

Tier 1 Remedial Criteria Development
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ABSTRACT

Contaminated sites must have target numerical objectives which guide delineation and remediation efforts. The setting of these criteria goals becomes a significant issue when the compounds of concern do not have suitable published criteria from Alberta Environment (AENV). The establishment of Tier 1 criteria, where previously no suitable criteria existed, allows proponents to set realistic, risk based, remedial objectives. Tier 1 criteria differ from the traditional site specific risk objectives (SSRO's) which often involve land use constraints, in that AENV will issue "closure letters" to sites that are remediated to Tier 1 criteria in contrast to the on-going risk management required at sites remediated to SSRO's.

The turn of the millennium brought with it significant changes in environmental remedial criteria with the release of the CCME Canada Wide Standards for Petroleum Hydrocarbons in Soil, 2000a. Following on the risk based protocols and toxicological data outlined in the CCME, 2000b document, AENV published a similar risk based guideline document: Alberta Soil and Water Quality Guidelines for Hydrocarbons at Upstream Oil and Gas Facilities, September, 2001. Along with changes to numerical remedial criteria in Alberta, came fundamental changes in the site assessment approach and regulatory framework. The new assessment approach allows proponents to eliminate groundwater protection pathways that may not apply, such as human ingestion and aquatic life use of the groundwater. The elimination of these pathways leads to the relaxation of groundwater remedial objectives to a Tier 1, non-potable status.

AMEC Earth and Environmental Limited has applied the same risk approach protocols and assessment techniques, contained within the latest Federal and Provincial guidance documents, to generate Alberta Tier 1 criterion for soil and groundwater contaminants. This paper presents the findings from the development of Tier 1 criterion for the toxic degradation product of chlorinated organic solvents – vinyl chloride. Once the applicable pathways and chemicals of concern are established at a site, the toxicological data is compiled and used to calculate the Tier 1 criterion. Human health criteria are calculated using standard generic risk assessment assumptions and transport models in the supporting scientific rationale which compliments both the CCME, 2000a and AENV, 2001 documents. Groundwater criteria designed to be protective of adjacent aquatic life receptors requires a suitable surface water criteria as a starting point, then generic, Alberta specific, transport and dilution models are employed to derive the protective soil and groundwater criterion. Tier 1 ecological soil contact criteria is derived based on the protocols described in CCME, 1996, with slight modification made in CCME 2000b. When there is insufficient, or inadequate eco-toxicological data available, such as with vinyl chloride, appropriate soil toxicity tests must be commissioned. Based on minimum data requirements in CCME, 1996 a toxicological data base can be established which enables the derivation of an eco-soil contact criterion.

INTRODUCTION

In Alberta, petroleum hydrocarbon criteria have been established through risk based protocols (AENV, 2001). Within the initial site assessment stages of the remedial process, proponents are able to eliminate groundwater protection pathways based on physical site evidence. The groundwater must be deemed to be incapable of supplying enough capacity for domestic use and proven not to be hydraulically connected to any potential domestic use aquifers. Furthermore, the groundwater must not be hydraulically connected to adjacent aquatic surface water bodies based on horizontal offset distances and hydraulic conductivity). A petroleum storage tank (PST) site for which there is no human or ecological use for the groundwater is to be remediated to a non-potable groundwater clean-up criteria. For volatile hydrocarbons, this non-potable groundwater remedial criteria is based upon protection against indoor vapour intrusion into both residential and commercial buildings.

The above approach to setting remedial criteria can apply to all organic contaminants within Alberta. Unfortunately, AENV only publishes non-potable groundwater criteria for petroleum hydrocarbons. In the absence of non-potable Alberta specific criteria, proponents are instructed to apply numerical criteria from other jurisdictions. For example, Ontario MOE publishes groundwater criteria for non-potable situations, thus, adopting these criteria may seem to be the easiest solution. However, the Ontario MOE estimates risks from indoor inhalation of volatile organics based on much more conservative transport models that assume 100% advective transport. This conservative transport approach can translate into non-potable groundwater criteria that is 2-3 orders of magnitude lower than that calculated with the Alberta approved transport model. The transport model used within the CCME, 2000a and Alberta, 2001 Tier 1 hydrocarbon criteria considers only diffusive transport. Under a “modified” criteria (*i.e.* Tier 2 and Tier 3 approaches) proponents are required to apply the advective component, which incorporates, pressure differentially driven, vapour intrusion through the cracks in the building slab (Johnson and Ettinger, 1991).

