

Review

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

Michael A. Nwachukwu

Department of Environmental Technology, Federal University of Technology, Owerri, Nigeria.

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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 m² (10,000 ft²) and extended to a depth of 10.7 m (35 ft), representing a total cleanup volume of 9930 m³ (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 TiO ₂ |
| 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, Trichlorobenzene, 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

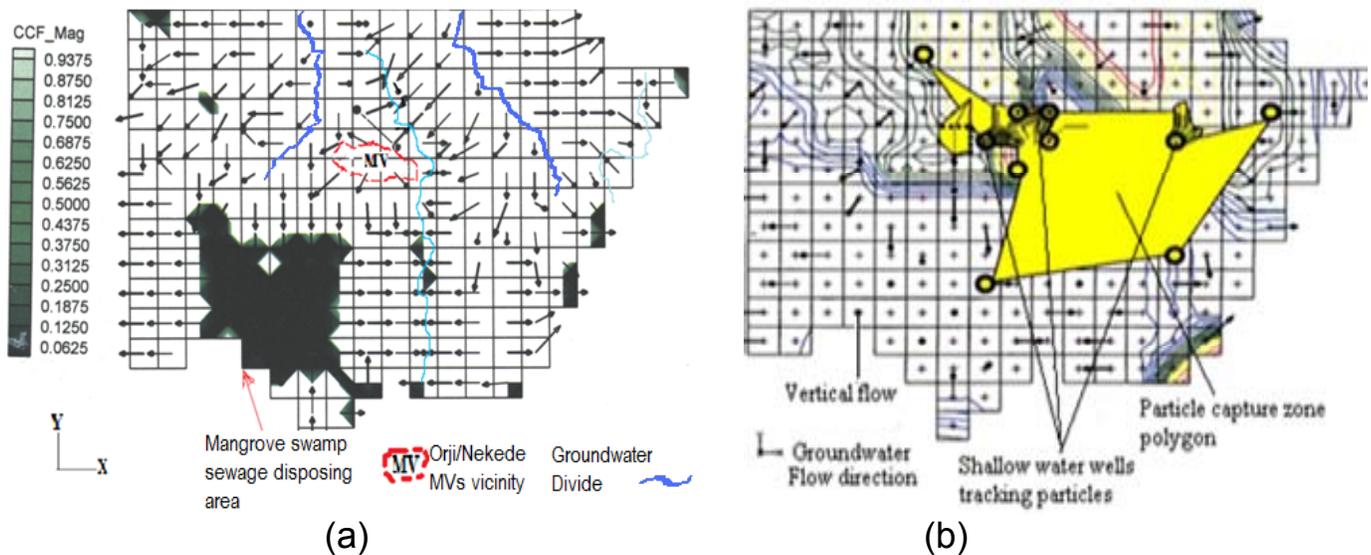


Figure 1. (a) Groundwater flow pattern based on model layer 5. In the SW portion is the highly contaminated sewage dump mangrove swamp area of Umuapu and Egbeda (b) Particle capture zone across Owerri metropolis (Source: Nwachukwu et al., 2010b).

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 ($\delta^{18}O_p$). The results collectively suggest that abiotic reactive transport processes exert minimal influence on the $\delta^{18}O_p$ 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

