The buffering capacity of soil materials for various contaminant types and the relationship between soil morphology, chemical properties and buffering capacity:
a literature review

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# 1.	INTRODUCTION

South Africa has limited water resources that are unevenly distributed. Some areas already experience water shortages and competition among various activities for the use of water has become more intense, requiring better management of the resource (Sililo et al., 2001). The economy is largely driven by mining and agricultural sectors that to a certain extent depend on groundwater (Table 1.1). Although groundwater contributes only about 15% of the total water consumption, it is estimated that 90% of extracted groundwater in South Africa is used by farmers (Colvin, 2001) and two-thirds of the country, including more than 280 towns and settlements, are largely dependent on groundwater (Sililo et al., 2001). The role of groundwater is thus very important and continues to grow across the country because of its availability and greater cost effectiveness than that of dwindling surface water resources (Sililo et al., 2001).

Table 1.1. Groundwater uses in South Africa (Colvin, 2001)

Use	Percentage
Irrigation	78
Domestic	7
Stock	6
Mining	5
Industrial	4

It is important that the quality of groundwater be closely monitored and that protection measures are put in place to safeguard groundwater from pollution.

Groundwater vulnerability is defined as the sensitivity of groundwater quality to an imposed contaminant load, which is determined by the intrinsic characteristics of the aquifer (Lobo-Ferreira, 2003). According to Focazio et al. (2003), the intrinsic susceptibility of a groundwater system to contamination depends on aquifer properties (hydraulic conductivity, porosity, hydraulic gradients) and the associated sources of water and stresses to the system (recharge, interactions with surface water, travel through the unsaturated zone, and well discharge). These aquifer properties are affected by several factors such as soil properties, properties of contaminants, hydraulic loading on the soil and crop management (Huddleson, 1994). Understanding the groundwater flow system will enable a better assessment of potentially important factors controlling the intrinsic susceptibility and vulnerability of the groundwater resource. This review focuses on soils and their role in attenuating contaminants (sometimes referred to as their buffering capacity) before they reach the groundwater table.

2.   SOURCES AND TYPES OF POLLUTION

The purpose of this section is to give some idea of the diversity of more common pollutants as a preamble to developing a perspective of the role of soil in arresting their mobility.

The chemical and biological quality of groundwater needs to be of acceptable standard for most uses. The South African Department of National Health and Population Development (1990) has drawn up guidelines for drinking water standards that specify maximum limits of various constituents for insignificant and low risk. These guidelines can be found in Colvin's (2001) report on groundwater quality protection for farmers. The quality of groundwater depends on quantity and quality of contaminants that pass through the soil to groundwater. The transport of those contaminants through the soil is governed by physical, geochemical and biological processes as influenced by soil properties, physical and chemical nature of contaminants.

The first step in addressing the problem of groundwater pollution and understanding the role of soil processes that affect the fate and transport of contaminants is to identify sources of contaminants and their properties. There are two basic types of groundwater pollution: point sources and non-point sources. Point-source pollution is contamination that can be traced to a particular source such as an industrial site, septic tank, or wastewater treatment plant. Non-point-source pollution occurs diffusely large areas and includes agricultural, human, forestry, urban, construction, mining and atmospheric deposition (Sparks, 2003). Sources are further classified in terms of time as either continuous or instantaneous (Focazio et al., 2003). Some of the main pollutant sources found in South Africa and their characteristics and impacts are listed in Table 2.1.

Tables 2.2 and 2.3 list some organic compounds and trace metals that are commonly found in groundwater as contaminants. The concentration of such contaminants is highly variable and acceptable limits are not in all cases known.

Table 2.1. Groundwater contaminant sources (modified after Sililo et al., 2001)