Traditionally, if a contaminated site is demonstrated to have potentially hazardous chemicals in various media, for which there are no appropriate remedial criteria, proponents have selected the option to develop risk based, site specific remedial objective (SSRO's) or chosen to remediate to background concentrations. This approach may be the only solution for complicated sites and provides adequate protection for the sensitive receptors. Nevertheless, the SSRO approach does not provide for regulatory closure. In contrast, sites that are remediated to a Provincially accepted, Tier 1 land use specific criteria are eligible for letters of regulatory compliance which can then be used to streamline real estate and legal transactions.

This paper presents a case example demonstrating the development of Tier 1 soil and groundwater criteria for vinyl chloride (VC), a highly toxic and mutagenic chloroethylene compound. As an environmental and occupational contaminant, VC is most frequently associated with the production of poly vinyl chloride (PVC). Additionally, VC is formed,

in groundwater and soil, as a degradation product following anaerobic de-chlorination of tetrachloroethylene (PCE) and trichloroethylene (TCE), both relatively common chlorinated solvents. Under ambient conditions, VC is a colourless, flammable gas with a slight sweet odour. The compound is extremely volatile with a high vapour pressure and Henry's Law constant, is heavier than air and displays a relatively low solubility in water, yet is soluble in almost all organic solvents. VC is expected to have a low organic carbon adsorption tendency and consequently a higher mobility in the sub-soil; partitioning into the soil vapour and pore water phases (WHO, 1999).

The site for which these Tier 1 criteria have been developed has subsurface soil and groundwater which contains VC generated from microbial degradation of PCE, TCE and dichloroethylene (DCE). The commercial/ industrial site is situated on fine grained clay till which does not contain, nor is it hydraulically connected to, any potential domestic use aquifers. Additionally, a surface water slough is present within the horizontal set back distance of 300 m. The applicable pathways, which have been accepted by AENV, are presented in Table 1.

Table 1: Summary of Applicable Criteria Pathways

Pathway Considered	Regulatory Justification
Aquatic Life (soil and groundwater)	Applicable: surface slough within 300 m off-set of the impacted soils.
Eco Soil Contact (soil only)	Applicable for all land use zonings within Alberta.
Inhalation of Indoor Air (soil and groundwater)	Applicable for commercial/ industrial and residential zoning
Human Soil Ingestion	Applicable for commercial/ industrial and residential zoning
Human Dermal Contact	Applicable for commercial/ industrial and residential zoning

METHODS/ PROTOCOLS

This section of the paper presents a terse overview of the methods and equations employed in the generation of the soil and groundwater criteria for each of the above noted pathways. For complete details on these mathematical equations and statistical techniques, the reader is referred to the Provincial and Federal guidance documents (AENV, 2001; CCME, 2000a and 2000b; and CCME, 1996). Other than chemical specific parameters describing environmental fate and toxicological thresholds, all receptor, soil and building parameters are generic values taken from AENV, 2001. The chemical and toxicological parameters were gathered from US EPA, 2000, 2001 and 2002.

Human Health Based Protocols

The US EPA IRIS databases lists VC as a human carcinogen. The evidence for VC's carcinogenic activity, primarily in the liver, is based upon several world wide epidemiological cohort studies of former PVC plant workers (WHO, 1999) and

benchmark life-time (> 3 years) laboratory animal studies from which the US EPA developed the current human “unit risk factor” and reference inhalation concentrations and oral doses (Til et al., 1983 and 1991).

