obtained. Groundwater flow model and changes in biogeochemistry as well as injection pathway are determined (Faybishenko et al., 2008; Hubbard et al., 2008).

Characterization studies should determine which general remedial approach is appropriate for each sub-area of the site. In many cases, the appropriate remedy for source areas will be containment, and the appropriate remedial level for pollution plume areas will be active restoration. Natural attenuation may be acceptable for some zones where it can show that natural biological, chemical and physical processes will lower pollutant concentrations to cleanup levels (Cherry, 1992). Once the level of remediation is established, site characterization studies should be designed to collect the data required in order to design a technically effective and cost effective remedial action to obtain the desired end result. *In-situ* treatment of polluted aquifer starts with mapping the pollution source(s), identifying stressors and migration pathway, estimating quantum of stress, and terminating release of
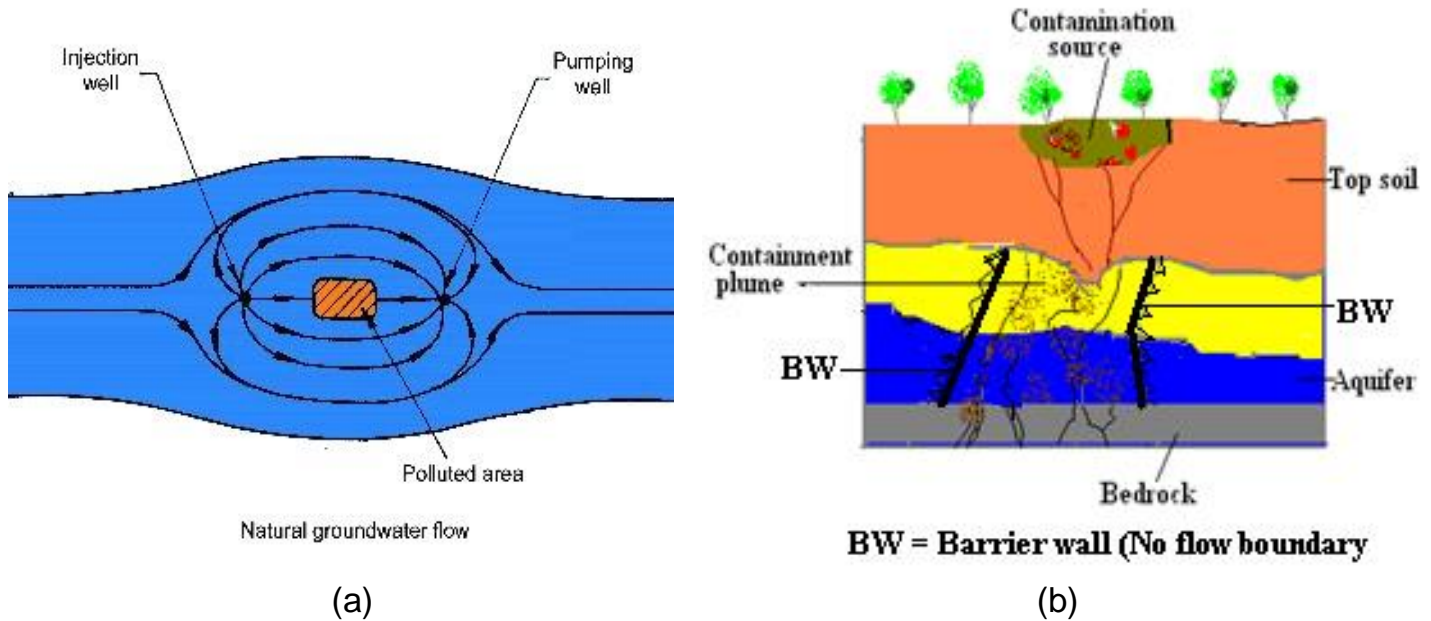
(a)   (b)

Figure 2. Scheme of containment systems (a) Hydraulic containment (Source: Fetter, 1993); (b) Containment barrier walls.

stressors from the source.

Aquifer treatment field techniques

Containment techniques

One of the most used alternatives to manage with groundwater pollution areas is to contain the future spread of the pollutant. This task may be achieved by subsurface barriers (Fetter, 1993) which are designed to prevent or control the groundwater polluted flow into the desired location. Two main types of subsurface barriers are used now: physical and hydraulic barriers. Physical barriers include slurry trench walls, grout curtains and cutoff walls. These barriers are no flow boundaries, made with materials that have a lower permeability than the aquifer. For example, compacted clay, geomembranes, soil and bentonite mixtures can be used.

Hydraulic barriers are used to isolate a plume of pollutant from the natural water flow pattern in order to prevent the increase of the polluted area. Another solution of the hydraulic barrier may be realized by controlling the hydraulic gradient of groundwater around and inside the polluted plume by using a pair of injection and pumping wells (Figure 2). The main disadvantages of a well system includes higher operation and maintenance costs, system failures, due to the breakdown of equipment or power outages, flexibility is reduced in fine soils and incorrect pumping rates can draw a significant part of the plume into the wells making treatment necessary before recharge into the aquifer (Barcelona et al., 1990).

