Review of the appropriateness of selected Canadian Soil Quality Guidelines (benzene, benzo(a)pyrene, ethylbenzene, toluene and xylenes) for incorporation into the Australian National Environment Protection (Assessment of Site Contamination) Measure and recommended Ecological Investigation Levels

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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) for their suitability to be incorporated into the Australian National Environment Protection (Assessment of Site Contamination) Measure (hereafter referred to as the NEPM) (NEPC, 1999). This was completed and a report submitted to NEPC (Warne, 2010). This review identified that the Canadian PHC CWSs (CCME 2008) specifically excluded benzene, benzo(a)pyrene, ethylbenzene, toluene and xylenes, which are important and common contaminants in Australian contaminated sites.

Therefore, in February 2010, Dr Michael Warne was approached by Ms Kerry Scott to review the Canadian Soil Quality Guidelines (SQGs) for benzene, benzo(a)pyrene, ethylbenzene, toluene and xylenes. 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 addressing the above objectives was to be provided to NEPC Service Corporation by March 12, 2010.

In undertaking this work, the following documents were read and critically evaluated:

- Environment Canada, 1999. *Canadian Soil Quality Guidelines for the Protection of Environmental and Human Health: Benzo(a)pyrene*. Scientific Supporting Document. National Guidelines and Standards Office, Environmental Quality Branch, Environment Canada. Ottawa, Canada. 46p.

- Environment Canada, 2004. *Canadian Soil Quality Guidelines for the Protection of Environmental and Human Health. Benzene*. 2004. Available from: http://ceqg-rcqe.ccme.ca/download/en/259/. Downloaded 1/3/2010.

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- Environment Canada, 2004. *Canadian Soil Quality Guidelines for the Protection of Environmental and Human Health. Toluene.* 2004. Available from http://ceqg-rcqe.ccme.ca/download/en/283/. Downloaded 1/3/2010.

- Environment Canada, 2004. *Canadian Soil Quality Guidelines for the Protection of Environmental and Human Health. Xylenes.* 2004. Available from http://ceqg-rcqe.ccme.ca/download/en/287/. Downloaded 1/3/2010.

- Environment Canada. 2005a. *Canadian Soil Quality Guidelines for the Protection of Environmental and Human Health: Benzene.* Scientific Supporting Document. Ecosystem Health: Science-Based Solutions Report No. 1-10. National Guidelines and Standards Office, Water Policy and Co-ordination Directorate, Environment Canada. Ottawa, Canada. 73p.

- Environment Canada. 2005b. *Canadian Soil Quality Guidelines for the Protection of Environmental and Human Health: Toluene, Ethylbenzene and Xylenes (TEX).* Scientific Supporting Document. Ecosystem Health: Science-based Solutions Report No. 1-9. National Guidelines and Standards Office, Water Policy and Co-ordination Directorate, Environment Canada. Ottawa, Canada. 94p.

2. Summary of the Canadian Methodology

A receptor and exposure pathway analysis was conducted for the contaminants in each of the four land-uses (residential, agricultural, commercial and industrial) and those that were relevant for each contaminant 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, none of the contaminants included in this review had sufficient toxicity data to meet the Canadian minimum data requirements to use a SSD method. For benzene and the TEX contaminants there were only toxicity data for four species (two plants, an earthworm and a collembolan). Therefore the Canadians used an 'Effects/No Effects Data Distribution weight of evidence (WoE) approach' (Environment Canada, 2005a) – which used a mixture of effects and no effects toxicity data, a modified SSD methodology (with relaxed minimum data requirements and different data reductions rules) and if deemed necessary uncertainty factors (the equivalent Australian term is assessment factors (ANZECC and ARMCANZ, 2000).

Normally the Canadian SQGs attempt to account for changes in contaminant bioavailability caused by soil properties. This is done, where appropriate data were available, by deriving SQG 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). With volatile contaminants, considerable decreases in soil concentrations can occur during the toxicity tests, which may need to be corrected for. In the case of benzene and the TEX contaminants, the measurement of loss was only done for the coarse soil and therefore the 'converted to "estimated effect" values using regression equations based on the analysis of samples collected 2 hours (for plants) and 24 hours (for invertebrates) after spiking' (Environment Canada, 2005a; 2005b).

There were insufficient data to meet the Canadian minimum data requirements to derive a direct soil contact SQG for benzo(a)pyrene (Environment Canada, 1999). Therefore only a provisional Canadian SQG was derived (Environment Canada, 1999). The provisional derivation process involves professional judgement "to evaluate the available information and recommend a provisional soil quality guideline" (Environment Canada, 1999). Benzo(a)pyrene has a very high octanol-water partition (K_{ow}) (with a log K_{ow} of over 6) and therefore it will preferentially bind to the solid phase (including organic matter) rather than

the liquid phase of soil.