The soil ingestion and dermal contact soil quality guidelines (SQG_{SI} & SQG_{DC}) are calculated by inverting standard risk assessment models used to estimate oral intake doses and dermal absorbed doses, respectively. Rather than using the models to estimate an exposure dose, soil guidelines are derived by ensuring the total daily intake is no greater than the toxicologically based tolerable daily intake (TDI).

The equation to calculate SQG_{SI} takes the following form:

$$SQG_{SI} = \frac{(TDI - EDI)(SAF)(BW)(10^3)}{(SIR)(AF_G)(ET)} + BSC \quad \text{Equation 1}$$

Where:

SQG_{SI}	=	human health soil quality guideline for soil ingestion (mg/kg)
TDI	=	tolerable daily intake (mg/kg/d)
EDI	=	estimated daily intake (mg/kg/d)
SAF	=	soil allocation factor (unitless)
BW	=	body weight (kg)
SIR	=	soil ingestion rate (g/d)
AF_G	=	absorption factor for gut (unitless)
ET	=	exposure term (unitless)
BSC	=	background soil concentration (mg/kg)

For dermal contact and oral ingestion of soil, it is assumed that the background soil concentration (BSC) and estimated daily intake (EDI) of vinyl chloride are negligible. The derivation of the criterion for a carcinogenic endpoint requires that the risk factor be converted into a risk-specific dose and inhalation concentration (RsD & RsC), determined by Equation 1a, with an acceptable background risk of developing cancer taken as 1×10^{-5} , or 1 in 100,000 (AENV, 2001).

$$RsD = \frac{\text{Acceptable Risk}}{\text{Unit Risk Factor}} \quad \text{Equation 1a}$$

The soil quality criteria for dermal contact with the soil is derived by Equation 2:

$$SQG_{DC} = \frac{(TDI - EDI)(SAF)(BW)(10^6)}{\{(SA_{HANDS} \times DL_{HANDS}) + (SA_{OTHER} \times DL_{OTHER})\}(AF_D)(EF)(ET)} + BSC \quad \text{Equation 2}$$

Where:

SQG_{DC}	=	human health soil quality guideline for soil dermal contact (mg/kg)
TDI	=	tolerable daily intake (mg/kg/d)
EDI	=	estimated daily intake (mg/kg/d)
SAF	=	soil allocation factor (unitless)
BW	=	body weight (kg)
SA_{HANDS}	=	surface area of hands (cm^2)

DL_{HANDS}	=	dermal loading for hands (mg/cm ²)
SA_{OTHER}	=	surface area of remaining parts of the body (cm ²)
DL_{OTHER}	=	dermal loading for remaining parts of the body (mg/cm ²)
AF_D	=	absorption factor for skin (unitless)
EF	=	exposure frequency (events per day)
ET	=	exposure term (unitless)
BSC	=	background soil concentration (mg/kg)

The overall equation used to derive the soil quality guideline for the indoor infiltration and inhalation exposure pathway SQG_{II} , is calculated by Equation 3:

$$SQG_{ii} = \frac{[(RfC - C_a)\{\theta_w + (K_{oc})(f_{oc})(\rho_b) + \frac{H}{RT}\theta_a\}(SAF)(DF_i)(10^3 \text{ g/kg})]}{\frac{H}{RT}\rho_b(ET)(10^6 \text{ cm}^3/\text{m}^3)} + BSC \quad \text{Equation 3}$$

Where:	SQG_{ii}	=	soil quality guideline by indoor infiltration (mg/m ³)
	RfC	=	substitute cancer risk specific concentration RsC (mg/m ³)
	C_a	=	background indoor/outdoor air concentration (mg/m ³)
	SAF	=	soil allocation factor
	θ_a	=	vapour-filled porosity
	θ_w	=	moisture-filled porosity
	K_{oc}	=	organic carbon partition coefficient (mL/g)
	f_{oc}	=	soil organic carbon fraction in contaminant partitioning zone
	ρ_b	=	soil dry bulk density in contaminant partitioning zone
	H	=	Henry's Law Constant (atm m ³ /mol)
	R	=	gas constant (8.21 x 10 ⁻⁵ atm m ³ /mol K)
	ET	=	exposure term
	BSC	=	background soil concentration (mg/kg)

