

## **2. Literature survey**

### **2.1 Introduction**

This study focuses on radionuclides and as such, a basic understanding of radionuclides and their chemical and geochemical activities are of importance to the project as a whole.

Some aspects that are specific to certain focus areas form part of the chapter pertaining to that focus area, and are not included in this chapter.

### **2.2 Environmental risk of radionuclides**

The main risk of gamma radiation to living organisms is the ionization of cellular atoms and molecules, especially DNA. The sensitivity of organisms to radioactivity is proportional to the chromosomal volume of cells in the organism, therefore humans are more susceptible to cellular damage caused by radiation than plants. Thus it is assumed that radiation exposure levels that are safe for humans are safe for other organisms. (ATSDR, 1999)

Frequent exposure to radiation causes unnatural distortions and harm to tissue in the human body. Common signs of radiation exposure include red and itchy skin, nausea, diarrhoea, kidney and liver problems, poor growth (children), reproductive problems, etc. (Valkovic, 2000)

The risk management of radiation and radionuclides in South Africa is strictly enforced by the National Nuclear Regulator and is backed by a number of legislations including:

- National Environmental Management Act no. 107 of 1998 (NEMA)
- NEMA Amendment Act, no. 8 of 2004
- Mineral and Petroleum Resource Development Act, no. 28 of 2002 (MPRDA)
- MPRDA Amendment Act, no. 49 of 2008
- National Water Act, no. 36 of 1998
- Hazardous Substance Act, no. 15 of 1973
- NEMA: Air Quality Act, no. 39 of 2004
- National Nuclear Regulator Act, no.47 of 1999
- Mine Health and Safety Act, no 29 of 1996
- NEMA Waste Act, no. 59 of 2008
- National Health Amendment Act, no. 12 of 2013

It can be seen that the importance of quantification of radionuclides as potential hazards to the environment and public health is of paramount importance. The quantification of radionuclide migration may assist in the prosecution, or prevention of prosecution, of mining companies with regard to radiation and radionuclides associated with ore and waste materials.

The average natural background radiation that every person is exposed to (through the air we breathe, contact with soil and the consumption of food and water) is 1 milli Sievert per annum (mSv/a), whilst the maximum dose limit that a radiation worker is exposed to is 50 mSv/a, which

is also the maximum dose limit for radiation exposure to skin of the general public. A dose rate of 50 mSv/a is the lowest dose rate where any evidence of cancer formation caused by radiation can be found, and is also the natural background concentration of Europe, Iran and India. (Department of Water affairs and Forestry, 2002., IAEA, 2007)

To compare, New Machavie has a high surface U measurement of 55 ppm which equates to approximately 1.8 mSv/a (WISE, 2009) for a worker completing 2000 working hours per year on the New Machavie TDF, which is only slightly higher than the natural exposure gained from food, water and air.

### **2.3 Basic radiometric theory and disequilibrium**

An atom is composed of a nucleus which is surrounded by negatively charged electrons. The nucleus is composed of positively charged protons and neutral neutrons. Particles of the same element that have higher or lower neutron numbers are called isotopes (Kotz *et al*, 2006). Some of these isotopes have too much energy and as a result they are unstable; they will then disintegrate into stable isotopes with lower mass numbers. Disintegration takes place in the form of a discharge of particles or energy. This process of disintegration is referred to as nuclear radiation and particles with this characteristic decay are referred to as radionuclides (Aswathanarayana, 1985., IAEA, 2003). Three types of radioactive decay may occur, namely: (Aswathanarayana, 1985., IAEA, 2003., Magill & Galy, 2005):

- Alpha - an alpha particle is released from the nucleus (2 protons and 2 neutrons).
- Beta - a beta particle similar to an electron is released;
- Electron capture – an electron is captured by the nucleus which excites the nucleus into a higher energy state. The excess energy is radiated away in the form of gamma radiation.