Pump and treat technique

Barely a few years ago, pump and treat was one of the most often used processes for polluted groundwater remediation. The basic concept of this technology is very simple; the polluted groundwater is extracted from the subsurface and treated using one of the methods that is currently applied for removing pollutants from industrial or domestic waste water. The clean water may be discharged into a surface water body, such as a stream, or it may be injected into the subsurface. Remediation by pump and treat is a slow process. The calculations for a variety of typical situations show that predicted cleanup times range from a few years to hundreds or even thousands of years. Because of the slow rates of pollutants' desorption and dissolution, pump and treat systems must displace many volumes of aquifer water to flush out pollutants. Pump and treat systems are generally an inefficient method for removing pollutants from the aquifer, but they may be used to clean up plumes of dissolved pollutants. A common private application of this method is the pump-treat-use. A number of treatment plants are available for different treatment purposes. Often treatment plants are abandoned for inefficiency in removing a number of pollutants, compelling operational stress and maintenance.

A very efficient and recommended application of pump and treat systems is to remove light non-aqueous-phase-liquids (LANPLs) from the subsurface. LNAPLs delineate the pollutant that is not miscible with water and is easier than it, so that it will accumulate as a mobile layer on the water table or the top of capillary fringes. These
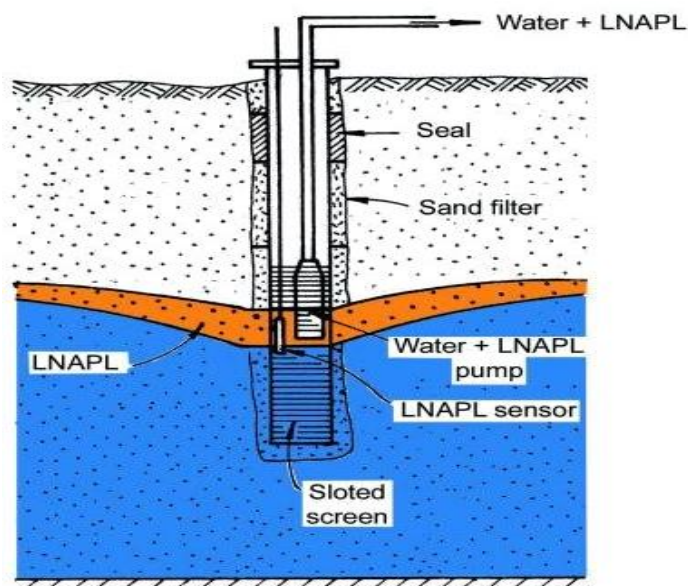
Figure 3. Examples of NAPL recovery by pump and treat system. Source: Beddient et al. (1993).

pollutants can be recovered by depressing the groundwater table with extraction wells in order to facilitate their accumulation in the well (Figure 3). For this application of pump and treat system, two alternatives can be employed: pumping the combined groundwater and LNAPL mixture with a single pump or using two separate pumps working under a control system to remove water and NAPL separately.

Soil vapor extraction technique

This technology is primarily applied to extract vapor of organic compound from an unsaturated zone by applying a vacuum at a sealed wellhead (Figure 4). Soil vapor extraction can be more efficient and cost effective in comparison to others remediation strategies like pump and treat. Soil vapor extraction involves passing large volumes of air through a polluted spill. The organic compounds or various fractions of a mixture of organic compounds volatilize or evaporate into air and are transported to the surface. The system may consist of one or more extraction wells, vacuum pump and a treatment system for the extracted vapors.

Bioremediation technique

The main feature of this method is to stimulate subsurface microorganisms to biodegrade pollutants (Figure 5a). In some proper conditions microorganisms can transform the chemical compounds pollutants of the groundwater to carbon dioxide and water (Figure 5b). Typical *in situ*

bioremediation systems inject electron acceptors and nutrients through the polluted area so as to enhance the bioactivity of the microorganisms. *In situ* bioremediation has been successfully applied for treating the soil and the groundwater polluted with hydrocarbons, phenols, acetone and cellulosic waste. *In situ* bioremediation has some advantages; it treats the pollutant on the spot and transforms it into an innocuous compound; so this method reduces the requirement for surface water treatment and disposal of recovered water.

In-situ bioremediation is looked upon as the best approach to deal with the underground water contamination. In order to increase microbial activity and to ensure the continuous growth of the bacteria in the Biologically Active Zone (BAZ), the limiting substances such as macro nutrient (nitrogen or phosphorus), electron acceptor (such as oxygen, nitrate) or carbon source has to be continuously supplied and injected to the system. Success of the whole program is largely dependent on the soil properties, selection of the right bacteria to use matching the type of contaminants present, hydrogeology and other factors. In the line of bioremediation is bioimmobilization. *In situ* bioimmobilization has recently gained attention as a potentially effective remediation strategy for metal- or radionuclide-contaminated groundwater (Tokunaga et al., 2003; Istok et al., 2004). During *in situ* bioimmobilization, electron donor additions are used to stimulate iron- and sulfate-reducing conditions, which promote the reductive precipitation of redox-sensitive metals and radionuclides from groundwater. Diverse or extreme geochemical conditions common to radionuclide-contaminated sites present unique challenges to successful implementation of bioimmobilization.

In situ chemical treatment technique

By this method, chemical compounds are used to transform pollutants in the subsurface. *In situ* chemical treatment processes generally consist of installing a series of injection wells for delivering chemical compounds at the head or within the plume of polluted groundwater. Chemicals that are added can oxidize or reduce pollutants, converting them to non toxic forms or immobilizing them to minimize their migration ability. Possible oxidizing compounds include hydrogen peroxide, ozone and potassium permanganate. The most often used reducing agent includes sulfur dioxide, sulfide salts, ferrous sulfate, metallic iron and zinc.

