Review of the Appropriateness of the Canadian Petroleum Hydrocarbon Country Wide Standards in Soil for Incorporation into the Australian National Environment Protection (Assessment of Site Contamination) Measure and Recommended Ecological Investigation Levels

By Dr Michael Warne

1. Background

In December 2009 Dr Michael Warne was approached by Ms Kerry Scott of the National Environment Protection Council Service Corporation to review the Canadian Petroleum Hydrocarbon (PHC) Country Wide Standards (CWS). The objectives of the review were to:

- consider the protocols used for the derivation
- provide advice on the sufficiency of the methods and selected values for ecological protection and any limitations to their application
- advise on the level of the reliability of the selected values for ecological protection.

A report of not more than five pages length addressing the above objectives was to be provided to NEPC Service Corporation by February 24, 2010.

In undertaking this work the following documents that were referred to in the scope of work were read and critically evaluated:

Canadian Council of Ministers of the Environment (CCME) 2008a. Canada-wide Standard for Petroleum Hydrocarbons (PHC) in Soil. Report no. PN 1398. January 2008. Ottawa, Canada. 8p.

Canadian Council of Ministers of the Environment (CCME) 2008b. Canada-wide Standard for Petroleum Hydrocarbons (PHC) in Soil: Scientific Rationale Supporting Document Report no. PN 1399. January 2008. Ottawa, Canada. 412p.

2. Summary of the Canadian Methodology

Petroleum hydrocarbons were divided into four fractions termed F1 to F4. These correspond to PHCs with: F1 – C6 to C10; F2 – C11 to C16; F3 – C17 to C34; and F4 – C35 to C50. The proposed Australian Health Screening Levels for PHCs have adopted the Canadian PHC fractions (Eric Friebell, *pers. comm.*). A receptor and exposure pathway analysis was conducted for PHCs in each of the four land-uses (residential, agricultural, commercial and industrial) and the appropriate ones were identified. Appropriate toxicity data were then collated for the identified receptors/exposure pathways.

The preferred method for deriving the standards is a risk-based species sensitivity distribution (SSD) method however, it was not always possible to use this approach and a weight of evidence (WoE) approach was necessary to derive the direct soil contact CWS values for F3 and F4. The methodology also attempted to take changes in PHC bioavailability caused by soil properties into account. This was done, where appropriate data were available, by deriving CWS values for fine and coarse soils (i.e., soils where >50% of particles have a diameter of < 75μm are classed as fine and soils where >50% of particles have a diameter of > 75μm are classed as coarse). Overall, the Canadian methodology is broadly consistent with the proposed Australian EIL derivation methodology (Heemsbergen et al., 2009).

3. Important points to consider

The Canadian PHC CWSs "are remedial standards" (CCME, 2008a) and therefore the aim of these guidelines is not the same as the Australian EILs. However, the toxicity data (EC/LC25 or 20%) and the level of protection that the Canadian CWSs provide (75% of species for residential and agricultural land and 50% for commercial and industrial land) are similar to those used in the proposed Australian EIL methodology (Heemsbergen et al., 2009) which uses EC/LC30 or LOEC data and provides 80% protection for species in residential and agricultural and 60% for commercial/industrial land). It would not be a small undertaking to obtain EC/LC30 or NOEC data that correspond to the Canadian data. However, it would be a relatively small task to recalculate the CWSs so that the % of species being protected matches those in the proposed Australian EIL derivation methodology (Heemsbergen et al., 2009) for each land use. These recalculations have been done and are presented in Section 5 of this report. However, there is an additional problem with the Canadian method which will be discussed in the next point.

The preferred method of deriving the CWS values is to use a SSD (however, that was not possible in all instances). Interestingly, the data reduction method that the Canadians use is different to that of the proposed Australian EIL derivation methodology (Heemsbergen et al., 2009) and that used by all other countries that use a SSD methodology. The normal approach is to manipulate the toxicity data using a set of rules, so that a single toxicity value is obtained for each species. This data reduction process ensures that the SSD method places the same importance (weight) on each species and it also means that the level of protection is expressed in terms of the % of species that should theoretically be protected. The Canadian PHC CWSs do not manipulate the data so that a single value is obtained for each species. Rather, they can end up with variable numbers of toxicity values for a species – one for each different biological effect.