Gamma radiation is an extremely high frequency type of electro-magnetic radiation (between  $10^{20}$  and  $10^{24}$  Hz compared to  $10^{15}$  Hz for visible light) with no charge or mass. However, the exact frequency of gamma radiation is distinctive to the isotope from which the radiation emanates. Thus, it is possible to detect the isotopes present in a sample by measuring different energy windows within the natural gamma range (Richards, 1981., Aswathanarayana, 1985., IAEA, 2003).

While many elements have radioactive isotopes, only four naturally occurring elements have a radioactive series with enough energy to be measured and to affect humans on a localised scale (Richards, 1981., Aswathanarayana, 1985., IAEA, 2003). These are the actinium (Ac), Th, U and potassium (K) decay series (Richards, 1981., Aswathanarayana, 1985., IAEA, 2003).



### 2.3.2 Thorium series

The Th decay series starts with  $^{232}\text{Th}$  and ends with the stable isotope of  $^{208}\text{Pb}$ . The half-life of Th is  $1.39 \times 10^{10}$  years (IAEA, 2003). The gamma emitter's in this series that is used to measure Th content is  $^{228}\text{Ac}$ , radium ( $^{224}\text{Ra}$ ),  $^{212}\text{Pb}$ , bismuth ( $^{212}\text{Bi}$ ) and thallium ( $^{208}\text{Tl}$ ). IAEA, 2003., Aswathanarayana, 1985., Richards, 1981.

The decay chain of the Th series is as follows:

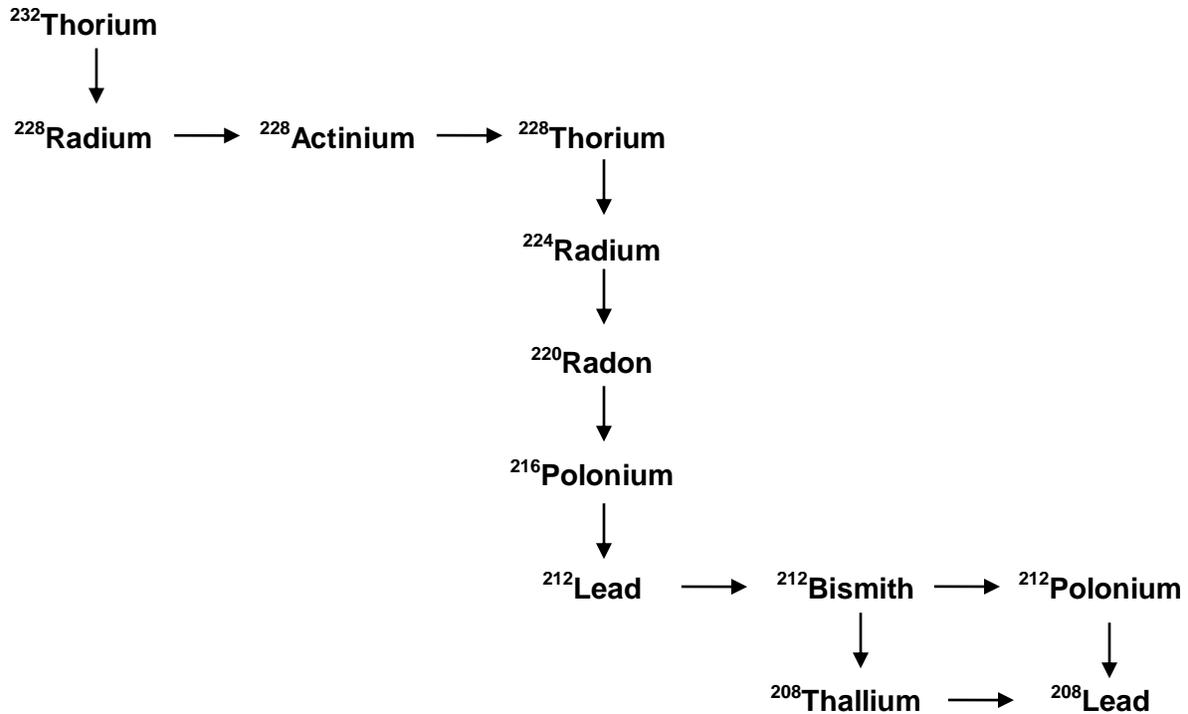


Figure 2.2: The Th decay series (Richards, 1981., Aswathanarayana, 1985., IAEA, 2003)

