

# Investigation into Cement Stabilisation of Settled Sludge from Port Slipway Runoff

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Prepared for  
Unimar Offshore Support Services Ltd  
(Envirolink Project 881-NLCC46)

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# 1. INTRODUCTION

In the last few years, Unimar Offshore Services Ltd (Unimar) has operated a system to separate particulate matter from the runoff from their Nelson slipway facility. The system comprises a series of three settling tanks through which the runoff wastewater is passed and particulates accumulate in the bases of the tanks as a sludge for eventual controlled disposal. This intercepted material contains a significant proportion of spent anti-fouling coatings from the grit-blasting of vessel hulls and is consequently very high in metal contaminants and organotins. In addition to the intercepted sludge, build up of sediments around slipway rails has also been found to be high in contaminants associated with anti-fouling paints.

## 1.1. Background

Testing carried out on the sludge material in 2009 showed that it did not meet the acceptance criteria of local managed landfill sites in Nelson. For York Valley Landfill, acceptance of potentially contaminated material is decided on the basis of two tiers of analysis. The screening level of testing is a measurement of total concentration for a given contaminant. For metals, this is based on digestion of the material. Material which fails the screening test may still be accepted if it passes the second tier; the USEPA's Toxicity Characteristic Leaching Procedure (TCLP), which uses exposure to an acetic acid-based extractant over an 18 hour time period to determine the quantity of contaminant released to solution. The TCLP test gives an indication of the mobility of contaminants. Where a contaminant is chemically bound in a stable mineral or exists in forms of low solubility, there is less concern that it will leach into groundwater or otherwise escape from the disposal site.

In February 2009, two samples of the sludge material were analysed for a variety of common port-related metals (copper, chromium, lead, zinc, mercury, tin and tributyltin) as well as semi-volatile organic compounds [e.g. pesticides, polycyclic aromatic hydrocarbons (PAHs)]. Results of these analyses are tabulated in Appendix 1 and a summary of metal and PAH analytes is listed in Table 1 along with the corresponding York Valley landfill acceptance criteria.

For the screening tests, acceptance limits were exceeded by copper, lead, mercury (one sample only), zinc and total PAHs. Although there is no listed screening criterion specifically for tributyltin (Tbt), the concentrations in the sludge (9.7 mg/kg and 20 mg/kg) were very high relative to national environmental guidelines for marine sediments [ISQG-Low = 0.005 mg/kg, ISQG-High = 0.070mg/kg (ANZECC 2000)]<sup>1</sup>.

TCLP testing of the two samples resulted in exceedences for copper and zinc only, indicating that the material will meet acceptance criteria for lead, mercury and PAHs (Table 1). No TCLP test was conducted for organotin compounds in these samples.

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<sup>1</sup> Interim Sediment Quality Guidelines (ISQG) and have two threshold levels under which biological effects are predicted. The lower threshold (ISQG-Low) indicates a **possible** biological effect, while the upper threshold (ISQG-High) indicates a **probable** biological effect.

**Table 1.** Results of analytical testing of Unimar settling tank sludge for selected contaminants; February 2009. Shaded cells (bold font) exceed corresponding York Valley landfill acceptance criteria. --- (Not Tested) ; <mdl (less than method detection limit); n/a (Not Applicable, No limit).

	Sample1		Sample2		York Valley Criteria	
	Total	TCLP	Total	TCLP	Screen	TCLP
METALS	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/L
Chromium	62	<0.011	72	<0.011	100	5
Copper	<b>3500</b>	<b>23</b>	<b>3200</b>	<b>15</b>	200	10
Lead	<b>400</b>	1.3	<b>560</b>	1.5	100	5
Mercury	<b>8.7</b>	---	3.7	---	4	0.2
Tin	---	<0.011	---	<0.011	400	20
Zinc	<b>3200</b>	<b>57</b>	<b>3000</b>	<b>55</b>	200	10
Tributyltin	9.7	---	20	---	n/a	n/a
PAHs - excluding naphthalene	<b>66.8</b>	<mdl	<b>85.8</b>	<mdl	1	0.05

As a result of acceptance criteria not being met for copper and zinc and the high Tbt concentrations in the material, a trial was set up to test the efficacy of using cement additions to the sludge material to stabilise the contaminants.