This technique can be considered in cases where specific pollutants, their concentrations and the extent of pollution plume in the aquifer are well-defined. The treatment chemical compounds specific to the class of pollutants are delivered in the subsurface by injection wells, as shown in Figure 6a (Barcelona et al., 1990). Figure 6b also illustrates a simple field technique of *in-situ* oxidation treatment method for contaminants like
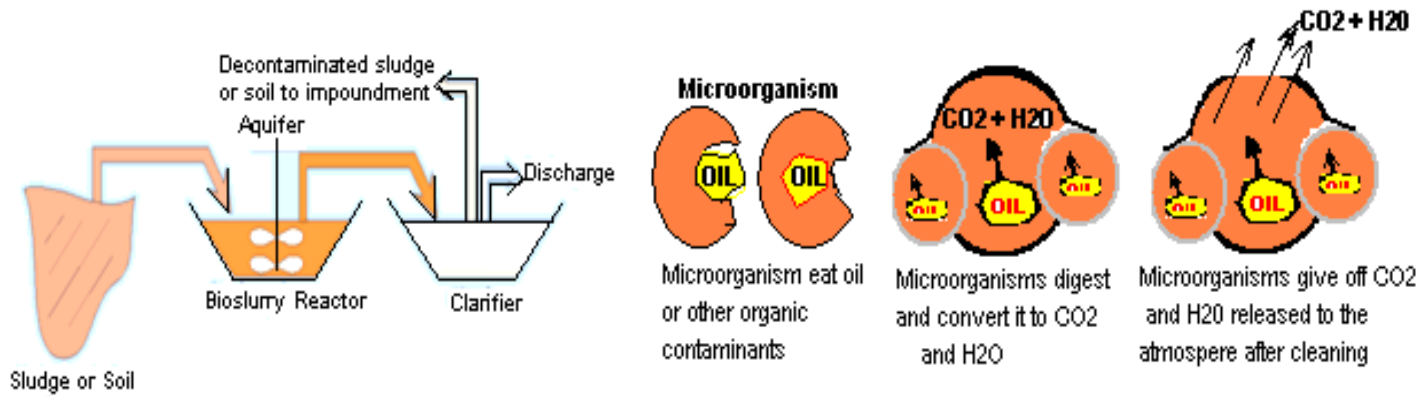
Figure 5. (a) Bioslurry bioremediation system (USEPA, 1991) (b) Bioremediation processes.
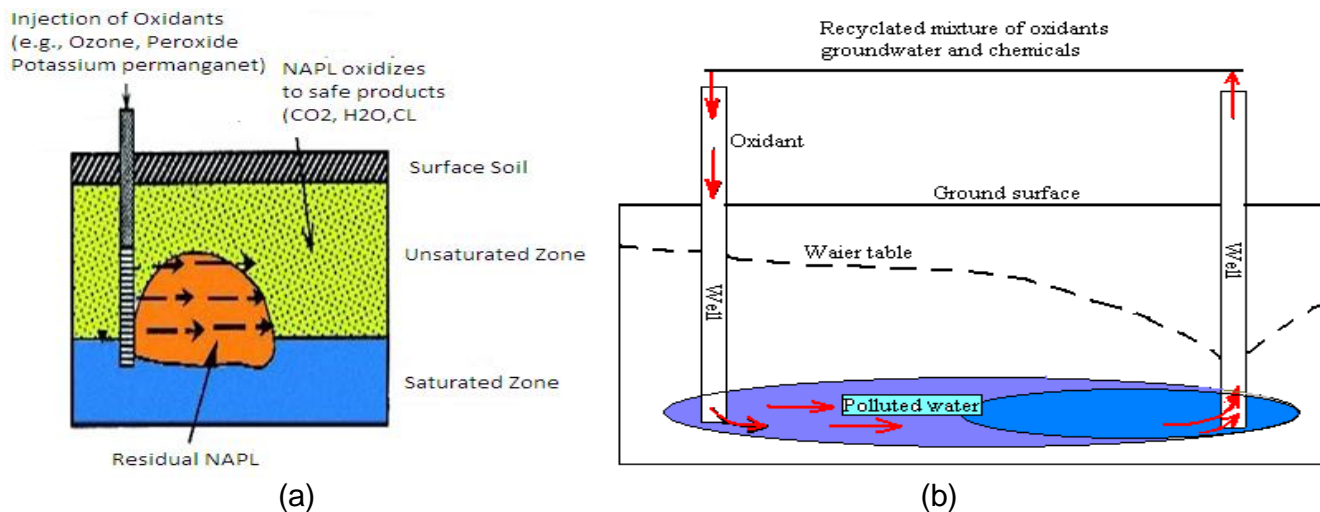

Figure 6. Techniques of chemical treatment system: (a) Barcelona et al. (1990); (b) Simple oxidation field technique.

amines, phenols, cyanides, halogenated aliphatic compounds, and certain pesticides in liquid waste streams.

In situ thermal technologies

In situ thermal technologies are designed to increase the temperature, of the subsurface to improve and accelerate the removal mechanisms of the pollutants. At the increasing of temperature the organic pollutants will mobilize more rapidly due to enhanced volatilization, enhanced desorption from soil, increased water solubility and increased fluid flow rates. Higher temperatures can also accelerate biodegradation and other certain abiotic transformation or decomposition reactions. Temperature can be increased by injection of heated fluids such as air, water or steam. Other means of heat addition include installation of vertical electrodes that provide resistance

heating by passing electrical current through the soil between the electrodes, with the amount of heat controlled by the amount of electrical current. *In situ* steam injection – extraction removes volatile and semi-volatile pollutants from soil and groundwater without requiring excavation. Application of steam injection and extraction (Figure 7) relies on the ability to deliver, control flow and recover the heating fluid.

