Three classes of pollutants have been examined:

1. **Cationic pollutants** (primarily inorganic i.e. metals, but including some organic pollutants the attenuation of which is primarily associated with cationic or polar character)

2. **Anionic pollutants** (primarily inorganic ligands such as phosphate, but ostensibly including a wide range of organic pollutants the attenuation of which is associated either with anionic or polar character or with a tendency to form covalently bonded complexes with soil mineral surfaces)

3. **Organic pollutants (non-polar)** with hydrophobic tendencies (non-polar) the attenuation of which is primarily related to soil organic carbon content.

**Experimental work**

The following experimental work has been completed. Adsorption characteristics of nearly 200 soils, representing the major diagnostic horizons and materials in South African soils and sourced from the archived, characterised collection associated with the South African land type survey (ARC Institute of Soil Climate and Water) have been assessed using batch type equilibration tests with varying concentrations of copper and phosphate salt solutions. Adsorption isotherms were developed (Fig.1) from which the sorption capacity at an equilibrium solution concentration of 1 mg L$^{-1}$ could be calculated as a basis for comparing the sorption capacity of different soils.

![Graph of logarithm plot (isotherm) of Cu sorption (mg/kg soil) vs solution Cu concentration](image)

Figure 1. Logarithm plot (isotherm) of Cu sorption (mg/kg soil) vs solution Cu concentration, demonstrating how sorption is estimated by extrapolation to 1 mg/L Cu in the equilibrium solution.
The data in Fig 2 represent soil Cu sorption (at 1 mg/L equilibrium solution concentration)) from about 170 soils sampled at sites across South Africa. Clearly there is a relationship between Cu sorption and soil pH, which can be described as one in which Cu sorption becomes increasingly confined to small values as acidic extremes of soil pH

Figure 2. Cu sorption data for 170 soils (each point determined as shown in Fig 1) as a function of soil pH (in CaCl₂). Individual data (above) were divided into 10 classes of equal size for calculation of means and standard deviations (SD), plotted below. The mean + 2SD curve represents a best-fit envelope subtending about 98% of the Cu sorption data across the pH range.
are approached. The data indicate that as an alkaline pH is approached the possibility of finding a high Cu sorption capacity is maximized. Whether this maximum potential is realised or not will depend on other factors such as CEC (reflected by the S value, for example) and clay content. The soil chemical interpretation of this relationship is relatively straightforward. The acidic extreme represents an environment in which Cu is most mobile because both hydrolysis of the Cu ion and the development of pH dependent charge on soil colloid surfaces is minimal. On the other hand the alkaline extreme represents a condition of minimum Cu solubility: with increasing pH, Cu is either adsorbed on colloid surfaces or is precipitated as sparingly soluble carbonate. If we fit a boundary line to the data the result is a wedge-shaped envelope of Cu mobility broadening across the pH range from acidic, where it is confined to low values, to alkaline values where its mobility is restricted by adsorption or precipitation reactions. The following approach has been used to depict the overall trend more clearly and to locate a boundary or perimeter objectively without sacrificing too many outliers.

1. Sort the data according to the independent variable (pH).
2. Divide the data into classes of equal size (in this case there are 10 classes, each with a population of about 17).
3. Calculate the mean and standard deviation (SD) of the dependent variable (Cu sorption) for each class, as well as the corresponding mean for the independent variable (pH).
4. Plot the mean and the mean + 2SD for Cu against mean pH for each class (Fig. 2). The mean + 2SD represents the maximum of about 98% of the Cu values in that class, discarding the uppermost 2% as outliers.
5. Fit a regression equation which describes most fittingly the relationship between mean + 2SD Cu sorption values and pH (in this case a 2nd order polynomial). The best equation is the one which has the highest \( r^2 \) value of those that are amenable to mechanistic interpretation (e.g. a 6th order polynomial has a better fit but reflects multiple fluctuation in Cu sorption over the pH range which defies explanation). The curve for mean + 2SD values (Fig. 2) represents a perimeter sans outliers (a normal ceiling) for the data set, and the interpretation of its shape is essentially identical to that arrived at originally.
6. Ideally data of this kind should be presented in both formats (Figs. 1 and 2). The first serves the purpose of discovering the measured outer limit to phenomena while the second provides a realistic estimate of the limit in terms of statistical validity. The perimeter line derived in this way we term a chemical envelope.