Despite there being no specific limits relating to organotin compounds, York Valley's acceptance criteria state that:

*“Where TCLP limits do not exist for a substance for which a disposal request is made, the TCLP limit shall be set at 100 times the drinking water standard for a substance.”*

In the case of tributyltin oxide, the drinking water provisional maximum acceptable value (PMAV) is 0.002 mg/L (MoH 2005), which puts the York Valley TCLP acceptance value for Tbt at 0.2 mg/L.

## 2. METHODS

### 2.1. Sludge preparation and casting

Samples of the sludge from the three settling tanks were air-dried for two weeks then broken up to a powder consistency with a mortar and pestle. The three samples were blended in proportions 75:20:5 by weight (Tanks 1:2:3, respectively, approximately relative to estimated bulk volumes). The blended material was mixed with ordinary Portland cement at 15%, 25%, 40% and 50% fractions by weight and water added incrementally until a consistency suitable for casting was attained. Relative proportions are listed in Table 2. The mixture was then split to be cast into single “block” and “biscuit” castings.

**Table 2.** Relative proportions for casting mixtures at the four cement addition rates.

Cement addition rate	Casting mixtures				Block castings	
	Dried sludge (g)	Cement (g)	Water (mL)	Water (%)	Casting height (mm)	Cured weight (g)
15%	300	53	200	57%	60	221
25%	300	100	210	53%	66	289
40%	300	200	255	51%	70	311
50%	300	300	270	45%	72	320

To fully complete the chemical reaction between cement and water, a water-cement ratio of approximately 1:4 (25%) is required. But where cement is mixed with other constituents, some of the water is taken up by the added material and is not available to participate in the hydration reaction. Hence a mix formed with 25% water is mostly too dry and does not flow well enough to be cast; so more water must be used than is technically necessary to react with the cement. In the case of concrete, more typical water-cement ratios of 35% to 40% are used, along with a plasticizer. For the relatively fine dried sludge material, it was found that water additions greater than 40% were required to attain the paste-like consistency necessary for casting, the fraction varying depending on the proportions used (Table 3).

Biscuit castings were made by spreading the mixture over the base of a small tray to a depth of approximately 1 cm thickness. The block monoliths were cast in 62 mm ID PVC tubing. Since the mixture was approximately halved, the castings at higher addition rates were larger (Table 3). This was allowed since the incorporation of approximately the same amount of dried sludge in each case would ensure better comparability of the results from the subsequent extractions<sup>2</sup>.

<sup>2</sup> Note that this was not the case with the standard TCLP extractions carried out on the crushed biscuit castings since strict standardisation of the procedure uses a set 100 g of material (see Section 2.2).

Both biscuit and block castings were left to cure for seven days before processing for analysis. The biscuit casts were roughly broken up with a mortar and pestle only to such point that all pieces would fit through a 1 cm aperture sieve.

## 2.2. TCLP method

The TCLP is used by the US Environmental Protection Agency as the basis for the promulgation of best demonstrated available technologies treatment standards under the land disposal restrictions program (USEPA 1989). The method requires crushing of the material to be tested to pass through a 9.5 mm screen. Two choices of buffered acidic leaching solutions (extractant) are utilised under the TCLP, depending on the alkalinity and the buffering capacity of the material. Both are acetate buffered; Solution 1 to pH = 4.93, Solution 2 to pH = 2.88. The leaching solution is added to a zero headspace extractor (ZHE) at a liquid solid ratio of 20:1 and the sample is agitated with a rotary tumbler at 30 rpm for 18 hours. The leaching solution is then filtered through a 0.6-0.8 µm borosilicate glass-fibre filter under 50 psi pressure and analysed. The standard TCLP was carried out by Hill Laboratories in Hamilton. The dried sludge (no cement addition) underwent extraction using Solution 2 (buffered pH = 4.93) and for the crushed castings, Solution 1 (buffered pH = 2.88) was required to balance the basic nature of the cement additions. Hill Laboratories also conducted the analysis of all extractant solutions for copper and organotin compounds as specified in Table 3.