Permeable reactive barriers technique

Permeable reactive barrier (PRB) is an *in situ* treatment zone that passively captures a plume of contaminants and removes or breaks down the contaminants, releasing uncontaminated water (Gillham et al., 2010). The primary removal methods include: (1) sorption and precipitation, 2) chemical reaction, and (3) reactions involving biological
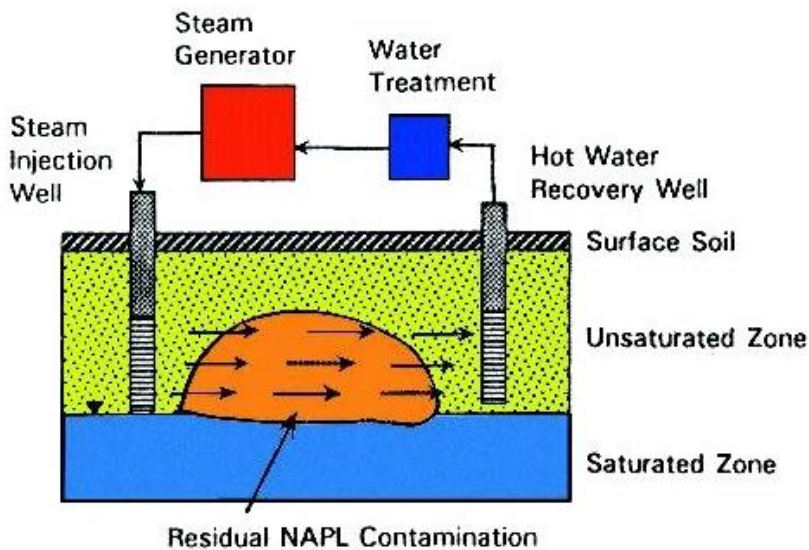
Figure 7. Scheme of a steam injection system (Barcelona et al., 1990).
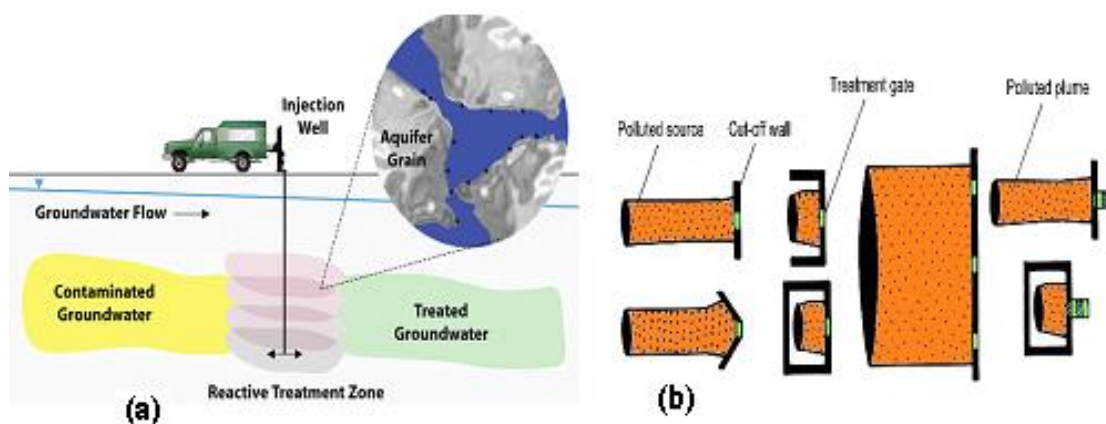

Figure 8. (a) Funnel and gate configuration (b) Field technique of PRB.

mechanisms involve construction of permanent or semi-permanent wall across the flow path of pollutant plume (Figure 8a). As the polluted groundwater moves passively through the wall, the pollutants are removed. Funnel and gate systems are used to channel the contaminant plume into a gate which contains the reactive material Figure 8b). The funnels are non-permeable, and the simplest design consists of a single gate with walls extending from both sides. An advantage of the funnel and gate system is that a smaller reactive region can be used for treating the plume, resulting in lower cost.

Denitrification technique

Most methods of nitrate removal that have been applied

for *in situ* groundwater treatment are based on chemical and/or biological denitrification. The methods apply redox reactions, often with biological catalysis, to reduce the nitrogen (N) oxides, nitrate (NO_3) and nitrite (NO_2), to the gases nitric oxide (NO), nitrous oxide (N_2O), and dinitrogen (N_2) to nitrogen gas. The appeal of using denitrification reactions for *in situ* application lies mainly in the fact that the main products of the reactions are gaseous and do not accumulate as hazardous by-products in the subsurface. Some of the techniques also do not require highly sophisticated technology. A series of factors influence the denitrification reactions and the most important ones for biological denitrification are listed below:

i) Temperature, preferably near 35°C; and pH, preferably

neutral to alkaline;
ii) Organic carbon present as substrate for bacteria; and Carbon: nitrogen ratio of 1:25;
iii) Presence of nutrients such as phosphate; and sufficient denitrifying bacteria;
iv) Low oxygen, that is, anoxic or anaerobic conditions; and high soil water content;
v) Anthropogenic disturbance of the soil and Porosity and permeability of aquifer.