Zinc and sulphate salt solutions were employed on a sub-set of soils to confirm that cationic and anionic sorption behaviour could be generalised with reasonable confidence from the copper and phosphate sorption results. Column leaching tests (Figs 3 & 4) with copper solution were carried out to find out whether this might be a viable alternative method for placing soils into pollutant attenuation classes. The quantity of soil available from the archived stocks of land type samples from the ARC-ISCW is very small and no more than 10g soil could be employed for these leaching tests. This required a small column (Fig.3) with its attendant difficulties of achieving a uniform flow rate and of ensuring minimal preferential flow during leaching. Although the breakthrough curves were satisfactory (e.g. Fig. 4), the analytical cost and limited sample size available rendered further column leaching work impractical.
In the case of non-polar organic sorption, reliance has been placed on the well-reported relationship between sorption and organic carbon content of the soil as a basis for creating attenuation classes.

Figure 3. Experimental set-up for determining sorption characteristics by leaching through a soil column.
Figure 4. Example of a breakthrough curve for Cu using the set-up in Figure 3 (10g soil from Paarl mountain reserve; 440 mg/L Cu as chloride input solution; flow rate ~ 1 ml/min).

Scheme for classifying soils in terms of pollutant attenuation

The following scheme has been developed for classifying soils in terms of expected pollutant attenuation behaviour:

1. Ascertain, from routine laboratory analyses, the following soil properties:
   a. pH (determined in 0.01M CaCl$_2$)
   b. S value (sum of exchangeable basic cations)
   c. Clay content
   d. Organic carbon content
   e. Free Fe and Al oxides (extractable in dithionite-citrate-bicarbonate)

2. Make use of equations for chemical envelopes which relate to Cu and P sorption, in the following tables, to calculate the potential maximum sorption (y) from the value of each variable (x). The result is given in the last column, based on input values in the previous column for the soil in question. The first four factors are reported as a percentage, and the last factor has units of cmol$_c$/kg.

   Each equation represents a line which encloses below it the expected range in Cu or P sorption values for particular values of the soil property in question (hence the term chemical envelope, which relates chemical behaviour (cation and anion adsorption) to specific soil properties.)
In the example above, the factor limiting Cu sorption the most is Al but this statement can be made with little confidence ($r^2=0.25$). The clay content suggests, with about double the reliability, that potential maximum Cu sorption is about 1500 mg/kg. With even more confidence ($r^2=0.96$), the S value and pH both point to potentially very high Cu sorption being possible. In all cases the prognosis for Cu sorption is potentially high, implying that there is no soil property among those routinely tested for which points to Cu sorption being confined to low values. The classification of this soil would therefore be that it presents a low risk for groundwater contamination with Cu (and related metals).

Conversely, the lower table points (mostly with a high degree of reliability) to certain factors exerting a confining influence on phosphate sorption, implying that relatively speaking this soil presents a high risk for groundwater contamination with phosphate and similar anions or ligands (including organic ones). The most impressive of these is the pH of 8.3 which appears to impose an especially low ceiling on P retention.

3. The chemical classification is completed by considering different classes of organic matter status as a basis for anticipating non-polar organic adsorption. In this case the sorption behaviour is so strongly affected by organic matter content that the consideration of other variables in the way that was done for cationic, anionic and polar organic contaminants is unnecessary, as is empirical testing of local soils with non-polar organic compounds. The properties that determine sorption are the n-octanol-water partition coefficient ($K_{ow}$), on the basis of which the $K_d$ (distribution coefficient) can be estimated knowing the soil organic
The above chemical scheme is essentially ready to be implemented once a consensus has been reached among interested researchers and environmental practitioners about how many contamination risk classes should be created (two, three or five, depending on how accurately the risk needs to be assessed). The physical or hydrological aspect also needs to be integrated with the chemical assessment and this will be done after consultation with the hydrological research community.