Given this, Environment Canada (1999) stated that it was desirable to develop or use an equation that converted food concentrations of benzo(a)pyrene that cause toxic effects to soil concentrations. They used the formula:

$$EC_{soil} = (f_{oms}/f_{omf}) \cdot EC_{food} \qquad (1)$$

where EC_{soil} is the concentration of benzo(a)pyrene in soil (mg/kg dry soil), f_{oms} is the fraction of organic matter in soil, f_{omf} if the fraction of organic matter in food (a value of95% from Jensen and Folker-Hansen (1995) was used), and EC_{food} is the concentration of benzo(a)pyrene in food that causes toxic effects. Environment Canada (1999) used a value for EC_{food} of 125 mg/kg which was the lowest concentration in leaves fed to slaters (a terrestrial invertebrate) that caused a statistically significant ($p \leq 0.05$) reduction in growth efficiency (Van Straalen and Verweij, 1999).

3.   Important points to consider

The Canadian SQGs prefer to use toxicity data that measure a 25% effect (e.g., LC50 or EC50 data) but in the case of benzene and the TEX contaminants they also used some lowest observed effect concentration (LOEC) data. The preferred toxicity data to be used to derive Australian EILs are those that measure a 30% effect or LOEC (Heemsbergen et al., 2009). It should be noted that in the Australian EIL derivation methodology (Heemsbergen et al., 2009) toxicity data that cause a 20 to 40% effect and LOEC data are considered equivalent. Therefore the data used by Environment Canada can be used without modification to derive Australian EILs.

The Canadian SQGs for benzene and the TEX contaminants were not derived to provide a specific level of protection (i.e. the percentage of species protected). As none of these contaminants meet the minimum data requirements, the SSD method was used and the25th and 50th percentile values were calculated (refer to the fourth point for an explanation of another difference between the Canadian and proposed Australian methods that relates to the SSD method). The 25th percentile values were then divided by an uncertainty factor of three for benzene and two for the TEX contaminants. The uncertainty factor of three was applied to benzene because of the limited number of species for which there were data and "greater than 50% of the data for soil invertebrate toxicity falls below the 25th percentile of the distribution" (Environment Canada, 2005a). The uncertainty factor of two was applied to the other contaminants because of "the limited number of species represented in the data distribution" (Environment Canada, 2005). Despite these explanations, it appears that the magnitude of the uncertainty factors is arbitrary.

For benzo(a)pyrene, a type of worst-known case approach has been combined with an approach that considers biomagnification. It is not possible to provide any estimate of the level of protection that is provided by the Canadian provisional SQG except that it is considerably (at least four orders of magnitude) lower than the three species for which there were toxicity data.

Due to the limited toxicity data, the Canadians used an 'Effects/No Effects Data Distribution weight of evidence (WoE) approach'. However, in conducting the SSD, the Canadians use a different set of data reduction rules to that of the 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 SQGs for the selected hydrocarbons do not necessarily 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. For example, in deriving the SQG for direct soil contact to benzene, four data values were used for both the Northern wheatgrass and alfalfa, while only a single value was used for both the collembolan and earthworm (Environment Canada, 2005). This means that the concentration that corresponds to a percentile (e.g., the 25th or 50th) should theoretically protect 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 SQG – rather the species that have the most data have most impact on the resulting SQG. This biases the analysis and the result. As all the data that the Canadians use are provided (Environment Canada, 1999; 2005a; 2005b), it would be possible to recalculate the Canadian SQGs using methods more consistent with the Australian EIL derivation methodology (Heemsbergen et al., 2009). These recalculations have been done and are presented in Section 5 of this report.

Both the Australian and New Zealand Guidelines for Fresh and Marine Water Quality (ANZECC and ARMCANZ, 2000) and the Australian EIL derivation methodology (Heemsbergen et al., 2009) specifically rejected using the SSD approach when the minimum data requirements were not met. In such circumstances both these frameworks use an assessment factor (AF) method[1] to derive the limits. The rationale for not using a SSD method to derive SQGs when the minimum data requirements are not met is provided in the following material. For statistical methods such as the SSD, the more data that are used the more powerful and reliable are the results of the analysis. The Danish EPA (Pedersen et al., 1994) and the OECD (1995) found that environmental quality guidelines (EQGs) derived using the SSD approach with data for less than 5 species were highly dependent on the spread of the data. While for EQGs derived using data for five or more species, this effect was markedly reduced. These findings were widely adopted as the minimum data requirement to use SSD methods in deriving EQGs (e.g. OECD 1995; Van de Plassche et al., 1994; ANZECC and ARMCANZ 2000; Crommentuijn et al., 2000).