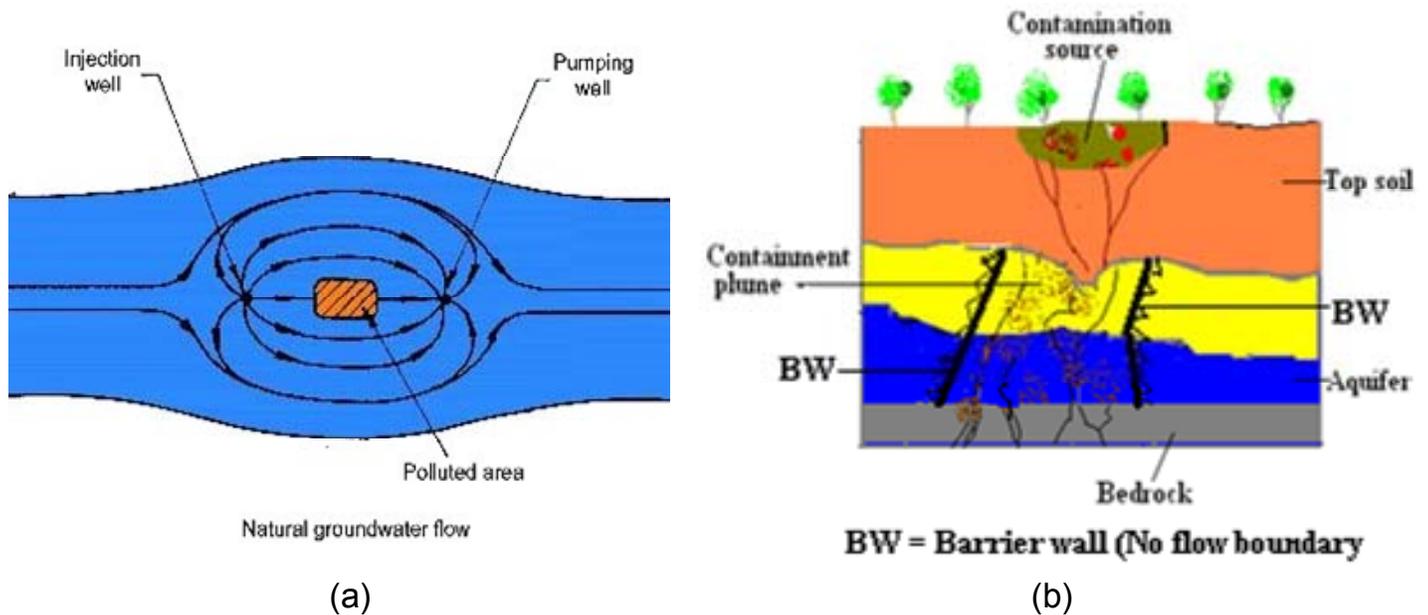


Figure 2. Scheme of containment systems (a) Hydraulic containment (Source: Fetter, 1993); (b) Containment barrier walls.

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 (LNAPLs) 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

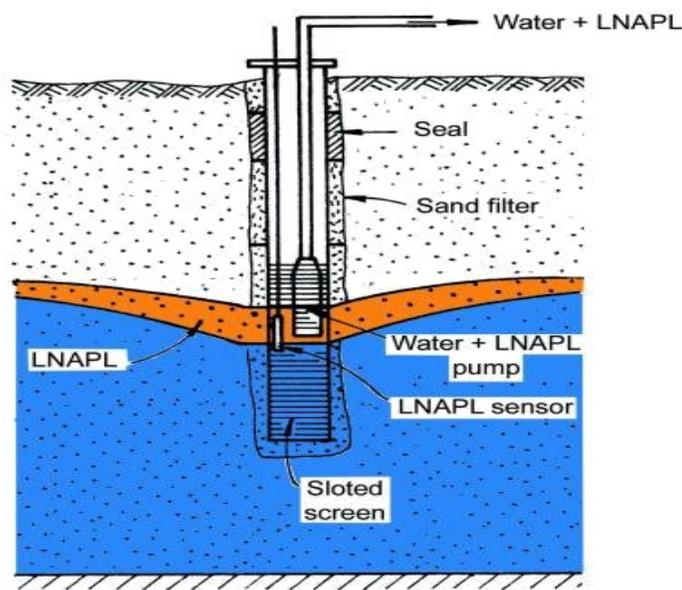


Figure 3. Examples of NAPL recovery by pump and treat system. Source: Beddient et al. (1993).