### 2.3.3 Uranium series

The U series starts with  $^{238}\text{U}$  and ends with the stable isotope of  $^{206}\text{Pb}$ . This series has a half-life of  $4.46 \times 10^9$  years. The gamma emitter's in this series that are used to measure U content is,  $^{214}\text{Pb}$  and  $^{214}\text{Bi}$ . The series can be graphically illustrated as follows. (Richards, 1981., Aswathanarayana, 1985., IAEA, 2003)

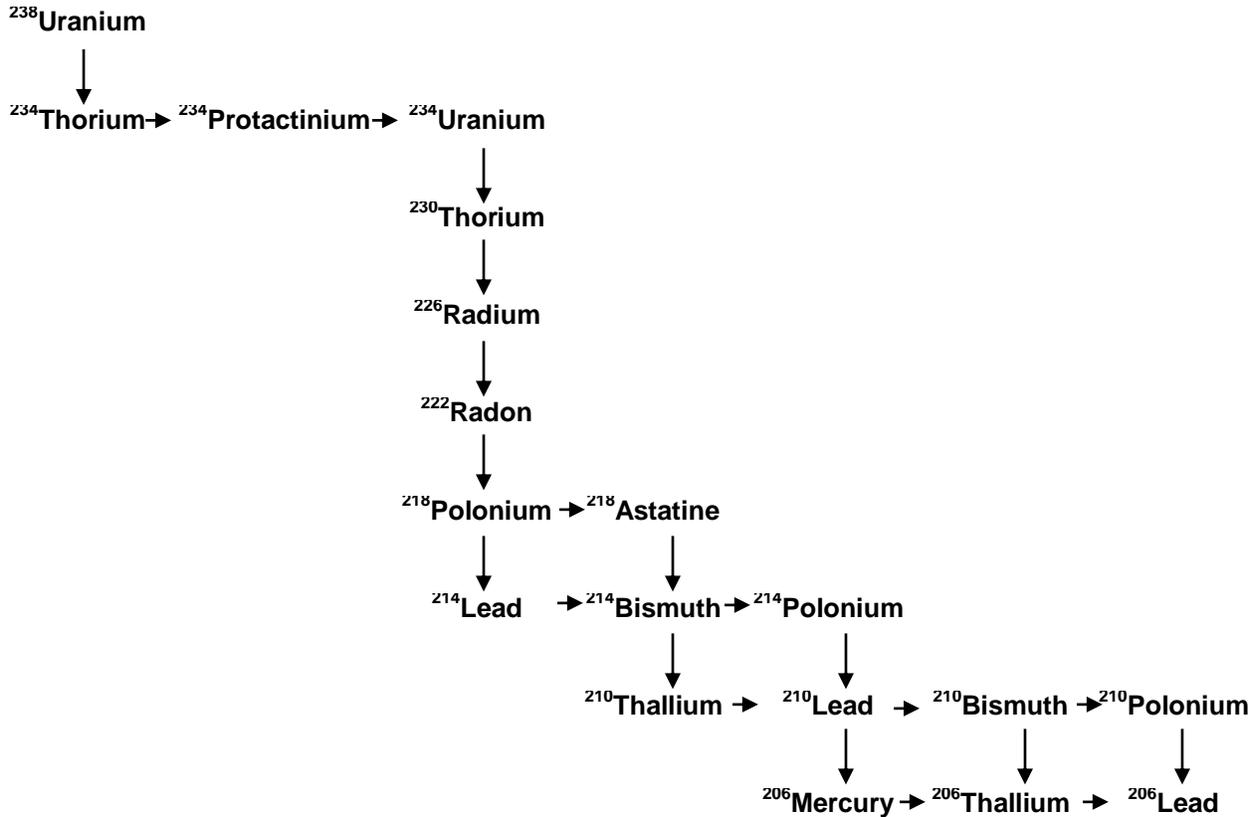


Figure 2.3: The U decay series (Richards, 1981., Aswathanarayana, 1985., IAEA, 2003)