Since 2000, a number of publications have shown the importance of using even larger datasets. For example, Newman et al. (2000) used non-parametric methods to estimate that the optimal number of species needed to minimise variation in EQG variation due to the random replacement of values ranged from 15 to 55 (with a median of 30). Wheeler et al. (2002) suggested that a minimum of 10 to 15 species were needed. Reflecting these findings, the EU has recommended (ECB 2003; ECHA 2008) that the minimum data requirement to use a SSD for aquatic ecosystems is toxicity data for ten species that belong to eight taxonomic groups. Therefore, the Canadians, by using a SSD method when there were only data for 4 species, derived unreliable SQGs. To overcome this, they modified the data reduction rules (to increase the number of data used in the SSD calculations) and divided the value generated by the SSD by an uncertainty factor.

The Canadian SQGs for the selected hydrocarbons 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 Canadian SQGs for the selected hydrocarbons are derived for a coarse and fine texture soil where appropriate data permit. This is in contrast to the 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 broadly consistent with the Australian EIL derivation methodology (Heemsbergen et al., 2009).

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[1] AF methods collate all the available data, then select the single most sensitive toxicity value and divide that by an AF, the magnitude of which depends on the number of data, the range of species and taxonomic groups for which there are data and the duration of the exposure. The more environmentally relevant the data the lower the AF is and *vice versa*.

The Canadian SQGs aim 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 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 Canadians derived SQG values based on all the individual exposure pathways and receptors that were identified as important for each land use. The lowest SQG 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 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 SQGs is microbiologically mediated nutrient cycling. However, no data were available and so this receptor was not included. In the 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 SQGs do not account for ageing and leaching in their derivation, unlike the Australian EILs. Their SQG values are essentially for fresh contamination. In contrast, the Australian EILs (Warne et al., 2009) have values for both fresh and aged contaminants. Therefore, as long as it is made perfectly clear that any limits for the selected hydrocarbons adopted from Canadian SQGs are for fresh contamination, they could be incorporated into the revised Australian NEPM.

4. Reliability of the Canadian Soil Quality Guidelines for the selected hydrocarbons

As two distinct methods were used to derive the SQGs for the selected hydrocarbons, the reliability of the benzene and TEX contaminants will be discussed separately to that of benzo(a)pyrene.

4.1 Benzene and the TEX contaminants

Each of these contaminants has toxicity data for 4 species that belong to three taxonomic groups (plants, earthworms and collembola). None of these contaminants have normalisation relationships[2] available. Therefore based on the method for assessing the reliability of toxicity data in the Australian EIL derivation methodology (Heemsbergen et al., 2009), these Canadian SQGs are all of low reliability. The limits calculated in Section 5 should also be classed as low reliability.

4.2 Benzo(a)pyrene

There were only benzo(a)pyrene direct soil contact toxicity data of suitable quality for one invertebrate and two plant species (Environment Canada, 1999). The Canadian SQG is based on toxicity data for a single invertebrate species (Environment Canada, 1999). Irrespective of whether the above toxicity data are considered combined or separately the Canadian SQG for benzo(a)pyrene would be classified as low reliability. The limits calculated in Section 5 for benzo(a)pyrene should also be classed as being low reliability.

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[2] Normalisation relationships are empirical relationships which model the toxicity of contaminants using soil physicochemical properties (e.g. soil pH, organic carbon content, cation exchange capacity). Examples of normalisation relationships can be found in Warne et al., 2008.

5. Options for recalculating the Canadian direct soil contact Soil Quality Guidelines to be more consistent with the Australian derivation method

The options available for recalculating the Canadian SQGs fall into two categories: the options available for benzene and the TEX compounds and the options available for benzo(a)pyrene. These are discussed separately below.

5.1 Options for Benzene and the TEX compounds

A literature search was conducted using ISI Web of Knowledge for any terrestrial ecotoxicology data for benzene and the TEX compounds that had been published since 2002. Unfortunately, while a few could be found, copies of the articles could not be obtained within the very tight timeframe for this project. Therefore, the limited amounts of data available for each contaminant could not be increased. Given the limited data there are three methods available to recalculate the SQGs for these compounds:

1. conform to the Australian EIL derivation methodology and therefore use an Assessment Factor method to derive the EILs:

2. use the Canadian data reduction rules and then the resulting data in the BurrliOZ SSD method (Campbell et al., 2000) but calculate the PC99, PC80 and PC60 values[3]; and

3. use the Canadian data reduction rules and then the resulting data in the BurrliOZ SSD method (Campbelll et al., 2000), calculate the PC99, PC80 and PC60 values[3] and divide these PC values by the Canadian uncertainty factors.