Pollution category	Pollution source	Main pollutant	Potential impact
Municipal	Sewer leakage Septic tanks, cesspools, privies	Nitrate, viruses and bacteria	Health risk to users, eutrophication of water bodies, odour and taste
	Sewage effluent and sludge	Nitrate, salts, organic compounds, viruses and bacteria	
	Stormwater runoff	Bacteria and viruses	Health risk to users
	Landfills	Inorganic salts, organic compounds, heavy metals, viruses and bacteria	Health risk to users, eutrophication of water bodies, odour and taste
	Cemeteries	Nitrate, viruses and bacteria	Health risk to water users
Agriculture	Feedlot wastes	Nitrate, ammonia, viruses and bacteria	Health risk to users (e.g. methaemoglobinemia)
	Pesticides and herbicides	Organic compounds	Toxic/carcinogenic
	Fertilisers	Nitrogen, phosphorus	Eutrophication of water bodies
	Leached salts	Dissolved salts	Increased TDS in groundwater
Industrial	Process water and plant effluent	Organic compounds and heavy metals	Carcinogens and toxic elements
	Industrial landfills	Inorganic minerals, organic compounds, heavy metals, viruses and bacteria	Health risk to users, eutrophication of water bodies, odour and taste
	Leaking storage tanks (e.g. petrol stations)	Hydrocarbons and heavy metals	Odour and taste
	Chemical transport Pipeline leaks	Hydrocarbons and chemicals	Carcinogens and toxic compounds
Atmospheric deposition	Coal fired power stations Vehicle emissions	Acidic precipitation	Acidification of groundwater and toxic leached heavy metals
Mining	Mine tailings and stockpiles	Acid drainage	
	Dewatering of mine shafts	Salinity, inorganic compounds, metals	Toxic concentrations of some compounds
Groundwater use	Salt water intrusion	Inorganic salts	Water deterioration

Table 2.2. Organic compounds found in groundwater (source: Diz, 2003)

Groundwater contaminants	
Acetone	Methylene chloride
Benzene	Naphthalene
bis- (2-ethylexyl)phthalate	Phenol
Chlorobenzenee	Tetrachloroethene
Chloroethane	Toluene
Chloroform	1,2-trans-dichloroethane
1,1-dichloroethane	1,1,1-trichloroethane
1,2-dichloroethane	Trichloroethene
di-n-butyl phthalate	Vinyl chloride
Ethyl benzene	Xylene

Table 2.3. Trace metals occurring in groundwater (Diz, 2003)

Groundwater contaminants		
Aluminium	Copper	Selenium
Antimony	Gold	Silver
Arsenic	Iron	Strontium
Barium	Lead	Thallium
Beryllium	Lithium	Tin
Boron	Manganese	Titanium
Cadmium	Mercury	Uranium
Chromium	Molybdenum	Vanadium
Cobalt	Nickel	Zinc

3. SOIL MINERALOGY AND CONTAMINANT BUFFERING

The capacity of a soil to sorb pollutants depends on physical, chemical and biological properties. Sorption mechanisms and soil mineralogy are briefly discussed in subsequent sections.

3.1 Sorption mechanisms

Sorption is a general term used when the retention mechanism at a surface is unknown and retention mechanisms include adsorption, surface precipitation and polymerisation (Sparks, 2003). Of the various phenomena that can contribute to sorption, chemical interactions constitute the major subject of interest in pollutant-soil interactions (Yong et al., 1992). Adsorption can be defined as the accumulation of a substance or material at an interface between the solid surface and the bathing solution (Sparks, 2003). Understanding the different sorption mechanisms involved in contaminant retention is a crucial step in assessing the vulnerability of aquifers as these processes (mechanisms) determines the fate and transport of most pollutants. Aquifers under soils with physical, chemical and biological properties that promote or increase the sorption of pollutants are considered less vulnerable to contamination.

The retention of contaminants through sorption mechanism in soils involves different kinds of bonding between adsorbate (solid surface) and adsorbent (contaminant). Physical forces such as van der Waal's forces and electrostatic outer-sphere complexes (Sparks, 2003) and chemical forces such as covalent bonding, hydrogen bonding and inner-sphere complexation that involve a ligand exchange mechanism (Stumm and Morgan, 1981) are involved in sorption of contaminants to adsorbate.

These sorption reactions are affected by quantity and type of surface functional groups on the exchange sites of the solid surface. A surface functional group is a chemically reactive molecular unit bound into the structure of a solid at its periphery such that the reactive components of the unit can be bathed by a fluid (Sposito, 1989). The surface functional group varies according to the solid surface (organic matter, clay mineral, oxide or carbonate) and the solution pH. The mechanism that dominates the sorption of a particular pollutant depends on the prevailing surface functional groups, solution pH and the functional groups of pollutants. The predominant sorption mechanism of cationic pollutants such as diquat^{2+} and paraquat^{2+} (herbicides) is apparently ion exchange (Best et al., 1972). Other mechanisms for this category of pollutants could be hydrogen bonding, ion-dipole and physical forces (Sparks, 1989).