### 3.3.4 Potassium series

Potassium ( $^{40}\text{K}$ ) decays directly to argon ( $^{40}\text{Ar}$ ) through electron capture, producing gamma radiation and calcium ( $^{40}\text{Ca}$ ) through beta particle emission (Richards, 1981., Aswathanarayana, 1985., IAEA, 2003).

During the radioactive decay of the parent nuclides, if the daughter isotopes remain in place and continue to decay to the last stable isotope then the decay chain is in equilibrium (Richards, 1981., Aswathanarayana, 1985., IAEA, 2003). However, if any isotope in the decay chain is removed from or added into the system, disequilibrium occurs (Richards, 1981., Aswathanarayana, 1985., IAEA, 2003). Disequilibrium occurs in nature through the weathering and oxidation of rocks and minerals, and the subsequent selective leaching of isotopes from the

system. It is rare that Th and K are in disequilibrium due to the fact that the gamma-emitting daughter isotopes are relatively close to the parent in the decay series, and little to no selective leaching of daughter isotopes occur. In the U decay series, this is not the case as the gamma emitters are low in the series, and selective leaching of isotopes in the series is a common occurrence. The assumption of equilibrium may be a major setback for natural gamma spectrometry as it is one of the most important errors that may occur during measurement. For this reason, one has to measure the degree of disequilibrium using either wet analytical methods like ICP-MS and ICP-ES or XRF, especially when working in weathered, oxidised or disturbed areas. Analytical results can then be used to correct the spectrometric data to account for disequilibrium. (Richards, 1981., Aswathanarayana, 1985., IAEA, 2003)

## **2.4 Natural gamma**

Natural gamma spectrometry and scintillometry has been widely used for decades in the mining exploration of various metals associated with radionuclides. The method has been developed to the point where numerous field manuals and guidelines with detailed descriptions of instruments, field procedures, data processing and interpretations can be found in the public domain. (IAEA, 2003)

### **2.4.1 Natural gamma scintillometry**

The most important component of a scintillometer is the detection material with a relatively high density, high enough to stop gamma rays. Usually a crystal of sodium iodide doped with thallium impurities is used; however, other materials can be used as well. The material also needs enough crystalline lattice energy to capture and react with high energy particles (electrons) in order to produce visible or ultraviolet light (depending on the type of detector). This process of electron capture and emission of light is called luminescence. The intensity of light produced is always proportional to the energy of the gamma ray that produced it. Connected to the crystal is a photomultiplier that detects the light pulse and converts it into an electrical signal. A photomultiplier consists of a photocathode and a series of dynodes. The cathode ejects an electron when it is hit with a photon (from the detector crystal), this electron hits the dynode and more electrons are released. This continues through a series of dynodes until enough electrical energy is produced to be further amplified by an amplifier, which in turn is connected to a counter that counts the electrical pulses. This pulse data or count rate is then displayed and/or recorded as counts per second (cps). By calibrating the scintillometer with known concentrations of radionuclides, information regarding concentration can be calculated from the cps data. Scintillometers only measure the rate of pulses, thus no information regarding specific elements is extracted even though data is usually converted to parts per million (ppm) equivalent  $U_3O_8$ . (Richards, 1981., Aswathanarayana, 1985., IAEA, 2003)