Summary and conclusions

Following earlier work reported in 2005 which sought relationships between chemical attenuation behaviour and existing soil classes or diagnostic horizons, it was concluded that generalisations about chemical attenuation cannot be made for specific diagnostic horizons or materials and that the existing general purpose classification of South African soils would therefore not be a suitable basis for assessing groundwater vulnerability to contamination. Most soil inventories, however, include routine analytical data which might provide a basis for anticipating chemical attenuation. For 170 representative soil materials the relationship was investigated between six commonly recorded soil properties (pH, S value, clay, organic carbon, and free aluminium and iron contents) and the sorption of copper (representing metals) and phosphate (representing anionic contaminants including organic ones) determined using sorption isotherms from batch equilibration tests. It was found that the sorption behaviour exhibited confinement over particular ranges of some of these variables, allowing prediction to be made as to whether particular properties would effectively imply more limited sorption and therefore a greater risk of contamination. The pattern of confinement has been termed a chemical envelope. Chemical envelopes were especially clearly defined for Cu sorption as a function of pH and S value, and for P sorption as a function of Al and Fe contents, which finding coincides with what would have been predicted on the basis of soil chemical theory. The chemical envelopes are described by regression equations for the relationship between mean + 2SD for sorption and the corresponding mean value for each class of the soil variable after creating classes by numerical subdivision of the data set. The regression coefficient for each equation provides a measure of reliability which can be incorporated into the risk assessment. This system for classifying soils according to their expected sorption capacity based on familiar properties, when combined with standard procedures for non-polar organic compounds that are based on soil organic carbon content, provides a comprehensive basis for assessing the chemical contribution of soils to groundwater protection.
Appendix: excerpts from Canadian guidelines for using organic matter as a basis for estimating sorption of non-polar organic compounds by soils

(http://www.ec.gc.ca/ceqg-rcqe/English/Html/soil_sitespecific.cfm)

Guidance Manual for Developing Site-Specific Soil Quality Remediation Objectives for Contaminated Sites in Canada

Canadian Council of Ministers of the Environment The National Contaminated Sites Remediation Program March 1996

1. Modify Based on Soil Organic Carbon Content

The characteristics of soils at contaminated sites have the potential to significantly alter the fate and effects of many contaminants. Ranges of organic carbon content and pH encountered in Canadian soil are reported in Alder et al. (1994). While pH, clay type, clay content, and cation exchange capacity of the soil are known to be strong influences, in some cases it was not possible to set a single range that would deal accurately with all types of contaminants. Site managers are strongly urged to read the sections in Alder et al. (1994) appropriate for contaminants of concern at the site.

The presence of atypical but not extreme levels of organic carbon content could affect the mobility and/or bioavailability of contaminants and provide sufficient grounds for a limited modification of the generic criteria. Following the review of Canadian soils by Alder et al. (1994), the Subcommittee nominated an applicable range of soil organic carbon content (foc), from 0.1 to 17%, for which the soil quality criteria would be widely applicable. The default value for foc used in the soil protocol (Evaluation of Derived Criteria Relative to Guidelines for Canadian Drinking Water Quality) was 0.1% soil organic carbon. However, if it can be demonstrated that soil organic carbon at the site is between 0.1 and 17%, the actual site value may be substituted in the equation. (See note in Explanation 16.)

2. If the soil organic carbon content at the site is outside the applicable range of 0.1 to 17% and if mobile organic contaminants are present, a risk assessment may be appropriate.

The site values of soil organic carbon content, foc, (5%), replace the default value of 0.1% in:

$$Y_a = DF \left[ C_{wa} \left( K_d + 2m \right) \right]$$

where

$Y_a =$ total contaminant concentration in soil in equilibrium with pore water at the drinking water guideline concentration

$DF =$ dilution factor

$C_{wa} =$ concentration in the aqueous phase, set at the drinking water guideline

$K_d =$ distribution coefficient, such that $K_d = foc \cdot K_{oc}$

$foc =$ organic carbon content
Koc = sorption coefficient for soil organic carbon, predicted form correlation with the water solubility, or n-octanol/water partition coefficient, Kow
2m = mass moisture content
Since Kd is much larger than 2m, the moisture content can be ignored. With all factors except foc staying constant, the resulting change in groundwater is to increase the human health soil quality guidelines for groundwater protection 50 times, hypothetically from 0.4 mg PCP/kg to 20 mg PCP/kg dry soil (Figure 7). The environmental guideline is hypothetically 1 mg PCP/kg dry soil. Therefore, when the modified human health soil quality guideline (20 mg PCP/kg dry soil) is compared with the environmental soil quality guideline (1 mg PCP/kg dry soil), the lower of the two (1 mg PCP/kg dry soil), is the recommended soil quality remediation objective.