Biological denitrification plants in the USA, France and parts of Europe generally use ethanol or methanol as carbon substrate. In one pilot plant in Israel, sucrose was used. Iron and manganese that are mobilized from the aquifer during the denitrification process are re-precipitated in the oxidation step.

Other field techniques

Natural attenuation

Natural attenuation defines the natural occurring processes in the subsurface environment such as dilution, volatilization, biodegradation, adsorption and chemical reactions with subsurface compounds that contain the spread of pollution and reduce the concentration and amount of pollutants at polluted sites. Consideration of this option requires modeling and evaluation of pollutant degradation rates and pathways. The processes contributing to natural attenuation are typically acting at many sites, but at varying rates and degrees of effectiveness, depending on the types of pollutants present and physical, chemical and biological characteristics of the soil and groundwater. To estimate how well natural attenuation will work and how long it will take requires a detailed study of the contaminated site.

Hydraulic and pneumatic fracturing

The pneumatic fracturing process involves injection of highly pressurized air into consolidated sediments that are polluted to extend existing fractures and create a secondary network of fissures and channels. In this way, the hydraulic permeability of the soil increases and the removal of the pollutants will be accelerated particularly by vapor extraction, biodegradation and thermal treatment. Hydraulic fracturing creates distinct fractures in low permeability and over-consolidated clays or sediments. High-pressure water is first injected into the bottom of a borehole to cut a notch that will serve as the starting point for the fracture. Slurry of water, sand and thick gel are pumped at high pressure into the borehole to propagate the fracture. These fractures will serve for steam or hot air injection or pollutant recovery and they can also improve pumping efficiency and the delivery for other *in situ* processes.

Air injection

This involves the injection of air with high pressure in a trench or in a borehole to form bubbles in a groundwater column. The bubbles will strip volatile organic compounds from the dissolved phase from NAPIs present along the path of the bubbles; they will add oxygen to the water to enhance the *in situ* bioremediation process and they will establish large circulation in the subsurface which tends to move polluted water to the surrounding wells for extraction. After the bubbles make their way to the unsaturated zone, a soil vapor extraction system is used to remove the vapors for treatment prior to release to the atmosphere. One major drawback of this technique consists in the risk of the potential off-site migration of vapors pollutant plumes so that an adequate monitoring system will be necessary.

Solidification and stabilization

Solidification and stabilization refers to treatment processes that mix or inject treatment agents into the polluted material to accomplish one of the following objectives: to improve the physical characteristics of the water by producing a solid form liquid or semi-liquid wastes; to reduce pollutant solubility; to decrease the exposed surface area across which mass transfer of pollutants may occur. Solidification refers to techniques that encapsulate hazardous waste into a solid material of high structural integrity. Stabilization refers to techniques that treat hazardous waste by converting it into a less soluble, mobile or toxic form. Solidification and stabilization technologies can immobilize many heavy metals, certain radionuclide and selected organic compounds while decreasing waste surface areas and permeability for many types of sludge, contaminated soils and solid wastes. Common solidification and stabilization agents include cement, lime, limestone, and various mixtures of these materials and various organic binders.

DISCUSSION OF PROSPECTS

Advantages

In situ treatment of contaminated groundwater uses the aquifer as a subsurface "treatment plant" to improve the quality of groundwater supplies. This has several advantages over conventional *ex situ* treatment technologies (pump-and-treat systems). The advantages are;

i) Cost and time savings
ii) Exposure to chemical reagents.
iii) There is a long period of operation (anything from 5 to 30 years) with less stringent control of operating conditions.

iv) Robust and require less plumbing.
v) Redox-based systems can often remove other contaminants e.g. chromate and organic chemicals, if these are also present.

Side effects

Some *in situ* treatment methods for removing groundwater contaminants may cause undesirable side effects, of which the most common problem is clogging in the subsurface. In the case of removal of organic compounds, the products of the treatment reaction may cause clogging of the aquifer due to biofilm build-up. If metals are removed by precipitation, the solid precipitates in the aquifer matrix may reduce the permeability of the aquifer over the long term. The specific hydrogeological conditions and the contaminant load will determine the extent of these phenomena. Side effects need to be managed to maintain the efficiency of the scheme and increase the treatment lifetime. Biofilm build-up in the aquifer, e.g. in biological systems still constitute a major disadvantage.

Design criteria

For the design of any treatment system, both the hydrodynamics of the flow system and the source of the pollution need to be exceptionally well characterized to optimize the system. The nature of the pollution source will affect the choice of system design. Trench and fill barrier methods are only suitable for shallow flow systems where the barrier can be constructed down to the impermeable bedrock. In deeper flow systems, treatment barriers can be created by borehole injection. *In situ* treatment methods are more likely to be successful in primary aquifers, where hydrodynamics are more easily understood and greater control over the treatment zone can be exercised than in fractured complex flow environments. For nitrate removal systems, management of nitrogen inputs to the subsurface is still required, as treatment of the nitrate in the aquifer does not remove the contamination source. Although the treatment systems generally have a long lifetime, it is still important that the source of contamination be eliminated wherever possible.