Intermediate calculations are required to derive the dilution factor (DF_i) in Equation 3, which is defined as the inverse of the attenuation coefficient. The equation describing the attenuation coefficient (Equation 3a) accounts for only diffusive vapour phase flow and is a function of the chemical molecular diffusivity and Alberta, 2001 generic soil and building characteristics. The complete attenuation coefficient (Johnson and Ettinger, 1991) accounts for advective flow through the building slab and is required for Tier 2 and Tier 3 “modified” criteria calculations (AENV, 2001).

$$\alpha = \frac{\frac{D_T^{eff} A_B}{Q_B L_T}}{1 + \frac{D_T^{eff} A_B}{Q_B L_T} + \frac{D_T^{eff} A_B L_{crack}}{Q_{soil} A_{crack} L_T}} \quad \text{Equation 3a}$$

Where:	α	=	attenuation coefficient
	A_B	=	building area
	L_T	=	distance from contaminant source to foundation
	L_{crack}	=	thickness of the foundation
	D^{crack}	=	effective vapour-pressure diffusion coefficient through the crack
	A_{crack}	=	area of cracks through which contaminant vapours enter the building
	Q_{soil}	=	volumetric flow rate of soil gas into the building (cm ³ /s)
	Q_B	=	building ventilation rate (cm ³ /s)
	D_T^{eff}	=	effective porous media diffusion coefficient (cm ² /s)

Human health groundwater quality guidelines (GWQG_{HH}) are calculated from the lowest human health soil quality guideline (SQG_{HH}) based on mass balance partition equation described in Gustafson et al., 1997. The mass fraction of SQG_{HH} expected to partition into the aqueous phase is described by Equations 4 and the critical groundwater value is calculated from Equation 4a.

$$MF_w = \frac{\rho_b}{n_w + k_s \rho_b + H n_a} \quad \text{Equation 4}$$

$$GWQG_{HH} = MF_w \times SQG_{HH} \quad \text{Equation 4a}$$

Where:	MF_w	=	mass fraction in water phase
	n_w	=	soil volumetric water content
	n_a	=	soil volumetric air content
	k_s	=	soil-water sorption coefficient defined as $K_{oc} \times f_{oc}$

Ecological Based Protocols

Aquatic Life

The exposure point freshwater quality criteria used in the calculations of SQG_{AL} was adopted from the Ontario Ministry of the Environment (MOE) for vinyl chloride (0.6 mg/L). According to the AENV (2001), two separate groundwater guidelines designed to be protective of aquatic life receptors are possible: 1) less than 10 m from a water body guideline, and 2) 10 m offset guideline. Within the 10 m buffer around an aquatic water body the exposure point guideline applies to the groundwater. Outside the 10 m buffer the soil and groundwater guidelines for protection of aquatic life receptors are back calculated from the exposure point concentration using a series of dilution factors. The soil quality guideline is calculated with Equation 5 and the groundwater quality guideline is calculated with Equation 6.

$$SQG_{AL} = C_w D F \quad \text{Equation 5}$$

Where:

SQG_G = soil quality guideline protective of groundwater for aquatic life, livestock, or wildlife watering (mg/kg);
 C_W = water quality guideline for aquatic life, livestock, or wildlife watering (mg/L);
 DF = $DF = DF1 \leftrightarrow DF2 \leftrightarrow DF3 \leftrightarrow DF4$