## 2.4.2 Natural gamma spectrometry

The detection method of spectrometers is similar to that of scintillometers; however, spectrometers measure the energy of each gamma ray that produced a pulse in the detector using a 256 channel detection system, outputting data in three spectrometric channels and one total count channel. As the intensity of light produced by the detector is proportional to the energy of the gamma ray, spectrometers are equipped with a pulse height analyser that measures the amplitude of incoming electrical signals from the photomultiplier, and then determines to which of several count rate meters the pulse should go. Spectrometers usually have four counters that receive pulses for the energy window of the specific radionuclides. In most cases total count, K, U and Th channels with their individual counters are present. (Richards, 1981., Aswathanarayana, 1985., IAEA, 2003)

## 2.5 Chemical and geochemical behaviour of radionuclides

The source of U and Th in the study area is the geologic formations from which gold was mined, in this case the Black Reef Formation at New Machavie and the Vaalreef at Harties (discussed further under section 3.4). As described by Aswathanarayana (1986) these economic formations show a “sympathetic relationship” between gold and U indicating that the enrichment event(s) that increased the gold content also mobilised and enriched U. The U content is fairly low compared to U ores in other areas of the world. However, it was still possible to extract U as a by-product from gold mining. Uraninite ( $\text{UO}_2$ , black colour, may be massive or crystalline) and thucholite (U-containing hydrocarbon complex, especially found in the Black Reef) are the major primary radionuclide-containing minerals in this area that are associated with gold (Aswathanarayana, 1986).

### 2.5.1 Uranium

Uranium occurs naturally in either a reduced state ( $\text{U}^{4+}$ ) or an oxidised state ( $\text{U}^{6+}$ ) (Vandenhove *et al.* 2009., Pulford, 2010.). Under un-oxidised conditions  $\text{U}^{4+}$  occurs in the insoluble form of uranium dioxide ( $\text{UO}_2$ ) which is believed to be immobile. However, micro-particles may be transported through porous materials and can be oxidised to  $\text{U}^{6+}$  if transported to an oxidising environment (Vandenhove *et al.* 2009., Pulford, 2010). Chemically,  $\text{U}^{6+}$  is significantly more active with a range of speciation possibilities. The speciation is pH-dependent with species being found at different pH ranges and environmental conditions/systems as seen in Table 2.1 (Vandenhove *et al.* 2009., Pulford, 2010).

Factors that affect the solubility of U include redox potential, pH, ligand content and type, and the presence of adsorbing materials like iron oxides, clay, phosphate minerals and organic matter. Uranium<sup>6+</sup> in the form of  $\text{UO}_2^{2+}$  is very soluble in water and thus also very mobile, but can be adsorbed onto iron oxides, clay, phosphate minerals and organic matter to decrease mobility. The presence of carbonates always increases the mobility of U through the formation of negatively charged U-complexes that cannot be adsorbed onto clays and iron oxide minerals. (Vandenhove *et al.* 2009., Pulford, 2010)

**Table 2.1: The pH range and system conditions of U<sup>6+</sup> chemical species (Vandenhove *et al.* 2009., Pulford, 2010., Alloway, 2012)**

pH range and system	Chemical species
< 5	UO <sub>2</sub> <sup>2+</sup>
> 5, neutral systems	UO <sub>2</sub> H <sup>+</sup> (UO <sub>2</sub> ) <sub>2</sub> (OH) <sub>2</sub> <sup>2+</sup> (UO <sub>2</sub> ) <sub>3</sub> (OH) <sub>5</sub> <sup>+</sup> (UO <sub>2</sub> ) <sub>3</sub> (OH) <sub>7</sub> <sup>-</sup>
9-10	UO <sub>2</sub> (OH) <sub>3</sub> <sup>-</sup>
> 6 – alkaline, carbonate rich system	UO <sub>2</sub> CO <sub>3</sub> UO <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> <sup>2-</sup> UO <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub> <sup>4-</sup>
< 4 (Concentration dependant , may occur at higher pH if concentration is high)	UO <sub>2</sub> SO <sub>4</sub> UO <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> <sup>2-</sup>
Neutral systems with abundant phosphate	UO <sub>2</sub> HPO <sub>4</sub> UO <sub>2</sub> PO <sub>4</sub> <sup>-</sup> UO <sub>2</sub> (HPO <sub>4</sub> ) <sub>2</sub> <sup>2-</sup>

