Uranium in Municipal Solid Waste Landfill Leachate

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ABSTRACT: Landfill leachates and leachate sediments were investigated in order to survey the discharge of uranium (U) from municipal solid waste (MSW) landfills and municipal solid waste incinerator (MSWI) bottom ash landfills. Concentrations of U in the leachates were as high as or higher than concentrations of Cd, a metal more often discussed when considering the environmental effects of landfill leachate. However, the U concentrations in leachate were no greater than levels occurring naturally in water. The U concentrations in leachate sediments were also the same as or lower than those reported in lake sediments around the world. Size charge fractionation of U in freshly sampled leachate showed that the metal was present mainly as either non-labile dissolved complexes or free anions, which have intermediate to high mobility and eco-toxicity. This is in contrast to other heavy metals, such as Cd, which are generally particulate bound in leachate. However, based on all the results of the investigations, it was concluded that leaching of U is not of major concern in MSW and MSWI bottom ash landfills.

Key words: Landfill leachate, Heavy metals, Uranium, Sediments, Speciation

INTRODUCTION

One of the main concerns associated with the deposition of waste in sanitary landfills is that of the release of potentially hazardous landfill leachate to the environment. Landfill leachate contains varying amounts of both organic pollutants and toxic metals (Christensen *et al.*, 2001; Kjeldsen *et al.,* 2002; Baig et al., 2007). When assessing the pollution potential of the leachate, the elements commonly analysed are Pb, Cd, Cu, Zn, Cr and Ni (Kjeldsen *et al.,* 2002; Baun and Christensen, 2004; Rieber *et al.,* 2005). Even though these metals are usually considered the most important from an eco-toxicological perspective, other elements, such as Tl, Sb, Be and U, which could also pose a hazard, are often ignored. Therefore, although there is broad knowledge of the concentrations and toxicity of the former elements in landfill leachate (Baun and Christensen, 2004; Kjeldsen *et al*., 2002; Øygard *et al.,* 2004; Øygard *et al.,* 2007), little information is available about the latter elements.

The toxicity of U, calculated on a molar basis, has been found to be approximately equal or slightly lower than that of Cu, depending on the pH of the solution (Franklin *et al*., 2000), and higher or equal to the toxicity of Pb for aquatic organisms (Labrot *et al*., 1999). For naturally occurring U, the toxicity is determined by chemical properties of the metal, rather than its radioactivity. The toxic potential of U in landfill leachate is unknown, as few studies have reported concentrations of U in leachate, and none have investigated its physico-chemical form. The physico-chemical form of an element is a critical factor, influencing its mobility, bioavailability, and toxicity (Øygard *et al*., 2007). This study aims, firstly, to determine total concentrations of U in leachate from MSW related landfills, and, secondly, to determine the physico-chemical forms of any U present. As such, this investigation will show whether the presence of U in the discharge from waste landfills should be an issue of greater concern.

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MATERIALS & METHODS

Fourteen solid waste landfills situated in western Norway (Fig. 1). were studied. All the landfills were in operation at the time of the sampling (Spring 2005). Landfills 1 and 5 received construction waste and municipal solid waste (MSW) incinerator bottom ash, landfill 11 received oil well sludge (after extraction of the oil) in addition to MSW, while the remaining landfills received only MSW. At landfill 3, the leachate was collected in a central collection point in a narrow valley downhill of the landfill. The other landfills had leachate collection systems, with leachate draining through pipes to a collection point, where the volume was continuously measured, and from where the samples were acquired. Not all the landfills had landfill liners. However, sampling of the groundwater at all sites had not detected any leaching from the landfills to the groundwater.

Samples for study by size charge fractionation were taken from the flowing leachate at the point immediately prior to its discharge into the environmental recipient, and fractionated in the field within 5 minutes. These samples were discussed previously by Øygard *et al.* (2007). Samples for total uranium determination were collected from the same locations. Leachate sediments were sampled either from the bottom of sedimentation tanks connected directly to the leachate discharge pipe, or from the bottom of the leachate volume sampling point.