$$GWQG_{AL} = \frac{C_W}{DF4}$$

Equation 6

Dilution factor 1 ($DF1$) considers the soil organic carbon and vapour phase partitioning of the compound. Dilution factor 2 ($DF2$) considers dilution of the contaminant as it percolates through the vadose zone toward the water table. For Tier 1 criteria, the contaminant is assumed to extend to the water table, thus $DF2 = 1$. Dilution factor 3 ($DF3$) takes into account infiltration rate and basic aquifer characteristics such as hydraulic conductivity and horizontal gradient to estimate dilution as the contaminated leachate mixes with the uncontaminated groundwater. Dilution factor 4 ($DF4$) dilutes concentrations according to the processes of dispersion and biodegradation as groundwater travels downgradient 10 m from the source. The single, additional chemical specific parameter, which has not yet been introduced in the human health based calculations, is the decay half life of the chemical in an aquifer ($t_{1/2}$). For VC, it was assumed that this biodegradation pathway was negligible ($t_{1/2} = 300$ years). Details on the calculation of these dilution factors are not presented within this paper, the reader is referred to the Provincial guidance document (AENV, 2001).

Ecological Soil Contact

Eco-soil contact criteria are generated based on direct toxicological testing on the plants and invertebrates likely to inhabit the shallow soils. The Canadian Council of Ministers of the Environment (CCME) publishes the only Canadian protocols for the derivation of environmental soil quality guidelines (CCME, 1996). Outlined within this document are three approaches to derive direct eco-soil contact criteria: 1) weight of evidence method requiring the most comprehensive toxicity database; 2) lowest observable effects concentration method when the minimum data requirements of method 1 cannot be met; and 3) median effects method when only minimal lethality or sub-lethal median effects (*i.e.* LC_{50}) data are available.

The weight of evidence method ranks the effects (commercial/industrial) or combined no-effects and effect (residential/parkland) data to estimate the effects concentration – low (EC-L) and threshold effects concentration (TEC), respectively. Selected databases are used to generate an empirical normal probability distribution, the so-called, species sensitivity distribution (SSD). The 25th percentile of the distribution is considered to be suitable to generate the benchmark EC-L and TEC values without applying uncertainty factors. As the quantity and diversity of the toxicological endpoints diminishes, alternative methods 2 and 3 are used and the EC-L calculated is further reduced by dividing by an uncertainty factor.

Within the Alberta (AENV, 2001) and Canadian (CCME, 2000b) hydrocarbon criteria, direct eco-soil contact guidelines were developed with modifications to the original CCME, 1996 protocols. The SSD used to generate the direct eco-soil contact criteria for commercial/ industrial sites excluded the invertebrate data and the benchmark percentile on the remaining plant SSD was set at the 50th, rather than 25th percentile.

The toxicity testing conducted for this study resulted in a database of 50 no-effects and effects endpoints covering microbes, invertebrates and plants (Table 2). The plant endpoints alone totaled 28. After removing the no-effects endpoints and averaging similar endpoint between the two different soil types, the databases used as input to the SSD's contained 23 and 15 data points for all species and plants alone.

Table 2: Soil Toxicity Tests Conducted

Organism	Effects (duration)	Endpoint	Test Substrate
Bioluminescent bacteria (<i>Photobacterium phosphoreum</i>)	Reduced light emission (15 minutes)	EC50, LOEC	Artificial sandy soil extracts:
		EC50, LOEC	Artificial clay soil extracts:
Earthworm (<i>Eisenia foetida</i>)	Mortality (14 day static test)	NOEC, LOEC , LC50	Artificial sandy soil:
		NOEC, LOEC , LC50	Artificial clay soil :
	Growth (14 day static)	NOEC, LOEC , TEC	Artificial sandy soil:
		NOEC, LOEC , TEC	Artificial clay soil :
Springtail (<i>Folsomia spp</i>)	Mortality (14 day static)	NOEC, LOEC , LC50	Artificial sandy soil:
		NOEC, LOEC , LC50	Artificial clay soil :
Lettuce (<i>Lactuca sativa</i>)	Seed emergence (21 day static)	NOEC, LOEC , EC50	Artificial sandy soil:
		NOEC, LOEC , EC50	Artificial clay soil :
	Root elongation (21 day static)	NOEC,LOEC ,IC50, IC10	Artificial sandy soil:
		NOEC,LOEC,IC50,IC10	Artificial clay soil :
Timothy (<i>Phleum pratense</i>)	Seed emergence (21 day static)	NOEC, LOEC , EC50	Artificial sandy soil:
	Root elongation (21 day static)	NOEC, LOEC, IC50, IC10	Artificial sandy soil:
Alfalfa (<i>Medicago sativa</i>)	Seed emergence (21 day static)	NOEC, LOEC , EC50	Artificial sandy soil:
	Root elongation (21 day static)	NOEC, LOEC, IC50, IC10	Artificial sandy soil:

Table 2 Footnotes: NOEC = no observable effect concentration; LOEC = lowest observable effects concentration (percentile effected); LC50 = lethality 50 %; EC50 = effects 50%; IC(50 & 10) = growth inhibition 50% & 10%; TEC = threshold effect concentration (averaged between NOEC and LOEC). Artificial sandy soil: 70% silica sand: 20% kaolinite clay: 10% peat moss; Artificial clay soil: 70% kaolinite clay: 20% silica sand: 10% peat moss.

RESULTS

The results of the Tier 1 criteria development for VC have yet to be reviewed and approved by AENV. Consequently, this paper will not provide absolute numerical criteria. However, expected ranges are presented (Table 3) and differences among the various pathways for human health and ecological protection are discussed.

Table 3: Expected Magnitude of Vinyl Chloride Soil and Groundwater Criteria for Commercial/ Industrial Site on Fine Grained Soils

Exposure Pathway	Symbol	Units	Criteria magnitude
Human Health (indoor vapour inhalation)	SQG _{HH}	mg/kg soil	10 ⁻²
Freshwater Aquatic Life	SQG _{AL}	mg/kg soil	10
Ecological Soil Contact	SQG _{SC}	mg/kg soil	10 ⁻²
Human Health (indoor vapour inhalation)	GWQG _{HH}	mg/L groundwater	10 ⁻¹
Freshwater Aquatic Life (>10 m)	GWQG _{AL}	mg/L groundwater	10
Freshwater Aquatic Life (< 10 m)	GWQG _{AL}	mg/L groundwater	0.6 [†]

Table 3 Footnote: [†]- within 10 m off-set exposure point surface water criteria applies (Ontario MOE)

The eco-soil SSD's are evaluated by taxon groups (Figure 1) and the overall SSD is portrayed in Figure 2. Figure 1 clearly indicates that among taxon sensitivity to VC varies considerably; invertebrates are more sensitive as compared to the plant taxon. A similar disparity was discovered following the analysis of the eco-soil toxicity data on petroleum hydrocarbons (CCME, 2000b). Figure 2 is the combined effects SSD used to generate the commercial/ industrial eco-soil contact soil quality guideline based on the original CCME, 1996 protocols. The 25th percentile on the combined SSD effectively protects 99% of the plant species, while failing to provide protection for the invertebrates. Based on this taxon disparity, and following the precedent modifications within the Federal and Provincial hydrocarbon criteria protocols, a recommendation has been made to focus the commercial/ industrial eco-soil protection objective on plant species alone.

The soil quality guideline calculated for the protection of aquatic life receptors at a 10 m off-set is two orders of magnitude higher than the range predicted for the direct eco-soil contact pathway. Because of the reduced molecular transport expected in the typical, "generic" Alberta fine grained soil, the aquatic life pathway is not expected to be a determining driver.

Of the three human health pathways evaluated, the carcinogenic endpoints for soil dermal contact and soil ingestion are within the same order of magnitude as the SQG_{AL}. Due to the extreme volatility of VC, the indoor vapour inhalation pathway is expected to be the determining driver for both the soil and groundwater criteria on commercial/ industrial lands. Based on the carcinogenic endpoint, the SQG_{HH} calculated for protection against

indoor vapour intrusion is within the same order of magnitude as that estimated for eco-soil contact.