**Table 3.** Analytical methods for determination of contaminant concentrations in TCLP extractant.

Test	Method Description
Total Copper (screen)	Nitric acid digestion APHA 3030 E 21 <sup>st</sup> ed. 2005. ICP-MS, screen level. APHA 3125 B 21 <sup>st</sup> ed. 2005.
Organotin compounds (Trace)	Solvent extraction, ethylation, SPE cleanup, GC-MS SIM analysis

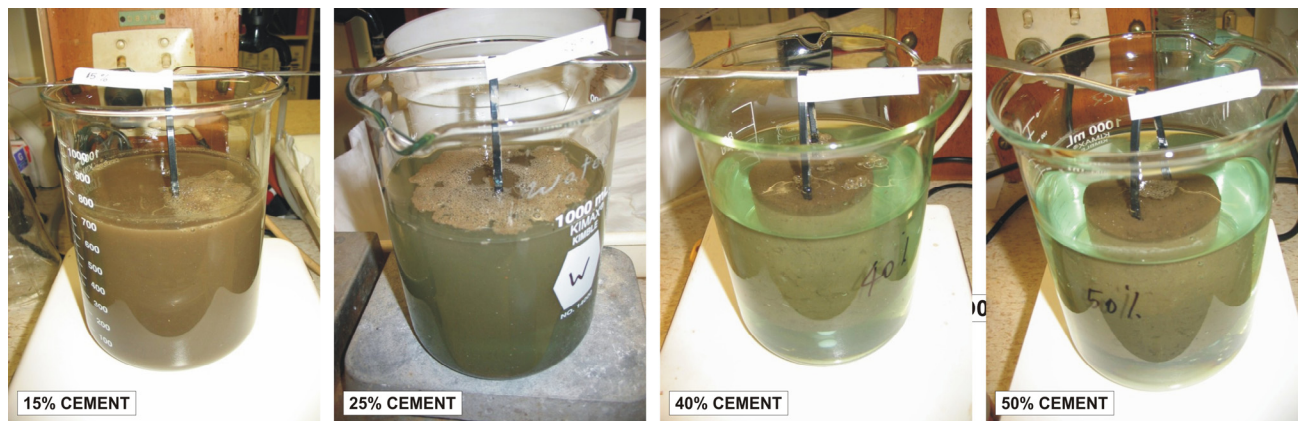
## 2.3. Modified TCLP for cast block monoliths

Once cured, the cast block monoliths were suspended in a 1 L beaker, fully immersed in 600 mL of TCLP extractant Solution 1 (buffered pH = 2.88). The beaker was stirred continuously for 18 hours. At the end of this contact period, the solution was filtered through a 0.6-0.8 mm borosilicate glass-fibre filter and the filtrate sent to Hill Laboratories for the analyses listed in Table 3.

### 3. RESULTS AND DISCUSSION

#### 3.1. Experimental observations

Photographs of the block monoliths after 18 hours exposure to the stirred TCLP extractant solution are shown in Figure 1. The turbidity of the treatments at lower cement addition rates is an indicator of the lack of structural integrity of the castings. Once filtered (0.6-0.8  $\mu\text{m}$ ), the leachates exhibited a green hue of decreasing intensity at higher cement addition rates (Figure 2). This may have been due to the presence of dissolved copper.



**Figure 1.** Beakers containing the suspended cast block monoliths and 600 mL of TCLP extractant solution after 18 hours continuous stirring.



**Figure 2.** Filtered leachate from the block castings, showing colour gradation. Increasing cement addition from left to right (15%, 25%, 40%, 50%).

### 3.2. Results of leachate analysis

A summary of the analysis results for the TCLP tests (on untreated dried sludge and crushed castings) and the block monolith leachates are provided in Table 4 and 5, respectively. Concentrations of copper and tributyltin in the leachates from each test series are plotted in Figure 3. In both tests, the analytical result represents the amount of the contaminant leached out of the cast material by a standard extractant<sup>3</sup> in 18 hours with agitation.

**Table 4.** Analysis results for standard TCLP extractions on untreated dried sludge (0% cement) and crushed and graded castings at four cement additions. Shaded cells represent values exceeding York Valley acceptance criteria.

Analyte	Cement addition (% by dry weight)					York Valley TCLP
	0	15	25	40	50	
Copper (mg/L)	360	40	3.6	3.8	3.3	10
Dbt (µg/L)	0.78	0.3	53	93	79	
Tbt (µg/L)	5	2.3	71	570	590	200
pH of leachate	6.1	6.6	10.1	11.8	12.0	

**Table 5.** Analysis results for extractions on cast blocks of dried sludge at four cement addition rates. Shaded cells represent values exceeding York Valley acceptance criteria.