Prospect case example

In Nigeria are great potentials for *in situ* treatment of shallow aquifers that constitute the accessible and economic sources of water supply to the ever growing population. From the basement complex rocks of the North and Western Nigeria to south-east and to the south-south sedimentary basins are shallow aquifers. About 85% of the population depends on shallow wells producing water from these water table aquifers

significantly polluted. The configuration of these wells range from 40 ft hand-dug tube wells to 100 to 120 ft hand driven mono pump wells and to between 120 to 200 ft hand-driven minor motorized pump wells. These are predominantly the private/commercial wells. Deep wells are usually the few public or government motorized rig drilled wells that are often non functional or abandoned. Aquifer contamination in most parts of Nigeria is mainly the product of poor domestic and industrial waste management and chemical fertilizer agricultural input across the country.

In the Niger Delta significantly, groundwater may have variable levels of pollution by petroleum products and wastes, and oil and gas spills. Another major pollution issue of the Niger Delta region of Nigeria is the saline intrusion to aquifer. The Niger Delta covers 20,000 km² within wetlands of 70,000 km² formed primarily by sediment deposition. It is home to 20 million people and 40 different ethnic groups. It is the largest wetland and maintains the third-largest drainage basin in Africa. The Niger Delta environment can be broken down into four ecological zones: coastal barrier islands, mangrove swamp forests, freshwater swamps, and lowland rainforests. A UNDP report states that there have been a total of 6,817 oil spills between 1976 and 2001, which account for a loss of three million barrels of oil, of which more than 70% was not recovered. 69% of these spills occurred off-shore, a quarter was in swamps and 6% spilled on land (UNDP, 2006). Some spills are caused by sabotage and stealing, while most are due to poor maintenance by oil companies such as Shell.

Presently, there is no significant research effort towards *in situ* treatment of groundwater in this region. A prospect model suggested for treating groundwater polluted by oil or gas in the Niger delta based on air sparging technique is illustrated in Figure 9.

Wells A, B, C are the compressed air injection wells, with injection nozzles extended from the water table. 1 and 2 are the air lifting wells connected to a blower that passes the aerated oil and gas to the atmosphere after some cleaning. X is the monitoring well with pump. This method is prospective in the Niger Delta where water table depth fluctuates to an average of 18 m or as shallow as 0 to 5 m in the swamps. A pilot study is necessary in order to determine the effectiveness of this technique in the area.

Prospect comparison

Capital investment for the *ex situ* plant may be between three and seven times higher than for the *in situ* systems. *In situ* methods have virtually no operating costs, and the permeable reactive barrier system have the lowest capital costs. This explains why *in situ* methods have already gained wide acceptance. *In situ* treatment systems for iron and manganese removal have been used successfully and economically for many decades, while *in*
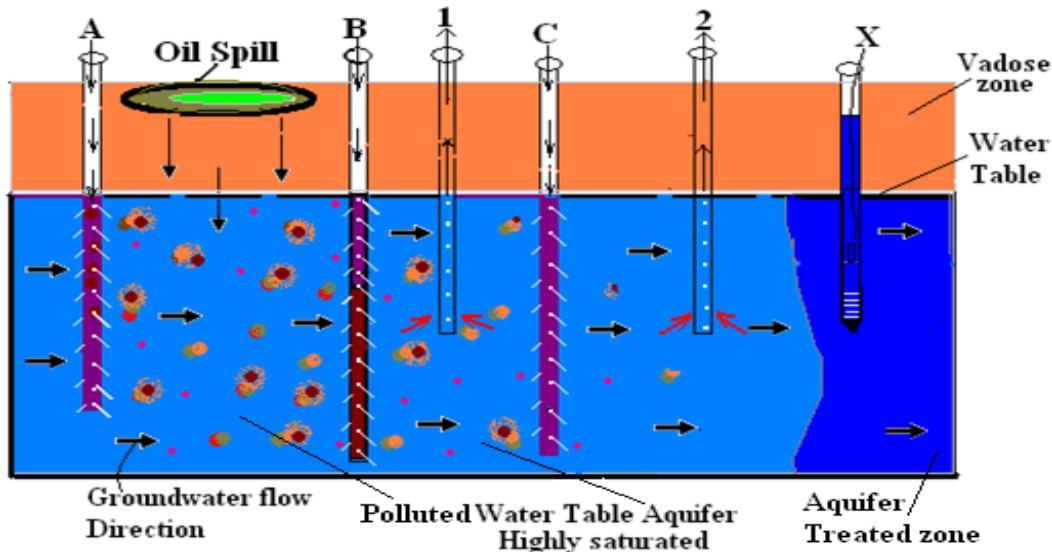
Figure 9. Air sparging field technique prospective for treating oil polluted areas of Niger Delta where the vadose and the shallow aquifer water consists of coastal plain sands.

situ nitrate removal has been in place for about two decades, with successful application in South Africa.