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

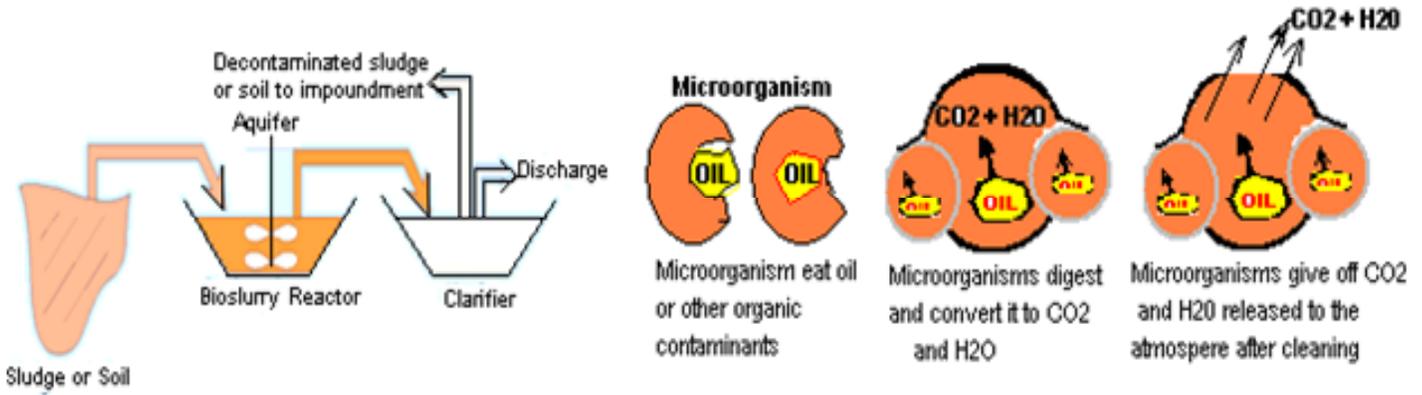


Figure 5. (a) Bioslurry bioremediation system (USEPA, 1991) (b) Bioremediation processes.

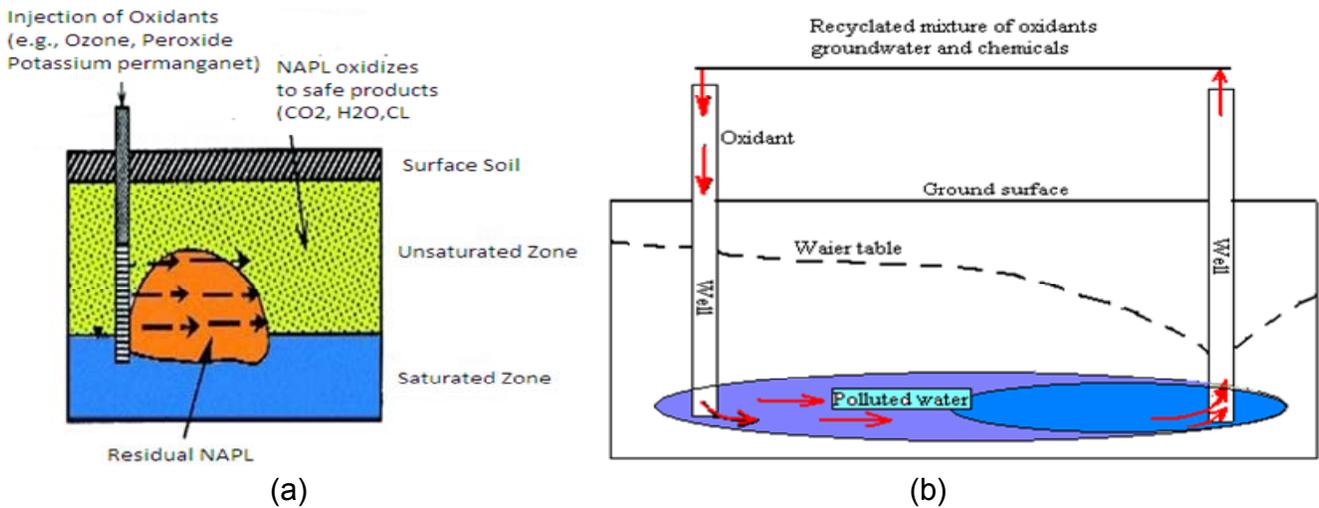


Figure 6. Techniques of chemical treatment system: (a) Barcelona et al. (1990); (b) Simple oxidation field technique.

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

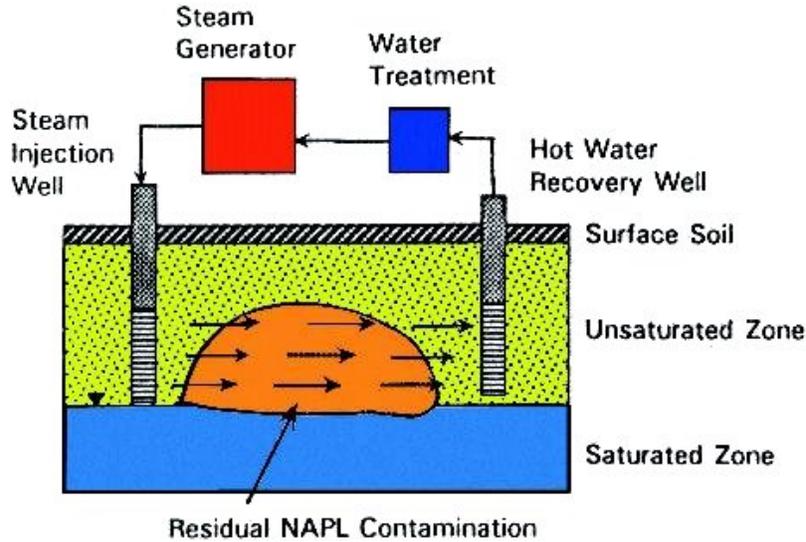


Figure 7. Scheme of a steam injection system (Barcelona et al., 1990).