The values generated using these three methods are presented in Table 1.

Theoretically the PC99, PC80 and PC60 values presented in Table 1 should protect 99, 80 and 60% of terrestrial species from experiencing chronic toxic effects of larger than 25% magnitude caused by direct soil exposure. As the number of species for which there are data decreases, the uncertainty that a limit will provide the desired level of protection increases. Given that for each of the four contaminants there are only toxicity data for four species, any proposed EILs should protect at least 99, 80 or 60% of the species for which there are data. An assessment of how the limits derived by each of the three methods (Table 1) meet the above criteria is provided below.

In method 1 the lowest toxicity value in each dataset was divided by an assessment factor of 50. Therefore this method protects 100% of the species for which there are toxicity data. In fact, the limits could be 50 times larger before any toxic effects would occur based on the available toxicity data. This is a substantial safety margin.

For methods 2 and 3 one set of the proposed limits (the PC80 values) were compared to the available toxicity data and a species was considered to be protected if the limit was lower than any of the toxicity values for that species. The results of this comparison for the PC80 values are presented in Table 2. It is clear that method 2 generates limits that regularly only protect 50% of species whereas method 3 generates limits that would always protect 75 to 100% of species.

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[3] The PC99 is the level of protection provided by the Australian method to areas of ecological significance. PC80 is the level of protection provided by the Australian method to urban residential and public open space land use while the PC60 is the level of protection provided by the Australian method to commercial and industrial land uses.

Table 1. The limits generated by three different methods (see Section 5.1) of recalculating the Canadian soil quality guidelines for benzene, toluene, ethylbenzene and xylenes. Limits were calculated for both coarse and fine soils. In addition, the lowest toxicity value in the dataset used to derive each limit is presented.

Chemical	Soil type	Lowest toxicity value (mg compound/ kg dry soil)	Limits calculated by various methods						
			Method 1	Method 2			Method 3		
				PC99	PC80	PC60	PC99	PC80	PC60
Benzene[4]	Coarse	63	1.2	24	150	230	8	50	75
	Fine	97	1.9	34	190	290	11	65	95
Ethylbenzene	Coarse	3	0.0	3.1	140	335	1.5	70	165
	Fine	112	2.2	84	255	370	42	125	185
Toluene	Coarse	68	1.3	21	170	275	10.6	85	135
	Fine	112	2.2	130	210	275	65	105	135
Xylenes	Coarse	78	1.5	20	210	365	10	105	180
	Fine	78	1.5	3.3	90	190	1.6	45	95

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[4] There appears to be an error in the Canadian documentation for the benzene SQG. Figure 1 of Environment Canada (2005) shows the lowest toxicity value in coarse soil to be approximately 30 mg/kg. But when Appendix IV is examined there is no invertebrate LOEC or LC25 value less than 63 mg/kg.

Table 2. The percentage of species for which toxicity exists that would be protected by the limits derived by methods 2 and 3 (see Section 5.1)

Chemical	Percent of species protected	
	Coarse soil	Fine soil
Method 2		
Benzene	75	50
Ethylbenzene	50	75
Toluene	75[1]	75[1]
Xylenes	50	50
Method 3		
Benzene	100[1]	100
Ethylbenzene	100	75
Toluene	100	100
Xylenes	75	75

[1] there was only a small difference between the limit and the lowest toxicity value therefore the percentage of protected species was nearly another 25% lower.

Thus method 1 will provide the greatest level of protection (100% of species for which toxicity data are available would be protected), followed in order of decreasing levels of protection being provided by method 3 (where either 100 or 75% of species would be protected) and method 2 (where 75 or 50% of species would be protected). It would appear that both methods 1 and 3 provide adequate protection. Which of these two methods should be adopted depends on the relative importance of the following factors:

(a) conforming to the Australian methodology for deriving EILs (Heemsbergen et al., 2009)

(b) how big a margin of safety is desired between the limit and toxicity data given the limited amounts of toxicity data

(c) how important it is to have EILs for the various land-uses.