Samples for determination of total U were acid preserved (to 1 % HNO_3) and stored for two weeks prior to analysis. Fractionated samples were also acid preserved to 1 % HNO_3. The sediment samples were dried at 40 ºC, sieved to 2 mm, ground and homogenized in an electrical agate mortar (Retsch Mortar Grinder KM 100), and kept in a desiccator prior to microwave assisted digestion (Anton Paar Multiwave microwave) and analysis.Total concentrations are of limited use when considering the eco-toxicological effects of metals, since they indicate neither the metal mobility nor the availability to aquatic organisms (Campbell, 1995; Batley *et al.*, 2005). Free/labile metals have a more harmful effect on aquatic
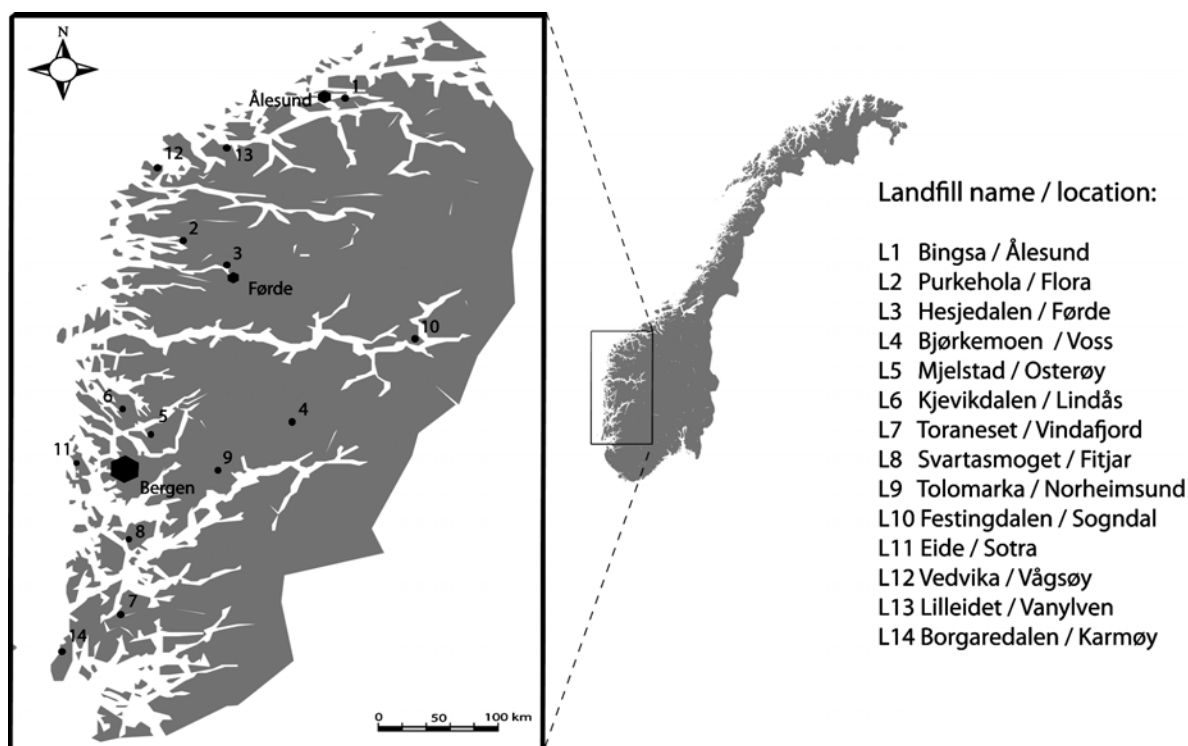

Landfill name / location:

L1 Bingsa / Ålesund
L2 Purkehola / Flora
L3 Hesjedalen / Førde
L4 Bjørkemoen / Voss
L5 Mjelstad / Osterøy
L6 Kjevikdalen / Lindås
L7 Toraneset / Vindafjord
L8 Svartasmoget / Fitjar
L9 Tolomarka / Norheimsund
L10 Festingdalen / Sogndal
L11 Eide / Sotra
L12 Vedvika / Vågsøy
L13 Lilleidet / Vanylven
L14 Borgaredalen / Karmøy

Fig. 1. Geographic location of the landfills where leachate and sediments were sampled

organisms than metals in non-labile colloids (Campbell, 1995; Batley *et al.*, 2004). It is therefore important to determine the physico-chemical form of the elements when assessing metal toxicity in landfill leachate. One method of doing this, used here, is size charge fractionation. This is a two-stage process. Firstly, filtration using a specific pore size (0.45 µm) was used to separate metals into two size classes (referred to as 'particulate' and 'dissolved' fractions). Ion exchange is subsequently used to fractionate the dissolved fraction into dissolved non-labile colloids / free anions and free cations/labile colloids. Data for the size charge fractionation of arsenic, cadmium, copper, chromium, iron, lead, manganese, molybdenum, nickel, and zinc in some of the leachate samples described in this work have been reported by Øygard *et al.*, (2007).High pure nitric acid (Merck suprapur), and deionised water (> 18 MΩ cm^{-1}) were used throughout. Total metal concentrations in the leachate were determined using a Thermo Finnigan Element 2 High Resolution ICP-MS. The certified reference material NRCC SLRS-4 was analysed along with the samples, and gave results within ±10 % for all available certified values. The metals in the leachate sediments were analyzed with a Perkin Elmer Sciex 6000 ICP-MS.