Analyte	Cement addition (% by dry weight)				York Valley TCLP
	15	25	40	50	
Copper (mg/L)	450	250	120	86	10
Dbt (µg/L)	0.142	0.107	0.079	0.08	
Tbt (µg/L)	3	3.5	1.74	1.81	200
pH of leachate	5.2	5.2	6.2	6.2	

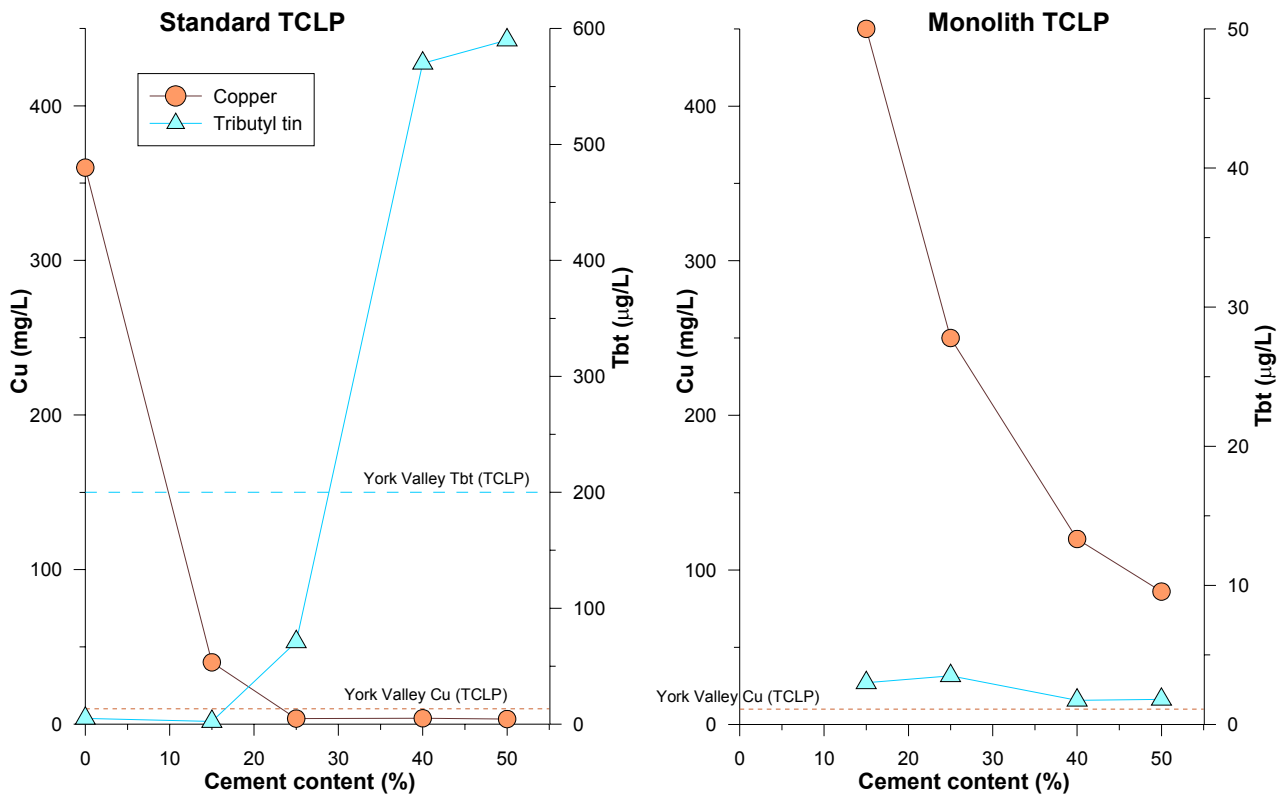
Both graphs in Figure 3 show the York Valley TCLP acceptance limit for copper (10 mg/L). However, due to scaling differences, the Tbt acceptance limit (200 µg/L) is shown only for the standard TCLP test (left hand graph). This is because very little Tbt was leached from the block monoliths at all cement addition rates (right and graph). Both graphs show consistent trends with changing cement addition but the trends in contaminant release from the solid material appear to be opposite for copper and tributyltin.