### 2.5.2 Thorium

Thorium has similar valence states as U (Th<sup>6+</sup> and Th<sup>4+</sup>); however, Th only exists as Th<sup>4+</sup> under environmental conditions (Vandenhove *et al.*, 2009). Thorium<sup>4+</sup> is responsible for Th being soluble under a wide range of pH conditions even though solubility is significantly lower than U (Alloway, 2012). Oxides of iron (Fe) and manganese (Mn) and organic matter are considered the main adsorption particulates of Th (US EPA, 1999., Vandenhove *et al.*, 2009). According to US EPA (1999), Th<sup>4+</sup> is the largest known tetravalent cation and is the most resistant to hydrolysis. Even so, Th may form a variety of hydroxyl species above a pH of 3. Most of the mineral forms of Th is considered insoluble and fairly resistant to weathering (US EPA, 1999., Vandenhove *et al.* 2009).

### 2.5.3 Bismuth

Bismuth can be found either as Bi<sup>3+</sup> or Bi<sup>5+</sup> under environmental conditions forming insoluble sulphide minerals in reduced environments. Bismuth is easily oxidized but forms fairly stable Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> molecules which tend to persist in soils (Kabata-Pendias, 2011).

### 2.5.4 Thallium

Little is known about the chemical speciation of Tl in soils and the environment; however it is known that Tl occurs predominantly as Tl<sup>+</sup> in an oxidised environment and behaves similarly to K<sup>+</sup>. Under strongly acidic and oxidising conditions, Tl<sup>3+</sup> becomes the dominant ion. Tl tends to persist in certain soil types with higher contents of clay, organic matter, and oxides of iron and manganese. (Madejón, 2012).

### 2.5.5 Lead

Under oxidising conditions, Pb occurs in the  $Pb^{2+}$  state while forming, PbS under reducing conditions (Steinnes, 2012). Higher pH conditions tends to decrease Pb solubility as Pb forms carbonates and is adsorbed onto clay, hydroxides and complexes with organic matter (Kabata-Pendias, 2011., Steinnes, 2012). Geochemically, Pb has the ability to replace K, barium (Ba), strontium (Sr) and Ca in soil adsorption sites and in isomorphic substitution sites within mineral crystal lattices (Kabata-Pendias, 2011). Lead is the least mobile of trace metals under environmental conditions but forms cations of  $Pb^{2+}$ ,  $PbCl^+$ ,  $PbOH^+$  and anions of  $Pb(CO_3)_2^{2-}$  and  $PbCl_3^-$  in soil solutions (Kabata-Pendias, 2011).

## 2.6 Witwatersrand gold tailings characteristics

Gold tailings of the Witwatersrand basin usually consist predominantly of quartz. The ore that was mined was either a quartz conglomerate or a quartzite. Mica and chlorite are usually present as well as pyrophyllite. K-feldspar may occurring on some TDFs. Pyrite ( $FeS_2$ ) dominates the geochemical nature of gold tailings due to oxidation reactions. Pyrite content in gold tailings usually ranges between less than 0.5 and 2 wt. %. (Bezuidenhout & Rousseau, 2005 and Yibas *et al.* 2010).

Yibas *et al.* (2010) thoroughly described the geochemistry of gold tailings as follows:

“Predominantly tailings are composed of  $SiO_2$ , in the active oxidation zone enrichment of metals such as Al, Fe, Mg and Ca occurs whilst these metals are depleted in the mature oxidation zone as leaching has removed them”.

Trace metal concentrations depend primarily on the sulphide mineralogy of the ore body. Bezuidenhout & Rousseau (2005) and Yibas *et al.* (2010) also found that the pH increased with depth due to the depth to which oxygen could penetrate, thus limiting the oxidation reaction of pyrite.