Pollutants such as the herbicides mentioned above are likely to compete with metal cations for the exchange sites on surface functional groups. Sorption of metal cations is pH-dependent and is characterized by a narrow pH range (known as the adsorption edge) where sorption increases to nearly 100% and for a particular metal cation, the adsorption edge is related to its hydrolysis or acid-base characteristics (Sparks, 2003). Sorption of inorganic and organic pollutants is dependent on sorptive concentration (molecule or ion in solution), surface coverage, and the type of sorbent (material that accumulates at the surface). Each sorbent has its own relative affinity or selectivity that is related to the hydrated radius (Sparks, 2003). For example, Kinniburgh and Jackson (1981) found that with monovalent alkali cations, electrostatic interactions predominate and the general order of selectivity is

$Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$ with Cs^+ having the smallest hydrated radius which therefore can approach the surface the closest and be held the most tightly.

Similarly, the sorption of anions varies with pH, usually increasing with pH. However, with phosphate ($H_2PO_4^-$, HPO_4^{2-}) and selenite ($HSeO_3^-$, SeO_3^{2-}), sorption decreases with increasing pH (Barrow, 1985). Anions such as NO_3^-, Cl^- and ClO_4^- are sorbed as outer-sphere complexes and sorbed only on surfaces that exhibit a positive charge. Sorption is sensitive to ionic strength (Sparks, 2003). The sorption of pollutants that are anions is likely to be governed by similar sorption mechanisms.

3.2 Soil organic matter

Both content and quality of soil organic matter play an important role in determining the sorption capacity for groundwater contaminants. The soil structure influences the size of soil pores (permeability) and layering through which pollutants pass through into underlying aquifer. Organic matter enhances the cation exchange capacity (CEC) of the soil, thus increasing the adsorption sites for metals and other cationic solutes. Huddleson (1994) regards organic matter content as the most important variable affecting sorption of pesticides as it provides the greatest number of binding sites because of an extremely large surface area and chemical reactivity.
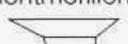
Rennert and Mansfeldt (2002) showed that sorption of the cyanide complexes ferricyanide $[Fe (CN)_6]^{3-}$ and ferrocyanide $[Fe (CN)_6]^{4-}$, depended on organic C, clay, and oxalate-extractable Al. They further stated that organic matter promotes sorption of both complexes, and destruction of soil organic matter reduced sorption by up to 99%. The chemical nature (quality) of organic matter enables it to adsorb different kinds of groundwater pollutants that are organic compounds. Several studies (Cruz-Guzmán et al., 2003; Hettiarachchi et al., 2003; Ran et al., 2003) have determined the adsorption capacity of humic acid for different organic pollutants in groundwater. A study by Terashima et al. (2003) on the distribution behaviour of pyrene on a humic acid (HA)-kaolin complex showed that the distribution coefficient (K_d) of pyrene on the HA-kaolin increased with the fraction (f_{oc}) of organic carbon adsorbed to the surface of kaolin. The results demonstrate that HAs, when adsorbed to clay minerals, play an important role in the deposition of polycyclic aromatic hydrocarbons (PAHs) in a soil environment.

The organic matter influence on soil pH also affects pH-dependent charge. Several studies (Stewart *et.al.* 2003; Dorronsoro *et.al.* 2002) have shown an increase in adsorption of certain contaminants with an increase in soil pH. Organic matter also provides energy to micro-organisms which degrade many organic compounds that are pollutants.

3.3 Clay minerals

Different clay minerals have different structures and properties that determine the CEC. The different structures affect the mechanism by which metals and other contaminants are retained in soil. Kaolinite has a 1:1 (silica: alumina layer) structure that has a low CEC and surface area whereas 2:1 clay minerals such as vermiculite and montmorillonite have high CEC and surface area and other 2:1 clays with non-expanded layers (illite, mica) or filled interlayers (chlorite) have intermediate reactivity (Table 3.1).