Irrespective of which set of limits is adopted into the NEPM they would all be low reliability EILs. The limits generated by method 3 provide an adequate level of protection and they derived limits for different land-uses. In comparison the limits generated by method 1 provide a high level of protection but only a single generic value is derived (i.e., a single limit applies to all land-uses). Considering the above, it is recommended that the limits derived by method 3 be adopted as low reliability EILs.

5.2   Options for benzo(a)pyrene

Benzo(a)pyrene would be classified under the Australian EIL derivation methodology (Heemsbergen et al., 2009) as a biomagnifier as it has a log K_{ow} value of greater than four. Therefore there are two methods available to derive EILs for benzo(a)pyrene. The preferred method is to use the BurrliOZ SSD method (Campbell et al., 2000) and for each land-use type increase the level of protection by a further 5% of species (Heemsbergen et al., 2009) except for the national parks and areas of high conservation value. Thus for example, the default level of protection for an urban residential site would be 85% rather than 80% for non-

biomagnifying contaminants. The alternate method is to use an Assessment Factor (AF) method and divide the lowest toxicity value by an appropriate AF (Heemsbergen et al., 2009).

There are only environmentally relevant toxicity data for three species (an earthworm and two plants) and essentially all the toxicity data are NOEC values with only one LOEC. A literature search was conducted using ISI Web of Knowledge for any terrestrial ecotoxicology data for benzo(a)pyrene published since 2000. Unfortunately, none could be located. Therefore the SSD method cannot be used to derive an EIL. In following the Australian EIL methodology, the AF method should therefore be used and given the available toxicity data the appropriate AF is 50. The lowest toxicity value for benzo(a)pyrene was 4400 mg/kg (Environment Canada, 1999). Therefore the EIL would be 88 mg benzo(a)pyrene/kg dry soil. However, it should be noted that the limit of 88 mg benzo(a)pyrene/kg dry soil does not account for the biomagnification properties of benzo(a)pyrene[5].

The other option is to adopt the Canadian SQG values for benzo(a)pyrene of 0.7 mg benzo(a)pyrene/kg dry soil for urban residential and public open space land uses and 1.4 mg benzo(a)pyrene /kg dry soil for commercial and industrial land uses. While this SQG accounts for biomagnification, it is derived from a single toxicity value for toxicity from contaminated food and therefore the confidence associated with this SQG is very low.

Despite there being a marked difference in the magnitude of the AF derived and Canadian derived limits (i.e. 88 vs 0.7 and 1.4 mg benzo(a)pyrene/kg dry soil) both sets of limits protect all the species for which there were toxicity data. As the method used by Environment Canada to derive a SQG for benzo(a)pyrene accounts for biomagnification, while the Australian method does not, it is recommended that the Canadian SQGs be adopted. Irrespective of whether the AF based or Canadian SQGs are adopted as the EILs they should be classed as low reliability EILs.

6.   Recommendations

1. That the Canadian direct soil contact SQG values for benzene, ethylbenzene, toluene and xylenes not be adopted but rather values derived using the Canadian data reduction methods, the Australian SSD method and the Australian levels of protection be adopted. The recommended EILs[6] are presented in Table 3. They should be classed as low reliability EILs.

2. That the Canadian SQG values for benzo(a)pyrene value of 0.7 mg benzo(a)pyrene/kg dry soil for the direct soil contact exposure pathway be adopted as the EIL[5] for areas of ecological significance, urban residential and public open space land uses. The limit of 1.4 mg benzo(a)pyrene/kg dry soil is recommended as the EIL for commercial industrial land use (Table 3). It is recommended that both be considered low reliability EILs.

3. The text associated with the recommended EILs should clearly state that the EILs were not derived using the Australian EIL derivation methodology (Heemsbergen et al., 2009) and a brief explanation of their derivation should be provided.

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[5] The AF value of 50 accounts for the limited amount of toxicity data and a laboratory to field extrapolation

(Heemsbergen et al., 2009).

Table 3. Recommended total soil concentrations for selected hydrocarbons to be adopted as low reliability ecological investigation levels (EILs) for various land uses.

Chemical	Soil type	Recommended low reliability EILs (mg/kg dry soil) for various land uses		
		Areas of ecological significance	Urban residential and public open space	Commercial and industrial
Benzene	Coarse	8	50	75
	Fine	11	65	95
Benzo(a)pyrene	Coarse	0.7	0.7	1.4
	Fine	0.7	0.7	1.4
Ethylbenzene	Coarse	1.5	70	165
	Fine	42	125	185
Toluene	Coarse	10.6	85	135
	Fine	65	105	135
Xylenes	Coarse	10	105	180
	Fine	1.6	45	95

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