For example in one calculation they have 3 species which have four data points each, one species with three data points, one species with two data points and one species with one data point. This means that the resulting level of protection is a certain percentage of the data points rather than a percentage of species. It also means that the same weight is not given to each species in determining the CWS – rather the species that have the most data have most impact on the resulting CWS. This biases the data.

As all the data that the Canadians use are provided (CCME, 2008b) it would be possible to recalculate the CWS values using the data manipulation method and SSD method of the proposed Australian EIL derivation methodology (Heemsbergen et al., 2009) and to address the issue raised in the preceding point. These recalculations have been done and are presented in Section 5 of this report.

The Canadian PHC CWS values are based on total concentrations and therefore they already take into account the ambient background concentration. They therefore should not have the ambient background concentration added to them.

The PHC CWSs are derived for a coarse and fine texture soil where appropriate data permit. This is in contrast to the proposed Australian EILs which are soil-specific, appropriate data permitting. The Canadian procedure is an attempt to account for soil-specific effects on the bioavailability of contaminants and is consistent with the proposed Australian EIL derivation methodology (Heemsbergen et al., 2009).

The Canadian PHC CWS aims to protect the following ecological receptors/exposure pathways: direct soil contact, groundwater and aquatic ecosystems, nutrient cycling and drinking water for livestock. This is not the case in the proposed Australian EIL derivation methodology (Heemsbergen et al., 2009) which aims to protect all types of organisms from direct soil contact and secondary poisoning if the contaminant bioaccumulates/biomagnifies and appropriate data are available. The PHC CWS values protect both human and ecological health but in addition there are a number of "management factors" for which there are also limits. These management limits include: (1) ignition hazard; (2) odour and appearance issues; (3) formation of non-aqueous phase liquids (NAPL); (4) exposure of workers in trenches etc; (5) effects on buried infrastructure; and (6) technology features. There are no equivalent limits in the proposed Australian EIL system. However, the Canadians derived CWS values based on all the individual exposure pathways and receptors that were identified as important for each land use, including limits for the management factors. The lowest CWS that applies for a particular land use is then adopted.

Therefore, it is possible to exclude the limits associated with human health and those ecological receptors and pathways or management factors that are not considered in the proposed Australian EILs derivation methodology (Heemsbergen et al., 2009).

A key receptor that is nominally protected by the Canadian ecological PHC CWSs is microbiologically mediated nutrient cycling. However, no data were available to the Canadians and so this receptor was not included. In the proposed Australian EILs (for arsenic, chromium III, copper, DDT, lead, naphthalene, nickel and zinc) there were such data and these were incorporated into the calculations (Warne et al., 2009).

The Canadian PHC CWSs do not account for ageing and leaching in their derivation, unlike the proposed Australian EILs. Their CWS values are essentially for fresh contamination, however it should be noted that some aged toxicity data were used in the derivation of the CWS values for F3 and F4. In contrast, the proposed Australian EILs (Warne et al., 2009) have values for both fresh and aged contaminants.

Therefore, as long as it is made perfectly clear that the PHC CWS values are for fresh contamination they could be incorporated into the revised Australian NEPM.

Although the PHC CWSs cover hydrocarbons from nC6 to nC50 they specifically exclude known carcinogens such as benzene and benzo(a)pyrene and also specific PHCs which have a long history of regulation i.e., toluene, ethylbenzene and xylenes. Therefore these chemicals are not to be included in the calculation of the PHC concentrations and must be managed separately. So if it is desired that these chemicals are to be included in the revised Australian EILs then the appropriate CWS values for these must be examined (for their appropriateness to the Australian system) and included or it must be made clear in the NEPM that they are omitted from the EIL.

4. Reliability of the Canadian PHC CWS values

As two vastly different methods were used to derive the CWS values for direct soil contact for F1 and F2 compared to F3 and F4 their reliability will be discussed separately.