Table 3.1. Common clay minerals and charge characteristics (Yong et al., 1992)

CLAY MINERAL	LATTICE DESCRIPTION	C.E.C (cmol/kg)	SURFACE AREA (sq.m/g)	SOURCE OF CHARGE	CHARGE CHARACTERISTICS
kaolinites	1:1, strong H - bonds	5 - 15	15	edges, broken bonds, (hydroxyl-ated edges)	variable and fixed charges
illites	2:1, strong K - bonds	25	80	isomorphous substitution, some broken bonds at edges	mostly fixed charges
chlorites	2:2, strong bonds	10 - 40	80	isomorphous substitution	mostly fixed charges
vermiculites	2:1, weak Mg - bonds	100 - 150	700	isomorphous substitution	mostly fixed charges
montmorillonites	2:1, very weak bonds	80 - 100	800	isomorphous substitution, some broken bonds at edges	mostly fixed charges

silica layer
alumina layer

2:1 = two silica layers to one alumina layer

The CEC and surface area can respectively range from 5–15 $cmol_c$/kg and 15 m^2g^{-1} (kaolinites), to 80 – 100 cmol/kg and 800 m^2g^{-1} (montmorillonites). These and other properties of clay minerals affect the nature and magnitude of contaminant retention in soil.

The buffer capacity of a soil is usually defined as the capacity to neutralise inputs of acid or base by generating additional CEC (or losing it) with changes in pH, thus buffering pH changes. Figure 3.1 illustrates the variation which can be expected for different clay minerals. This indicates that besides inherent differences in CEC and surface area, the pH dependent adsorption behaviour of metal cations will also vary with clay mineral type, explaining to some extent why managing metal mobility in soils critically depends on controlling soil pH in the correct range.
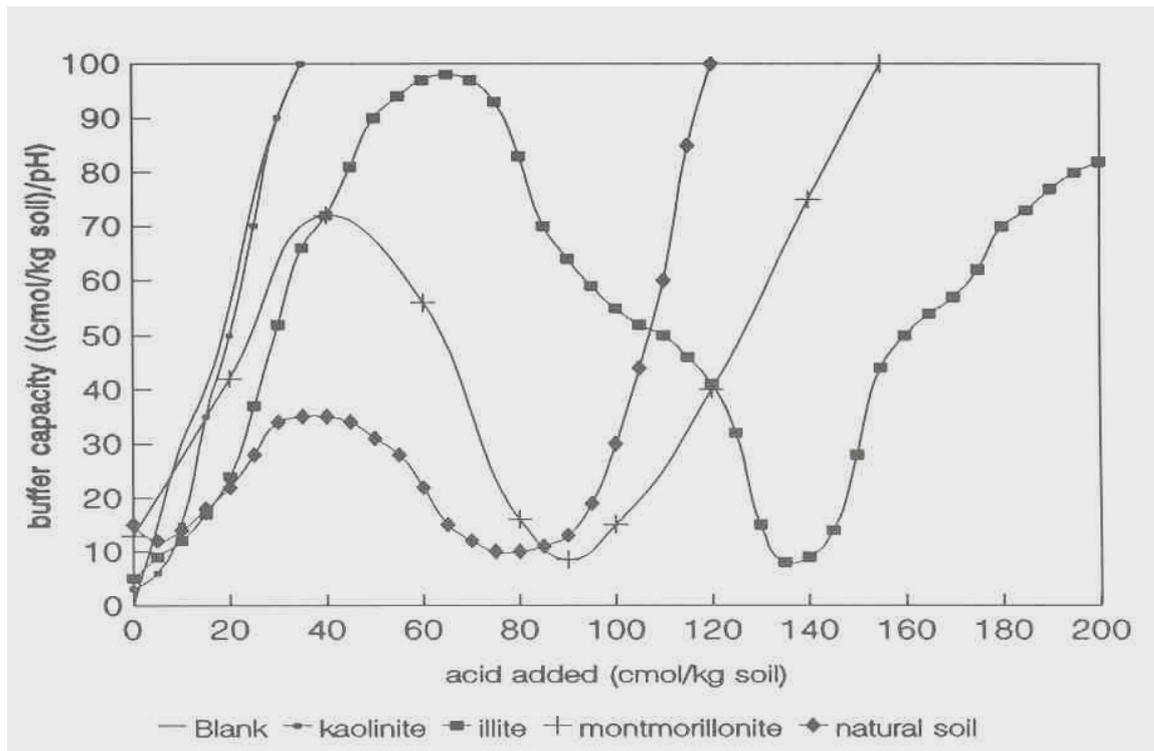
Figure 3.1. Buffer capacity curves for three clays and natural soil in relation to acid input (Yong et al., 1992)