In consideration of the post-extraction leachate pH listed in Table 4 and 5, it is suspected that pH is the key factor in the very different results from the two methods. It is likely that copper becomes more mobile/leachable under acidic conditions (sub-neutral pH) and that Tbt leaches under basic conditions.

<sup>3</sup> The exception was the untreated dried sludge (0% cement addition) for which TCLP Solution 2 (pH = 4.93) was used as predicated by the TCLP standard protocol.



The narrow cross-over region within both acceptance criteria means that the stability of the material may depend on very stable pH in the receiving environment (something almost impossible to guarantee in a landfill situation).



**Figure 3.** Concentrations of dissolved copper and tributyltin in leachates from the standard TCLP test (left) and the block monolith tests (right) at different cement addition rates. York Valley landfill acceptance criteria are plotted for comparison. Note differences in scales.

The contrasting behaviour of the two contaminants when the sludge material is cast with cement is cause for some concern with respect to their potential mobility subsequent to disposal. Even though there is a point (at 25% cement addition, standard TCLP) where the leachate is within the York Valley acceptance criteria for both Cu and Tbt, we can have only very limited confidence in the reproducibility of this result. The results of the block monolith extraction underscore this concern; since at 25% cement, they show a copper concentration at 25 times the acceptance limit (Table 45).

For the standard TCLP tests, the end-point pH for the extractant was 10 and greater for all cement additions greater than 20% (Table 4). The high pH arises from the action of cement itself, which is very basic. Bone *et al.* (2004) report that problems with the retention of organic compounds may be encountered with cement stabilisation of sediments, noting that release to solution may occur if the organic contaminant is soluble in water and/or has a low pKa, which suggests that transformation to a water-soluble species would occur at the higher pH of the cementitious system. Tributyltin has a pKa of 6.25 (Vreysen *et al.* 2008), which is

significantly lower than the final leachate pH of the standard TCLP tests at 40% and 50% cement addition rates where the Tbt acceptance criterion was exceeded (Table 4).

Leachates from the block monolith tests all had pH end-points in the sub-neutral range (Table 5) and this is consistent with pH being the main influence on contaminant release to solution. The reason for the difference in end-point pH of the two leaching test series may be explained by differences in the solid:extractant ratio and especially the potentially large difference in solid surface area exposed to the extractant solution in each case.

Bone *et al.* (2004) further noted that, because organic compounds do not generally form chemical interactions to the same extent as inorganics, stabilisation of many organic compounds tends to be in the form of physical rather than chemical immobilisation. Compounds that are retained purely by physical mechanisms may leach from the waste form more readily, since their entrainment depends on the physical characteristics of the solid.

The problem of differing chemical properties for these contaminants is not limited to waste stabilisation treatments. In a study of the efficacy of adsorption processes applied to contaminant removal from shipyard wastewaters, Vreyson *et al.* (2008) reported their screening experiments as showing that there was no single adsorbent with a significant ability to remove both elemental metals (Cu, Zn) and organotin compounds.

It is not clear why the February 2009 TCLP performed on the sludge (Table 1) resulted in significantly less copper in solution than for the “0% cement” control TCLP carried out for the current study. Although at 23 mg/L and 15 mg/L, the earlier test still exceeded the York Valley criterion; it was significantly less than the 2010 result (360 mg/L, Table 4). In both cases, the TCLP Solution 2 (pH = 4.93) was used, although the samples were collected some 10 months apart and sample preparation may have differed.

Strength testing of the castings was not carried out but general observations indicated very poor strength at low cement additions (15%, 25%) with poor resistance to impact (relative to concrete) even at 50% addition. Bone *et al.* (2004) noted that many organic compounds interfere with the hydration of cement or lime, resulting in retardation of set and a reduction in strength. The slipway sludge has significant quantities of resinous particulate matter derived from paints. Oils also appear to be present in the sludge.

It is possible that a destructive treatment of the waste, such as controlled incineration, would be successful in completely degrading the organotin species, following which the metal contaminants could be successfully immobilised using cement stabilisation. A secondary advantage to this route is likely to be improved strength of the stabilised end product arising from the combustion of organic materials associated with paint materials.