4.1 F1 and F2

The amount of appropriate ecotoxicity data was limited (6 species belonging to 3 taxonomic groups for F1 and 5 species belonging to three taxonomic groups for F2) but met the minimum data requirements of the Canadians and would meet those of the proposed Australian EIL derivation methodology (data from five species that belong to three taxonomic groups) (Heemsbergen et al., 2009). However, the number of data is not extensive and considerably less than that used to derive the vast majority of the proposed Australian EILs (Warne et al., 2009). For example, the smallest dataset used to derive any of the proposed Australian EILs (Warne et al., 2009) was for 14 species belonging to five taxonomic groups for naphthalene. The toxicity data for F1 and F2 meet the minimum data requirements to use a SSD method (see above) but there are no normalisation relationships, therefore the resulting CWS values would be classified as moderate reliability (Heemsbergen et al., 2009). However, in order to improve their agreement with the proposed Australian EIL derivation method they should be recalculated as discussed previously.

4.2 F3 and F4

There are considerable limitations in the ecotoxicity data available for these fractions which include: limited biological endpoints being examined in some studies; some studies only used one of two concentrations; some studies used fresh PHC contamination while some used aged. Each of the available studies has "issues which make interpretation of the data challenging" (CCME, 2008b). Therefore, they felt that the most appropriate way forward "was not to attempt to combine all the data in a single distribution, but rather to calculate guideline values for each dataset individually" (CCME, 2008b). A variety of different methods were used to maximise the information obtained for each dataset. These methods were in many instances not consistent with the preferred SSD method. A weight of evidence approach was then used to determine which study provided the most reliable limit and whether the other less-optimal studies supported this value.

The method for assessing the reliability of EILs can not be applied directly to the CWS values for F3 and F4 as the type of data used to determine the CWS were not envisaged in the proposed Australian EIL derivation methodology (Heemsbergen et al., 2009). However, given the deficiencies in most of the ecotoxicity studies and the non-standard methods of determining the CWS values I believe that the Canadian PHC CWS values for F3 and F4 have low reliability. I recommend that if these CWS values are adopted that they be adopted as either 'low reliability EILs' or 'interim low reliability EILs".

5. Recalculation of the Direct Soil Contact CWSs Using the Proposed Australian EIL Derivation Method

The ecotoxicity data used to calculate the Canadian F1 CWS values for direct soil contact and the values that would be used if the proposed Australian EIL derivation methodology was followed are presented in Table 1. The SSD plot of data using the proposed Australian method is presented in Figure 1 and the Canadian PHC CWS values and the corresponding Australian values are presented in Table 2. Comparing values within a column of Table 2 illustrates the effect of using the different toxicity data while comparisons within a row illustrate the effect of changing the level of protection. It would appear using the proposed Australian methodology leads to lower limits (Table 2).

Table 1. Ecotoxicity data (based on total soil concentrations) used to derive the Canadian direct soil contact standard for fraction one petroleum hydrocarbons and the values that would be used if the proposed Australian EIL derivation methodology (Heemsbergen et al., 2009) was used.

Species	**Endpoint**	**LC/IC20 (25) values used by CCME (2008b) (mg/kg)**	**Recommended LC/IC20 (25) values to be used[1] (mg/kg)**
alfalfa (plant)	shoot length	280	190
	root length	230	
	shoot weight	190	
	root weight	230	
barley (plant)	shoot length	610	490
	root length	500	
	shoot weight	490	
	root weight	610	
corn (plant)	shoot length	380	160
	root length	160	
	shoot weight	740	
	root weight	830	
red fescue (plant)	shoot length	300	190
	root length	190	
	total weight	400	
Orthonychiurus folsomi (collembola)	adult mortality	230	220
	no. progeny	220	
Eisenia andrei (earthworm)	mortality	510	510

[1] These data were selected using the data reduction and manipulation methods set out in Heemsbergen et al., (2009).