Besides the influence of CEC, soil pH and buffer capacity, clay minerals tend to be selective in adsorbing heavy metals, preferring certain metals over another species at a particular pH. A good example is montmorillonite where two different patterns can be observed: where soil solution pH is ≤ 3, Pb> Cd> Zn> Cu, while for pH > 3, Pb> Cu> Zn> Cd (Yong et al., 1992).

3.4 Metal oxides and carbonates

Besides the silicate clay minerals, other reactive compounds that occur in large amounts in some soils include iron, aluminium and manganese oxides and carbonate minerals (chiefly calcite). These minerals may have disproportionately large effects on many soil chemical processes such as sorption and redox status because of their high specific surface area and reactivity (Sparks, 2003).

The effect of metal oxides on some heavy metals is synergisitic, with the one oxide enhancing the effect of the other. Brown et al. (2003) showed a significant reduction of bioavailability of soil Pb, in both *in vivo* and *in vitro* studies, by 37 and 43 %, respectively, with the addition of compost high in Fe and Mn. In a study by Warren and Alloway (2003), iron oxides produced a highly significant reduction in lettuce of arsenic (As) concentration. When soil pH was kept constant by application of lime, arsenic concentration exponentially decreased with increasing $FeSO_4$. However, ferrous sulphate with insufficient lime lowered soil pH and caused mobilization of Al, Ba, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sr, and Zn. In a study by Hettiarachchi and Pierzynski (2002), where phosphorus and manganese were used to adsorb lead, addition of either P fertilizer and /or Mn oxide significantly reduced bioavailable Pb. The results also suggested that removal of P from soluble P sources by

plants could negate the beneficial effects of P on bioavailable Pb, unless sufficient soluble P was added or soluble P was combined with Mn oxide. Satapanajaru et al. (2003) treated an aqueous solution of Metalochlor with Fe^0, and found that destruction kinetics were greatly enhanced when Al, Fe (II) or Fe (II) salts were added, with the following order of destruction kinetics observed: $Al_2(SO_4)_3$> $AlCl_3$> $Fe_2(SO_4)_3$> $FeCl_3$.

The most characteristic effect of metal oxides in soils is their variable surface charge which is governed by pH and ionic strength, and the fact that this charge will change from negative to positive as conditions become more acidic. The point of zero charge ZPC) of Al and Fe oxides is typically between about pH 5 and pH 8 whereas Mn oxides only develop positive charge below a pH of between 2 and 4.5, depending on the mineral species. This implies that at low pH the dominant surface sorption mechanism is anion exchange (sometimes termed ligand adsorption) with a wide range of organic and inorganic anions showing not only simple electrostatic adsorption but also specific adsorption by covalent bonding to the oxide surface. This constitutes a critically important process for contaminant attenuation, the chemistry of which is well understood because it forms the basis of much water purification chemistry, in which Al or Fe (and sometimes Mn) salts are precipitated in water through lime addition, resulting in a multiple scavenging effect on soluble contaminants.

A particularly novel process of metal and ligand attenuation has recently been developed in our laboratory (Hardie, 2004) which involves the extreme acidification or alkalization of the soil followed by neutralization back to the original pH. This process generates new hydrous precipitates of Al, Fe and Si which then serve to augment the existing capacity of the soil for pollutant attenuation. When sulphuric acid and calcium hydroxide are employed for this priming reaction, the salt generated during neutralization is gypsum which is environmentally benign, allowing subsequent plant growth to take place normally following treatment. The process was developed with the enhancement of groundwater protection from surface pollution as one of its main objectives.

Carbonate minerals are also strong sorbers of metal ions, with Cu, Mn, and Zn, for example, typically being reduced to levels that are deficient for many plants in calcareous soils. The sorption is partly due to the effect of pH (normally > 8 in calcareous soils) in causing metal hydroxide precipitation, but most transition metals and the so-called heavy metals have a tendency to form insoluble carbonates and will sorb strongly on the surface of minerals such as calcite that are widespread in many South African soils.