Bezuidenhout & Rousseau (2005) stated that hydraulic separation of particle sizes causes differential permeability in TDFs, which may either increase or decrease the flow of contaminants, depending on the site conditions. Moisture content of TDFs is extremely variable and depends on a number of factors including climatic conditions, local geology (dolomite tends to decrease moisture content as fluid is freely leached into the groundwater), physical properties of the TDF, the presence of very fine-grained layers that limit water penetration and coarse-grained layers that act as capillary breaks (Photo 2.1).

The Black Reef also consist of quartz conglomerate and quartzite containing pyrite, thus the tailings characteristics are similar to the Witwatersrand tailings.



**Photo 2.1: Typical hydraulic separation layering in gold TDFs (Photo by P.W. van Deventer)**

The oxidation of pyrite can be summarised in three balanced chemical reactions, initially described by Garrels and Thompson (1960) and later improved by Singer and Stumm (1970) (as cited by Chandra *et al.*, 2010).

The reactions are as follows:



From these reactions it is clear that oxygen (O<sub>2</sub>) and Fe<sup>3+</sup> act as oxidizing agents with Fe<sup>3+</sup> being more aggressive and effective than O<sub>2</sub> at oxidizing pyrite, but O<sub>2</sub> is needed to sustain the oxidation process as Fe<sup>3+</sup> becomes depleted fairly quickly (Chandra *et al.*, 2010). This also indicates how the formation of different zones in TDFs is dependent on oxygen penetration as a rate limiting factor.

## **2.7 Geostatistics and modelling**

All information gathered at both study locations were geographically based as latitudes and longitudes were recorded for each borehole. At New Machavie, the aim was to create 3D models of different parameters which were either measured on surface, in boreholes or from samples taken from boreholes.

### **2.7.1 Elevation survey**

In order to create a 3D model an elevation survey was conducted to accurately define the structure of the New Machavie TDF. The method used is based on levelling as described by Bhalla & Larroquette (2004) and discussed under Methodology (Section 4.5).

### **2.7.2 Interpolation**

It is not practical or possible to measure every location that may exist on a surface, therefore interpolation between measured points was used to quantify the extent of the surface. Two interpolation methods were employed; inverse distance weighting (IDW) and kriging. For the purpose of this study, only a description of IDW and kriging will be given.

- Inverse Distance Weighting

Inverse Distance Weighting interpolates values between points based solely on the distance from the measured points. No spatial relationships are assumed except for the concept that points closer to each other should be more related than points further apart (Naoum & Tsanis., 2004). Inverse Distance Weighting allows for the importance of known points to be defined by the user and thus to control the weight of these points with regard to the output points (Isaaks & Srivastava., 1989 and Naoum & Tsanis., 2004). Inverse Distance Weighting was used to interpolate concentration data and ratios within the TDF as this is an omnidirectional method for which one can define the type of relationship, isotropic, anisotropic, and the directional weight of relationships. IDW is computationally less exhaustive than kriging and other interpolation methods.

- Kriging

Kriging uses spatial relationships within the known data set to interpolate unknown points between the known points (Isaaks & Srivastava., 1989 and Naoum & Tsanis., 2004). Isaaks & Srivastava (1989) describe kriging as linear (weights are estimated linearly between points), unbiased (aims to have the error as close to zero as possible) and aims to minimize the variance of the errors. Bohling (2005) gives the advantages of kriging as:

- Compensating for the effects of clusters by giving less weight to points in clusters than isolated points; and
- Giving an estimation of the variance is given which produces greater statistical reliable data.

Variograms are used to give the spatial relationship between points. These variograms are then fitted to the data. Kriging assumes that the variation is the same at all points on the surface (statistically homogeneous), therefore data with trends and sudden spatial variations are not suitable for kriging. (Isaaks & Srivastava., 1989 and Naoum & Tsanis., 2004).

Kriging was used to interpolate elevation data from the elevation survey as well as borehole data to generate the surface of the New Machavie TDF and the soil below the TDF. These surfaces were then used to constrain the radionuclide data during the modelling of these parameters.