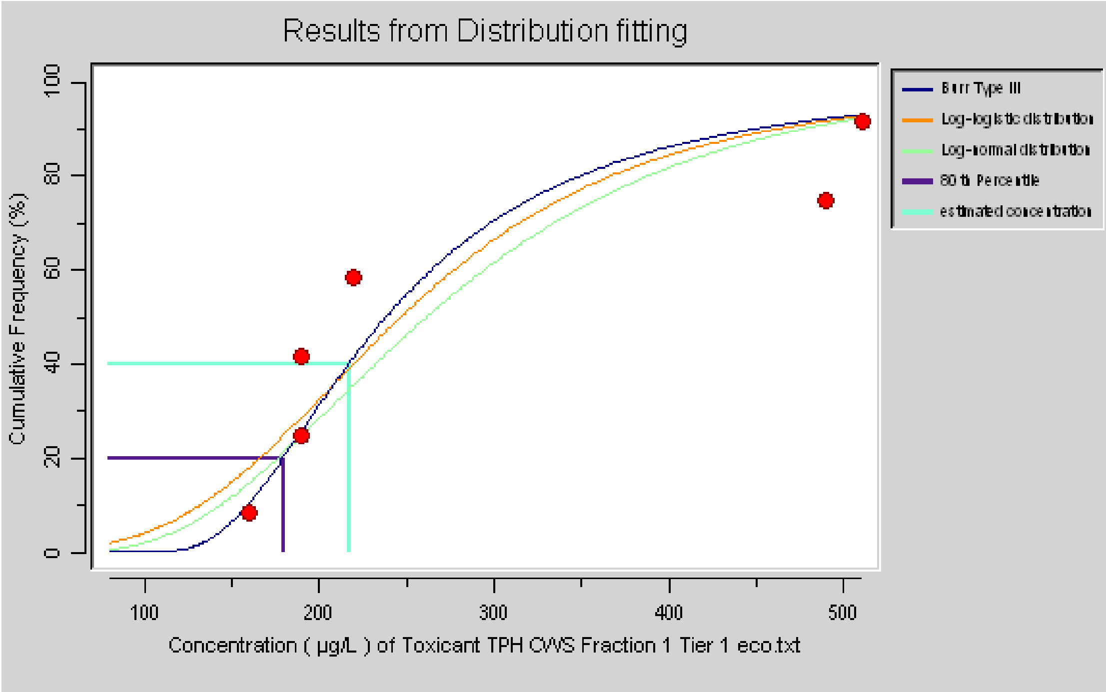

Figure 1. The species sensitivity plot for the fraction 1 petroleum hydrocarbon ecotoxicity data selected using the proposed Australian EIL derivation methodology (Heemsbergen et al., 2009) (column 4 of Table 1). The plot was generated using BurrliOZ (Campbell et al., 2000). The purple and aqua green horizontal and vertical lines indicate the concentration that should theoretically protect 80 and 60% of species. The units of the x axis are mg/kg not µg/L as stated, unfortunately the units of the BurrliOZ output graph can not be changed from µg/L.

Table 2. Limits calculated using fraction 1 ecotoxicity data by the Canadian method and the proposed Australian method. The pink and blue shaded values are the Canadian standards and the values recommended for adoption as Australian ecological investigation levels (based on total soil concentrations), respectively.

Calculation method	**Protective concentrations (mg/kg)**				
	75%[1] species	**80%[2] species**	**50%[3] species**	**60%[4] species**	**99%[5] species**
Canadian	210	222[6]	319	282[6]	142[6]
proposed Australian	190	180	238	217	126

[1.] the level of protection provided by the Canadian method to residential and agricultural soils. [2.] the level of protection provided by the proposed Australian method to residential and agricultural soils.

[3.] the level of protection provided by the Canadian method to commercial and industrial soils.

[4.] the level of protection provided by the proposed Australian method to commercial and industrial soils.

[5.] the level of protection provided by the proposed Australian method to national parks and areas of high ecological value.

[6.] these values were not calculated or presented in CCME (2008b) but were calculated in the present study using the Canadian data and method but the Australian levels of protection.

The ecotoxicity data used to calculate the Canadian F2 CWS values for direct soil contact and the values that would be used if the proposed Australian EIL derivation methodology was followed are presented in Table 3. The SSD plot of data using the proposed Australian method could not be generated due a glitch in the BurrliOZ software that prevented the graph being copied and pasted into the current report. The Canadian PHC CWS values and the corresponding Australian values are presented in Table 4. The effect of using the different toxicity data and the effect of changing the level of protection can be determined using the same method as for Table 2. Again, using the proposed Australian methodology leads to lower limits (Table 4).