4.   SOIL MORPHOLOGY AND CONTAMINANT ATTENUATION

All morphological features (colour, texture, structure, consistence) evaluated during soil profile description are related to soil properties and environmental conditions affecting soil formation processes. The same soil properties and environmental conditions govern processes that influence the movement (transport) and fate of pollutants in the soil. Therefore, pollutant retention in soil is related to soil morphology that is easily evaluated and applied in the South African classification system.

4.1 Soil colour

In many cases, the most striking morphological feature of a soil profile is soil colour from which a good indication can be obtained from the prevailing soil environment (Grey et al., 1994). Soil colour develops from soil properties such as organic matter (dark values and chromas) iron oxides (red, yellow) and manganese oxides (black) and pale colours of silicate minerals as influenced by moisture and aeration status (Lambrechts, 1994).

4.2 Soil texture

Soil texture is used to characterise the morphology of the soil profile since it determines the intensity of a host of soil processes including water retention, infiltration and drainage, the retention and availability of plant nutrients, and other features such as erodibility and sensitivity to compaction.

Soil texture (as well as organic matter) determines the soil structure, which largely governs the size of soil pores (permeability) through which groundwater contaminants pass. The proportion of sand, silt and clay in soils plays a vital role in contaminant sorption processes. Soils with a high clay content have small pore spaces that reduce infiltration and permeability rate (Huddleson, 1994), increasing the residence time both for adsorption or biodegradation and for evaporative concentration of the soil solution. Glover et al. (2002) conducted an experiment on Pb and Cd adsorption on goethite at pH 6 for one week and 20 weeks. They found that Pb adsorption was nearly complete after 4 hours, while Cd showed a continuous and slight increase in the remaining adsorption time of 20 weeks. Their results demonstrate the varying time needed by different pollutants to be adsorbed by soil. In soils with low clay content the high infiltration rate will allow some pollutants to reach the groundwater with minimal attenuation. Stewart et al. (2003) showed that Cr (III) sorption (both adsorption and surface precipitation) in soils was strongly and positively correlated to clay content, total inorganic C, pH, and CEC.

Soil texture also plays a large role in the sorption of organic contaminants. A study by Krauss and Wilcke (2002) showed that in most of a wide range of soils studied the concentration of polycyclic aromatic hydrocarbons (PAHs) decreased in the order silt> clay> fine sand> coarse sand, and those of the polychlorinated biphenyls (PCBs) in the order clay> silt> fine sand> coarse sand.

4.3 Soil structure

Soil structure refers to the natural aggregation of primary soil particles into compound units or peds, which are separated from one another by planes and surfaces of weakness (Lambrechts, 1994). Structural development is a function of clay type, clay content, the dominant cation, amount of iron and aluminium oxides and hydroxides, amount and type of organic matter, climatic conditions and soil depth (Lambrechts, 1994). Soils with weak structure or large compound units or peds typically have lower CEC and smaller surface area and therefore a lower capacity for contaminant adsorption, while fine or small peds provide large surface area and high CEC, thus increasing contaminants retention in soils. On the other hand, strongly developed structure is often caused by a high concentration of expansible smectitic clays. When wetted, these clays will swell and become relatively impermeable and although highly adsorptive, the permeability is low and therefore the capacity for attenuating pollutants may be reduced because of less contact as a result of reduced infiltration and increased runoff.

4.4 Soil consistence

Soil consistence expresses the degree of cohesion or adhesion of the soil material within the soil mass and its resistance to deformation or rupture (Grey et al., 1994). The relation between soil consistence and land quality is tied up with many soil properties and in most cases, harder consistence commonly implies slower permeability, low porosity and high bulk density (Lambrechts, 1994). Slow permeability and low porosity imply low infiltration rate that favours contaminant retention because of increased attenuation time, although enhanced runoff may also result, meaning that less chemical reaction can take place within the soil.

The principles summarised above have formed the basis for converting the South African soil classification system, which is general-purpose in nature, to a special purpose system specifically designed to accommodate soil differences that are relevant to groundwater vulnerability. This proto-type system, the details of which are still to be developed, is described in detail by Sililo et al. (2001).