RESULTS & DISCUSSION

Total concentrations of uranium in the sampled leachates are shown in (Table 1). All the heavy metal concentrations are in the lower part of the concentration ranges reported by Christensen *et al.* (2001). All the leachate samples had pH values between 6.5 and 7.5. In many of the samples, the molar U concentrations were considerably higher than those of Cd. In a few samples, the U concentrations came close to those of Pb, but were always considerably lower than the concentrations of the other heavy metals (Cu, Zn, Ni and Cr).

In general, the concentrations of uranium found in natural waters range from 0.1 – 7 µg/L, whilst concentrations in seawater range from 2 – 4 µg/L (Langmuir, 1997). A Japanese study found average background concentrations of 28 ± 33 µg /L in river waters and 24 ± 30 µg /L in lakes (Tsamura and Yamasaki, 1992), whilst another large study found median concentrations of 20 µg /L in Russian lake water and 41 µg /L in Norwegian

lakes (Reimann *et al.*, 1999) Compared to these values, the U concentrations in the leachate samples are quite high, although well within the naturally occurring concentration ranges reported by Langmuir (1997). Background water concentrations depend upon the geology of the rock in contact with the water (Bakaç and Kumru, 2000). With the exception of L4, all the landfills discharged their leachate into the ocean. Since background levels of U in seawater are the same or higher than the concentrations found in the leachates, the environmental strain on the marine recipient due to U can be assumed to be insignificant.

U concentrations in natural waters depend upon the geology of the rock in contact with the water (Bakaç and Kumru, 2000). Some of the landfills were constructed without bottom liners and had an inwards directed groundwater flow, suggesting that U concentrations in the leachate could have been influenced by U from the groundwater. To investigate this, groundwater samples were taken from the vicinity of selected landfills, from sample points known not to be influenced by the landfills themselves or by any other sources of contamination. The concentrations of U are shown in (Table 2).

With the exception of landfill L8, the U concentrations in the leachates were considerably higher than concentrations in the corresponding local groundwater, indicating that the primary source of U in MSW landfill leachate generally is the deposited MSW. Only in landfill L8 could groundwater infiltration be contributing significantly to the U in the leachate.For some of the landfills, samples were taken directly from the flowing leachate, and immediately size charge fractionated in the field. These samples represent the leachate discharged into the environment, and the various U fractions thus represent the actual environmental load on the leachate recipients. The percentages of the total U concentration found in the various leachate fractions are shown in (Fig. 2).

Uranium was found to be present mainly as dissolved free anions or non-labile colloids (on average 81 ± 26 %), with only a small amount as free cations or labile colloids (7 ± 11 %). The proportion of U in the > 0.45 µm fraction was, on

Table 1. Concentration of heavy metals (µg/L) in leachate from thirteen landfills