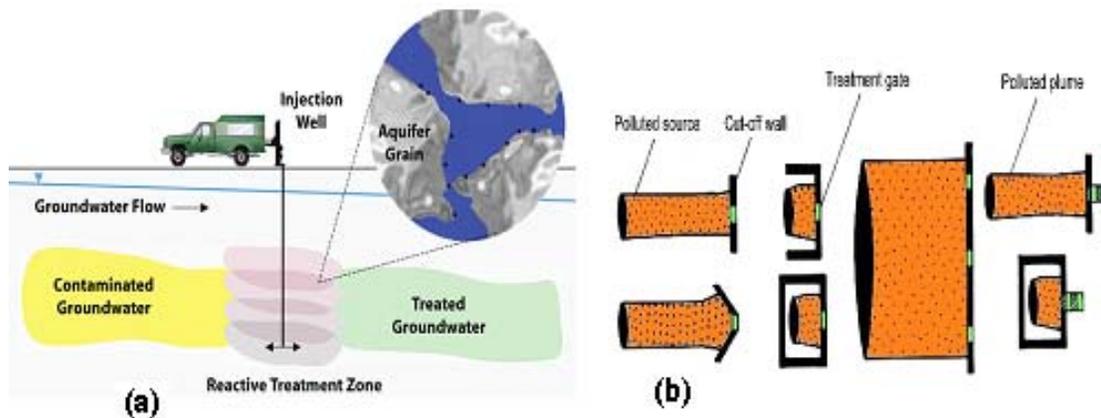


Figure 8. (a) Funnel and gate configuration (b) Field technique of PRB.

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 (NO₃) and nitrite (NO₂), to the gases nitric oxide (NO), nitrous oxide (N₂O), and dinitrogen (N₂) 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*

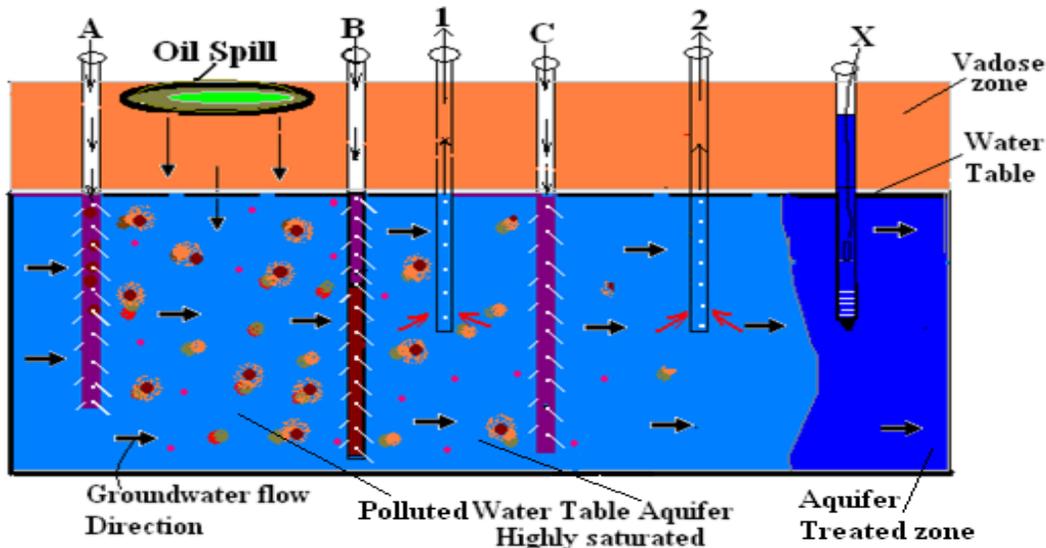


Figure 9. Air sparging field technique prospective for treating oil polluted areas of Niger Delta where the vadose and the shallow aquifer water consists of coastal plain sands.

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.

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