Table 3. The ecotoxicity data (based on total soil concentrations) used to derive the Canadian direct soil contact standard for fraction two petroleum hydrocarbons (modified from CCME, 2008b) and the values that would be used if the proposed Australian EIL derivation methodology (Heemsbergen et al., 2009) was used.

Species	**Endpoint**	**LC/IC20 (25) values used by CCME (2008b) (mg/kg)**	**Recommended LC/IC20 (25) values to be used[1] (mg/kg)**
alfalfa (plant)	shoot length	455	167
	root length	221	
	shoot weight	167	
	root weight	764	
barley (plant)	shoot length	494	284
	root length	381	
	shoot weight	284	
	root weight	311	
northern wheatgrass (plant)	shoot length	1092	79
	root length	86	
	shoot weight	308	
	root weight	79	
Eisenia andrei (earthworm)	mortality	305	116
	no. progeny	116	
	progeny biomass	135	
Orthonychiurus folsomi (collembola)	mortality	211	211

[1.] These data were selected using the data reduction and manipulation methods set out in Heemsbergen et al., (2009).

Table 4. The limits calculated using the fraction two ecotoxicity data using the Canadian method and the proposed Australian method. The pink and blue shaded values are the Canadian country wide standards and the values recommended for adoption as Australian ecological investigation levels (based on total soil concentrations), respectively.

Calculation method	**Protective concentrations (mg/kg)**				
	75%[1] species	**80%[2] species**	**50%[3] species**	**60%[4] species**	**99%[5] species**
Canadian	150	146[6]	260	216[6]	46
proposed Australian	133	118	195	172	23

[1.] the level of protection provided by the Canadian method to residential and agricultural soils. [2.] the level of protection provided by the proposed Australian method to residential and agricultural soils.
[3.] the level of protection provided by the Canadian method to commercial and industrial soils.
[4.] the level of protection provided by the proposed Australian method to commercial and industrial soils.
[5.] the level of protection provided by the proposed Australian method to national parks and areas of high ecological value.
[6.] these values were not calculated or presented in CCME (2008b) but were calculated in the present study using the Canadian data and method but the Australian levels of protection.

6. Recommendations

1. That the overall methodology used for to derive the Canadian Country Wide Standards (CWS) for Petroleum Hydrocarbons (PHC) be adopted and incorporated into the NEPM.
2. That the Canadian CWS values for PHC fractions one and two not be adopted but rather values derived consistent with the proposed Australian EIL derivation methodology be adopted. The recommended EILs[1] for both fractions one and two are presented in Table 5. For these fractions the recommended EILs apply to both fine and coarse soil.
3. That the Canadian CWS values for PHC fractions three and four be adopted[1] (Table 5), but as low reliability EILs or possibly interim low reliability EILs.

[1] The ambient background concentration does not need to be added to these recommended values as they are based on total soil concentrations.

Table 5. Recommended soil concentrations for all petroleum hydrocarbon fractions to be adopted as ecological investigation levels for various land-uses.

Fraction (F) and soil type	Recommended EILs (mg/kg) for land-uses		
	National parks and areas with high ecological value	Urban residential and open public space	Commercial and industrial
F1[1] (both)	126	180	217
F2[1] (both)	23	118	172
F3[2] (fine)	na[3]	1300	2500
F3[2] (coarse)	na	300	1700
F4[2] (fine)	na	2500	6600
F4[2] (coarse)	na	1700	3300

1. it is recommended that these be adopted as 'moderate reliability EILs'.

2. it is recommended that these be adopted as either 'low reliability EILs' or as 'preliminary low reliability EILs'.

3. na = not available.

7. References

Campbell E, Palmer MJ, Shao Q, Wilson D. 2000. BurrliOZ: A computer program for calculating toxicant trigger values for the ANZECC and ARMCANZ water quality guidelines. Perth, Western Australia, Australia.

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Heemsbergen D, Warne MStJ, McLaughlin MJ, Kookana R. 2008. A Proposed Australian Methodology to Derive Ecological Investigation Levels in Contaminated Soils. CLW Science Report. Prepared for the NEPM Review Team. 76p.

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