Summary

Although most water table aquifers are polluted, they are the easily accessible primary sources of urban and rural water supply. Sustainable hydrology this millennium will capture *in-situ* treatment of polluted aquifers particularly in developing countries. The most important *in situ* groundwater treatment methods can be divided into the following three main groups: Permeable Reactive Barrier (PRB), Biological and Electrochemical methods with Air and Steam injections techniques. *Ex-situ* pump and treat method is slow, costly and unsustainable. *In-situ* treatment of polluted aquifer starts with mapping pollution source(s), identifying stressors and migration pathway, estimating quantum of stress, and terminating release of stressors from the source. Sustainable hydrology shall include developing a hydrologic model code that can predict pollution, treatment method; amount and period of treatment. The model code shall be based on the characteristics of the aquifers; the pollution stress and the subsurface. *In situ* treatment however has shown potential for total groundwater cleanup and considered as a 21st century aspect of sustainable hydrology. Inorganic contaminants susceptible to this cleanup include Arsenic (As), Cadmium (Cd), Chromium (Cr), Copper (Cu), Mercury (Hg), Iron (Fe), Manganese (Mn), Molybdenum (Mo), Nickel (Ni), Lead (Pb), Selenium (Se), Technetium (Te), Uranium (U), Vanadium (V), Nitrate (NO_3^-), Phosphate (PO_4^-), and Sulphate (SO_4^{2-}). Organic compounds can also be removed by *in situ* treatment.

Conclusion

Permeable reactive barriers can be constructed from cheap, readily available materials and would be relatively simple for sub urban communities in Nigeria to install with limited training. *In situ redox manipulation* (ISRM) should be tested for deeper primary aquifers in South and West African countries. The dithionite chemical reagent should be readily available, since it is used in the pulp and paper industry. The electrokinetic method is, however, the only one found that has been claimed to be suitable for fractured aquifers with high technical skill. *Vyredox* method for Iron and manganese removal is imperative in many high volume abstraction situations to avoid or minimize borehole clogging effects. Advancement in groundwater geophysics, to advanced hydrological or hydrodynamic model codes is inevitable for sustainable hydrology this 21st century. Though global, the aspect of sustainable hydrology needs to be well infused into groundwater management in Africa, and now is the time.

REFERENCES

Barcelona M, Keely J, Pettijohn W, Wehrman A (1990). Contamination of ground water: Prevention, assessment, and restoration. Pollution Technology Review No. 184. Noyes, Park

Benaabidate L, Cholli M (2011). Groundwater stress and vulnerability to pollution of Saiss basin shallow aquifer, Morocco. 15th International Water Technology Conference, IWTC-15 2011, Alexandria, Egypt.

Brown CL, Pope GA, Abriola LM, Sepehrnoori K (2010). Simulation of surfactant-enhanced aquifer remediation. Water Resour. Res. 30(11):2959-2977.

Key KC, Sublette KL, Johannes TW, Raes E, Sullivan E, Duba J, Ogles D, Baldwin BR, Biernacki A (2013). An *In Situ* Bioreactor for the Treatment of Petroleum Hydrocarbons in Groundwater. Remed. J. 23(3):55-84.

http://journals.ohiolink.edu/ejc/article.cgi?issn=10515658&issue=v23i 0003&article=55_aisbfttophig

Cherry AJ (1992). Developing rational goals for *in situ* remedial technologies. Subsurface Restor Conf, Dallas.

Elliott DW, Zhang WX (2001). Field assessment of nanoscale bimetallic particles for groundwater treatment. Environ. Sci. Technol. 35:4922-4926

Fetter CW (1993). Contaminant Hydrogeology. Macmillan Publishing Company, New York.

Faybishenko B, Hazen TC, Long PE, Brodie EL, Conrad ME, Hubbard SS, Christensen JN, Gavaskar A, Tatar L, Condit W (2008). Cost and Performance Report Nanoscale Zero-Valent Iron Technologies for Source Remediation. Port Hueneme, CA: Naval Facilities Engineering Command; CR-05-007-ENV: at www.clu-in.org/download/techdrct/td_CR-05-007-ENV.pdf.

Glazier R, Venkatakrishnan R, Gheorghiu F, Walata L, Nash R, Zhang W (2003). Nanotechnology takes root. Civ. Eng. 73(5):64-69.

Gillham R, Vogan J, Gui L, Duchene M, Son J (2010). Iron barrier walls for chlorinated solvent remediation. In: Stroo, H. F.; Ward, C. H. (eds.), *In Situ* Remediation of Chlorinated Solvent Plumes. Springer Science+Business Media, NY, p. 537. doi:10.1007/978-1-4419-1401-9

Henn KW, Waddill DW (2006). Utilization of nanoscale zerovalent iron for source remediation - A case study. Remediation 16(2):57-77.

Hubbard SS, Williams KH, Conrad ME, Faybishenko B, Peterson J, Chen J, Long PE, Hazen TC (2008). Geophysics for monitoring of hydrological and bio-geochemical transformations associated with contaminant remediation. Environ. Sci. Technol. 42:3757-3765.

Istok, JD, Senko JM, Krumholz LR, Watson D, Bogle MA, Peacock A, Chang YJ, White DC **(**2004). In situ bioreduction of Technetium and Uranium in a nitrate-contaminated aquifer. Environ. Sci. Technol. 38:468-475.

Jaisi DP (2013). Stable isotope fractionations during reactive transport of phosphate in packed-bed sediment columns. J. Contam. Hydrol. 154:10-16.

Macé C, Desrocher S, Gheorghiu F, Kane A, Pupeza M, Cernik M, Kvapil P, Venkatakrishnan R, Zhang W-x (2006). Nanotechnology and groundwater remediation: A step forward in technology understanding. Rem. J. 16(2):23-33.

Matheson LJ, Tratnyek PG (1994). Reductive dehalogenation of chlorinated methanes by iron metal. Environ. Sci Technol. 28(12):2045-2053.

Melloul AJ., Collin ML (2002). Prioritization of Sustainable Groundwater Management Needs: Case of Israel's Stressed Coastal Aquifer. Environ. Dev. Sustain. 4(4): 347-360.