5.   APPROACHES TO GROUNDWATER VULNERABILITY ASSESSMENT

Different research institutions (e.g. USGS, USNRC) around the world are working on strategies to assess groundwater vulnerability to contaminants in order to manage and contain groundwater pollution. These strategies involve identifying sources of contaminants, factors influencing transport and fate of contaminants, identifying vulnerable aquifers and creating maps that guide decision makers on land use management. Over the years, geologists and hydrologists have developed a wide range of methods for assessing groundwater vulnerability based on an understanding of the factors that affect the transport of contaminants introduced at or near the land surface (Hamerlinck et al., 1998). Assessment methods are generally classified into three categories: process-based simulation models, empirical statistical methods and overlay and index methods. An overview of methodologies used to assess groundwater vulnerability by Focazio et al. (2003) grouped methodologies into subjective rating and statistical and process-based methods. Statistical and process-based methods focus on producing products or maps that achieve science objectives rather than policy or management guidelines. Such products or maps will require further explanation by the scientist to policy or decision makers in order to implement information provided in the map.

5.1 Process-based methods

Process-based simulation model methods involve mathematical models that approximate the behaviour of substances in the sub-surface environment. They predict how long a contaminant will take to reach a given depth and/or the amount of contaminant by mathematically modelling the processes influencing contaminant fate and transport (Hamerlinck et al., 1998). Loague et al. (1998) conducted a study on simulation of DBCP groundwater contamination in Fresno County, California using PRZM-2. Most of their data consisted of approximations and many assumptions were made for different factors affecting transport and fate of DBCP in the soil. Process-based methods refer to approaches that either simulate or otherwise take into account physical processes of water movement and the associated fate and transport of contaminants (Focazio et al., 2003). These processes are used either to determine intrinsic susceptibility of an aquifer or to assess the vulnerability of groundwater to a targeted contaminant or contaminants. Therefore, process-based methods account for one or few important processes but do not account for all processes controlling vulnerability (Focazio et al., 2003). Harbaugh et al. (2000) developed MODFLOW, a computer modelling code that solves the governing equations of groundwater flow, which is often used for quantitative modelling of groundwater flow and assessment of intrinsic susceptibility. It includes several process-based models to simulate the interactions of key interacting components of the groundwater flow system.

5.2 Empirical statistical methods

These methods calculate the probability of contamination by characterizing contamination potential for the specific geographic area using data from known contamination distribution in the area (Hamerlinck et al., 1998). Statistical methods range from a simple summary or descriptive statistics of concentrations of targeted contaminants to more complex regression analyses that incorporate the effects of several predictor variables (Focazio et al., 2003). Most maps produced or developed using statistical methods such as those of Ryker (2001),

Rupert (1998), Tesoriero and Voss (1997) and Squillace et al. (1999) give ranges of likelihoods or probabilities.

5.3 Overlay and index methods

Overlay and index methods assign a numerical index or rating to mapped physiographic and anthropogenic attributes of a region. The ratings are then combined to generate a composite sensitivity/vulnerability rating. The ratings can be considered equally or weighted according to the relative magnitude of their influence in the overall assessment determination (Hamerlinck et al., 1998). The overlay and index methods were the earliest to be used in assessing groundwater vulnerability and are still favoured by many states and regulatory and planning agencies (Carbonell, 1993). Hamerlinck et al. (1998) found overlay and index methods less complex than empirical statistical and process-based simulation model methods and applied them in mapping groundwater vulnerability in Wyoming. Their approach was a two step process, in which aquifer sensitivity was first assessed as a function of geohydrology, depth to water, soils, and recharge. Sensitivity was then combined with ratings of land use practices and pesticide use to determine relative ground water vulnerability to pesticides across the state.

A widely used index in assessing groundwater vulnerability is the **DRASTIC** index. This index uses the following attributes: **D**epth to water table, **R**echarge, **A**quifer media, **S**oil media, **T**opography, **I**mpact of the vadose zone and **C**onductivity. These seven parameters constitute the Pollution Potential equation:
$$PP = D_rD_w + R_rR_w + A_rA_w + S_rS_w + T_rT_w + + I_rI_w + C_rC_w$$
Where *PP* is the pollution potential, *r* is the rating and *w* is the weight for each factor. The major assumptions outlined in DRASTIC are that:
The contaminant is introduced at the surface
The contaminant reaches groundwater by precipitation
The contaminant has the mobility of water
The area of the study site is greater than 40 ha.