Figure 1: Normal Probability Plots

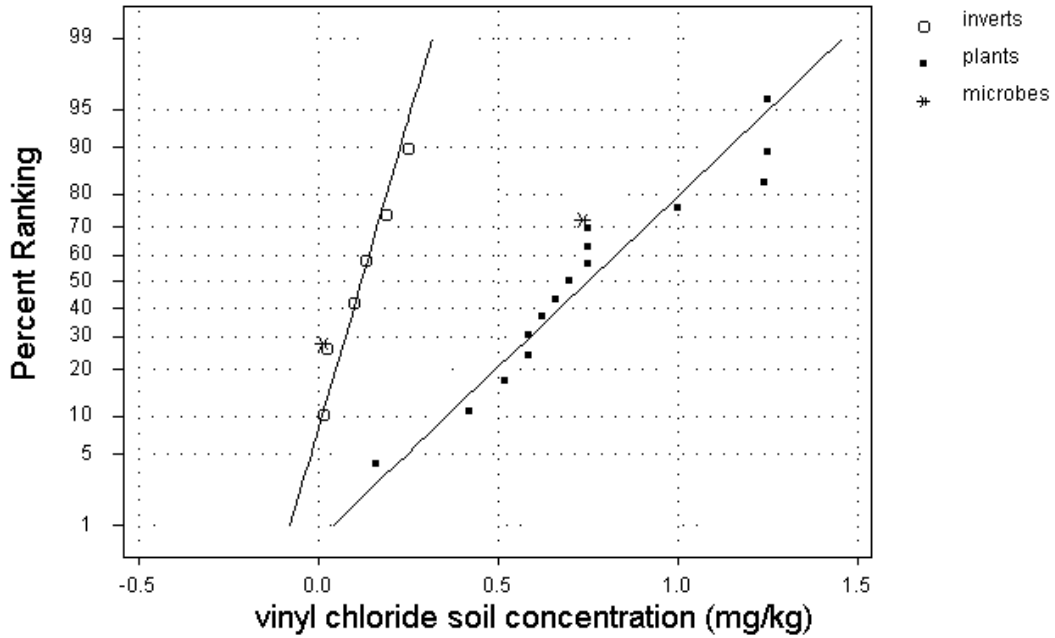
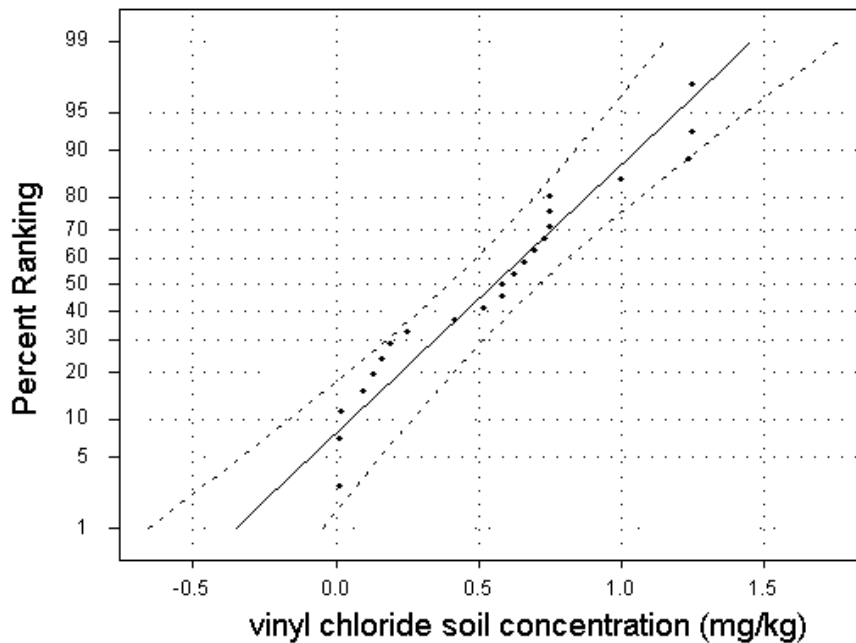


Figure 2: Normal Probability Plot for Combined Data



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