Melloul AJ, Collin ML (2000). Sustainable groundwater management of the stressed Coastal aquifer in the Gaza Region. Hydrol. Sci-J-des Sci. Hydrologiques 45(1):1-47.

McDonald MG, Harbough AW (1988). A modular three-dimensional finite-difference groundwater flow model, MODFLOW. U.S. Geo Survey Open-file Report 83-875.

Nwachukwu MA, Osoro E (2013). Assessment of environ hazards: Linking borrow pits, gully erosion, and road failure. J. Geotech. Eng. Construct. Tech. 4(6):199-210,

Nwachukwu MA, Huan F (2012). *In-situ* Remediation of Shallow Aquifer. Pollut. J. Hydrol. Eng. Editorial, 1:1.

Nwachukwu MA, Ohuawunwa C, Nwachukwu I, Nnorom U (2012). Sustainable water supply from boreholes in neighborhood communities besieged by off-campus students. Int. J. Water Res. Environ. Eng. 4(11):352-362.

Nwachukwu MA, Huan F, Ophori D (2010). Groundwater model and particle track analysis, for water quality monitoring and pollution assess around contaminated sites. J. Spatial Hydrol. 10(1).

Nwachukwu MA, Feng H, Amadi MI, Umunna FU (2010). The Causes and the Control of Selective Pollution of Shallow Wells by Coliform Bacteria: Imo River Basin Nigeria. Water Qual. Expo. Health 2:75-84.

Nowack B (2008). Pollution prevention and treatment using nanotechnology. In: Krug H, Nanotechn, Environ Aspects. Weinheim: Wiley-VCH Verlag. 2:1-15.

Nandakumar T (2012). Aquifer atlas reveals groundwater stress. The Hindu, Today's Paper (October, 12) Otto M, Floyd M, Bajpai S. Nanotechnology for site remediation. Rem. J. 19(1):99-108.

Plaza G, Ulfig K, Hazen TC, Brigmon RL (2001). Use of Molecular techniques in bioremediation Acta. Microbiol. Pol. 50:205-218.

Pollock DW (1994). User's guide for MODPATH/MODPATH PLOT, version 3: A particle tracking post processing package for MODFLOW: The U.S. Geological Survey finite-difference groundwater flow model

Piotrowski MR, Doyle JR, Carraway JW (2006). Integrated bioremediation of soil and groundwater at a superfund site. Rem. J. 2(3):293-309.

Rickerby DG, Morrison M (2007) Nano-technology and the environment: A European perspective. Sci. Technol. Adv. Mater. 8:19-24.

Rao PS, Annable MD, Sillan RK, Dongping D, Hatfield K, Graham WD, Wood LA, Enfield CG (2010). Field-scale evaluation of *in situ* cosolvent flushing for enhanced aquifer remediation. Water Res. 33:2673-2686,

Royal Commission on Environmental Pollution (2008). Novel Materials in the Environment: The Case of Nanotechnology. London: Royal Committee on Environ Pollution. Accessed at: http://www.official-documents.gov.uk/document/cm74/7468/7468.pdf

Saleh N, Sirk K, Liu Y, Phenrat T, Dufour B, Maty-jaszewski K., Tilton RD, Lowry GV (2007). Surface modifications enhance nanoiron transport and NAPL target-ing in saturated porous media. Environ. Eng. Sci. 24:45.

Suthersan S, John H, Denice N, Scott P (2010). *In situ* air sparging remediation engineering design. Ground water Monit. Rem. 30(3):39-44,

Theron J, Walker JA, Cloete TE (2008). Nanotechnology and water treatment: Applications and emerging opportunities. Crit. Rev. Microbiol. 34:43-69.

Tratnyek PG, Johnson RL (2006). Nanotechnology for environmental cleanup. Nanotoday 1(2):44-48.

Tokunaga TK, Wan JM, Firestone MK, Hazen TC, Olson KR, Herman DJ, Sutton SR, Lanzirotti A (2003). *In situ* reduction of chromium (VI) in heavily contaminated soils through organic carbon amendment. J. Environ. Qual. 32:1641-1649.

U.S. EPA. (2001). Cost Analysis for Selected Groundwater Cleanup Projects: Pump and Treat Systems and Permeable Reactive Barriers. Washington, DC: Environ Protect Agency 542-R-00-013.

U.S. EPA (2008b). Nanotechnology for Site Remediation: Fact Sheet. Washington, DC: EPA 542-F-08-009 at http://www.epa.gov/tio/download/remed/542-f-08-09.pdf

U.S. EPA (1991). "Sampling and analysis plan for a bench-scale bioslurry test of soil from the 9th Ave Dump Superfund site, U.S. Army Engineering Waterways Experiment Station, Vicksburg, Washington, DC.

UNDP (2006). "Niger Delta Human Development Report." UNDP p. 76. Retrieved 19 June, 2013

Zhang W-X (2003). Nanoscale iron particles for environmental remediation: An overview. J. Nanopart. Res. 5:323-332.

Zhang W-X (2005). Frontiers in Nanotechnology: U.S. EPA Millenium Lecture Series. Nanotechnology for Water Purification and Waste Treatment July 18, 2005 Washington D.C.: http://www.epa.gov/ncer/nano/lectures/zhang0705.pdf

Zhang W-X, Elliott DW (2006). Application of iron nanoparticles for groundwater remediation. Rem. J. 16(2):7-21.