Subjective rating methods focus on policy or management objectives and range from basic index methods to subjective hybrid methods. Index methods are closely associated with overlay methods in combining maps of physical attributes by assigning scores that generally include subjective rankings of vulnerability. A widely used method is DRASTIC, described above. It has been used to develop maps in many parts of the world including the United States (Durnford et al., 1990), Israel (Melloul and Collin, 1998), Nicaragua (Johansson et al., 1999), Portugal (Lobo-Ferreira and Oliveira, 1997), South Africa (Lynch et al., 1997) and South Korea (Kim and Hamm, 1999).

5.4 Hybrid methods

Focazio et al. (2003) defined hybrid methods as any method that combines components of statistical, process-based and/or index methods. A typical example of such methods is that employed by Vowinkel et al. (1996) using pesticide-use intensity near public supply wells, distance of the wells from aquifer recharge areas, soil organic matter content, well construction data and land use as parameters to develop a map showing wells with low, medium and high groundwater vulnerability to pesticides. Other studies were done by Nolan et al. (1997) using nitrogen loading, population intensity, soil hydrologic group and woodland

to cropland ratio, and by Rupert (2001) using land use and non-parametric statistical correlation between nitrate concentration in groundwater and depth to groundwater and soil drainage.

The SEEPAGE model (System for Early Evaluation of Pollution potential of the Agricultural Groundwater Environment) is a combination of three models that was adapted to meet the needs of field personnel (Moore et al., 1990; Richert et al., 1992; Engel et al., 1992). SEEPAGE considers various hydrogeologic settings and physical properties of soil that affect ground water vulnerability to pollution potential. The following parameters are considered in SEEPAGE: soil slope, depth to water table, vadose zone material, aquifer material, soil depth, and attenuation potential, which further incorporates the following factors: texture of surface soil and subsoil, surface layer pH, organic matter content of the surface, soil drainage class and soil permeability (least permeable layer).

Huddleston et al. (1998) used two basic factors to determine soil sensitivity rating for Oregon Water Quality Decision Aid (OWQDA). These are leaching potential and sorption potential, which depend on different soil properties. Factors that were considered for leaching potential are:
Through flow potential, which is the relative time required for water to pass through the soil to groundwater. The time of travel is calculated using soil permeability and soil depth. It is affected by type of aquifer (apparent or perched).
Runoff potential, which is hydraulic loading as a result of the balance between infiltration and runoff.
Intrinsic leaching potential – determined by through flow and runoff potential. It also corrects the effect of irrigation on hydraulic loading by increasing the rating if the soil being assessed is under irrigation.
Sorption potential rating is done through rating organic carbon content in different soil families of soil orders, and clay content rating as a surrogate for cation exchange capacity. For example, coarse silty and sandy families of Aridisols are rated very low in organic matter, and loamy, fine silty and fine families of Aridisols are rated low.

Sililo et al. (2001) proposed a ground water vulnerability assessment method for South African soils that uses available soil information. This method involves an assessment of the pollutant attenuation capacity of soil horizons, other regolith materials and a diagnostic description of the key morphological and chemical properties of soils. These soil properties automatically convey information on contaminant transport potential quantitatively and/or qualitatively. A provisional, special purpose classification of SA soils based on the binomial system with attenuation capacity ratings as a basis for higher order groupings, and incorporation of hydrological inferences into the classification by identifying chemical affinities between ground water and the overlying soil/regolith and their relationship to recharge characteristics, was proposed in the work by Sililo et al. (2001) which is currently being developed in more detail.

6. SUMMARY

There is a wealth of modern literature on the reaction between a diversity of chemical pollutants and different soil types. On the whole, however, the incorporation of soils information into groundwater vulnerability assessment methods is confined to the accommodation of key soil properties into a rating system and there has been little attention given to translating existing soil classification systems into ones that cater specifically for groundwater vulnerability assessment. There is a significant opportunity to make important strides in this respect, the advantage being that existing soil maps can then be used to produce vulnerability maps without the need for large scale laboratory analyses and attenuation tests.

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