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## 4. REFERENCES

- ANZECC 2000. Australian and New Zealand guidelines for fresh and marine water quality 2000 Volume 1. National Water Quality Management Strategy Paper No. 4. Australian and New Zealand Environment and Conservation Council and Agriculture and Resource Management Council of Australia and New Zealand, Canberra.
- Bone BD, Barnard LH, Boardman DI, Carey PJ, Hills CD, Jones HM, MacLeod CL, Tyrer M. 2004. Review of scientific literature on the use of stabilisation/solidification for the treatment of contaminated soil, solid waste and sludges. Environment Agency (UK).
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- Vreysen S, Maes A, Wullaert H 2008. Removal of organotin compounds, Cu and Zn from shipyard wastewaters by adsorption – flocculation: A technical and economical analysis. Marine Pollution Bulletin 56 (2008) 106–115.

## 5. APPENDICES

**Appendix 1.** Results of analytical testing of Unimar settling tank sludge; February 2009. Shaded cells (bold font) exceed corresponding York Valley landfill acceptance criteria. --- (Not Tested); <mdl (less than method detection limit) ; n/a (Not Applicable, No limit).

	Sample1		Sample2		York Valley Criteria	
	Total mg/kg	TCLP mg/L	Total mg/kg	TCLP mg/L	Screen mg/kg	TCLP mg/L
<b>METALS</b>						
Chromium	62	< 0.011	72	< 0.011	100	5
Copper	<b>3500</b>	<b>23</b>	<b>3200</b>	<b>15</b>	200	10
Lead	<b>400</b>	1.3	<b>560</b>	1.5	100	5
Mercury	<b>8.7</b>	---	3.7	---	4	0.2
Tin	---	< 0.011	---	< 0.011	400	20
Tributyltin	9.7	---	20	---	n/a	n/a
Zinc	<b>3200</b>	<b>57</b>	<b>3000</b>	<b>55</b>	200	10
<b>SEMI-VOLATILE ORGANIC HYDROCARBONS</b>						
<i>Acid &amp; Base Fractions</i>						
o-Cresol	<mdl	<mdl	<mdl	<mdl	4000	200
m-Cresol	<mdl	<mdl	<mdl	<mdl	4000	200
p-Cresol	<mdl	<mdl	<mdl	<mdl	4000	200
Cresol Total	<mdl	<mdl	<mdl	<mdl	4000	200
Pentachlorophenol	<mdl	<mdl	<mdl	<mdl	20	1
2,4,6-Trichlorophenol	<mdl	<mdl	<mdl	<mdl	40	2
1,4-Dichlorobenzene	<mdl	<mdl	<mdl	<mdl	150	7.5
2,4-Dinitrotoluene	<mdl	<mdl	<mdl	<mdl	2.6	0.13
Hexachlorobenzene	<mdl	<mdl	<mdl	<mdl	2.6	0.13
Hexachlorobutadiene	<mdl	<mdl	<mdl	<mdl	10	0.5
Hexachloroethane	<mdl	<mdl	<mdl	<mdl	60	3
Nitrobenzene	<mdl	<mdl	<mdl	<mdl	40	2
Pyrdine	---	---	---	---	100	5
<i>Pesticides</i>						
Chlordane	---	---	---	---	0.6	0.03
Endrin	<mdl	<mdl	<mdl	<mdl	0.4	0.02
Heptachlor	<mdl	<mdl	<mdl	<mdl	0.16	0.008
Lindane	<mdl	<mdl	<mdl	<mdl	8	0.4
Methoxychlor	---	---	---	---	200	10
Toxaphene	---	---	---	---	10	0.5
Organophosphate pesticides	---	---	---	---	2	0.1
<i>Organics</i>						
Formaldehyde (as HCHO)	---	---	---	---	1000	50
Phenols -excluding chlorinated phenols	<mdl	<mdl	1.1	<mdl	100	50
Chlorinated phenols	<mdl	<mdl	<mdl	<mdl	0.4	0.02
Halogenated aliphatic compounds	---	---	---	---	20	1
Monocyclic aromatic hydrocarbons	---	---	---	---	100	5
PAHs - excluding naphthalene	<b>66.8</b>	<mdl	<b>85.8</b>	<mdl	1	0.05
Naphthalene	3.8	0.0084	4.6	0.0048	n/a	n/a