Landfill	Uranium	Cadmium	Lead	Copper	Zinc	Nickel	Chromium
L1 (n=4)	0.27 ± 0.05 (0.21 – 0.34)	0.13 ± 0.06 (0.09 – 0.21)	2.3 ± 1.6 (1.4 – 4.7)	8.3 ± 2.1 (6.0 – 11)	61 ± 12 (49 – 73)	18 ± 15 (6 – 37)	7.1 ± 2.9 (4.5 – 9.9)
L2 (n=4)	0.49 ± 0.21 (0.18 – 0.61)	0.11 ± 0.04 (0.06 – 0.14)	2.6 ± 1.4 (1.2 – 4.5)	16 ± 6.4 (10 – 22)	88 ± 64 (41 – 180)	30 ± 11 (19 – 40)	41 ± 7.0 (33 – 48)
L3 (n=4)	0.28 ± 0.21 (0.11 – 0.69)	0.24 ± 0.07 (0.18 – 0.32)	11 ± 2.8 (5.6 – 12)	19 ± 3.9 (14 – 23)	380 ± 73 (300 – 450)	14 ± 3.6 (9.3 – 18)	7.1 ± 2.2 (4.1 – 8.9)
L4 (n=4)	0.95 ± 0.40 (0.56 – 1.5)	0.21 ± 0.14 (0.11 – 0.41)	1.7 ± 0.89 (0.99 – 2.9)	2.8 ± 0.99 (1.7 – 3.9)	240 ± 97 (120 – 340)	41 ± 15 (23 – 60)	110 ± 81 (55 – 230)
L5 (n=4)	2.1 ± 1.2 (1.3 – 3.6)	0.20 ± 0.09 (0.09 – 0.29)	2.6 ± 1.1 (1.3 – 3.6)	46 ± 25 (21 – 78)	360 ± 160 (150 – 510)	50 ± 32 (14 – 91)	140 ± 78 (72 – 250)
L6 (n=7)	0.27 ± 0.06 (0.24 – 0.34)	0.05 ± 0.01 (0.04 – 0.06)	1.5 ± 0.41 (0.67 – 1.6)	7.2 ± 2.4 (4.7 – 10)	41 ± 16 (21 – 57)	15 ± 3.4 (14 – 22)	27 ± 6.7 (23 – 37)
L7 (n=4)	3.1 ± 0.73 (2.2 – 4.0)	0.73 ± 0.98 (0.20 – 2.2)	3.2 ± 3.6 (1.2 – 8.5)	52 ± 91 (4.8 – 190)	670 ± 1200 (50 – 2500)	32 ± 38 (11 – 89)	64 ± 44 (35 – 130)
L8 (n=4)	0.54 ± 0.1 (0.44 – 0.64)	0.09 ± 0.15 (0.04 – 0.07)	1.5 ± 0.75 (0.96 – 2.6)	12 ± 7.0 (3.8 – 18)	180 ± 220 (49 – 500)	14 ± 2.7 (11 – 17)	30 ± 5.8 (22 – 35)
L9 (n=7)	0.77 ± 0.35 (0.48 – 1.3)	0.03 ± 0.01 (0.01 – 0.05)	0.87 ± 0.30 (0.34 – 0.97)	4.9 ± 3.2 (1.1 – 7.8)	22 ± 6.8 (12 – 25)	9.2 ± 6.4 (6.2 – 20)	6.7 ± 2.0 (4.3 – 8.5)
L11 (n=4)	0.64 ± 0.24 (0.41 – 0.97)	0.37 ± 0.23 (0.16 – 0.65)	21 ± 9.2 (13 – 34)	150 ± 180 (49 – 420)	1100 ± 1300 (410 – 3100)	77 ± 94 (13 – 210)	320 ± 290 (90 – 690)
L12 (n=2)	0.39 ± 0.13 (0.12 – 0.16)	0.17 ± 0.16 (0.05 – 0.28)	2.1 ± 0.64 (1.7 – 2.6)	9.2 ± 2.0 (7.8 – 11)	1900 ± 860 (1300 – 2500)	20 ± 9.8 (13 – 27)	3.3 ± 0.78 (2.7 – 3.8)
L13 (n=4)	0.27 ± 0.11 (0.15 – 0.37)	0.15 ± 0.05 (0.07 – 0.19)	1.5 ± 0.61 (0.89 – 2.3)	19 ± 7.1 (12 – 29)	70 ± 23 (39 – 91)	13 ± 2.5 (9 – 15)	22 ± 7.6 (11 – 28)
L14 (n=4)	0.37 ± 0.11 (0.21 – 0.48)	0.17 ± 0.05 (0.13 – 0.25)	2.0 ± 0.77 (1.3 – 2.8)	11 ± 4.5 (7.0 – 17)	101 ± 27 (74 – 140)	10 ± 2.9 (6.7 – 13)	61 ± 26 (32 – 89)

Table 2. Concentration of uranium in non-polluted groundwater close to some of the investigated landfills (N=4)

Landfill	Uranium (µg/L)
L6	0.54 ± 0.03
L7	1.1 ± 0.54
L8	3.1 ± 2.1
L9	0.02 ± 0.01
L12	0.01 ± 0.02
L13	0.01 ± 0.01

average, 12 ± 15 %. The U distribution in the leachate from landfill L3 deviates somewhat from the pattern shown by the other landfills. The reason for this is unknown to the authors. Waite and Payne (1993) reported that uranium is present mainly as an anionic hydroxides complex at neutral pH

conditions. Alternatively, when carbonate is present in the solutions, uranium may form carbonate containing anionic complexes (Katsoyiannis, 2007). The uranyl ion and its complexes are considered to be the U species most bioavailabile and toxic to freshwater biota (Markich, 2002; Unsworth *et al.*, 2005). Complexes with humic acids are readily formed, however (Markich, 2002; Unsworth *et al.*, 2005). Unsworth *et al.*, (2005) found that naturally occurring U in river water was largely (80 % of total U), bound to organic matter, and by computer simulation (WHAM) also predicted U to be bound to organic matter. The formation of organic complexes was proportional to the humic acid concentration in the water samples. It is thus likely that the dissolved non-labile U complexes found

Uranium

Particulate/ colloidal bound metals . 0.45 µm

Free anins or non-labile metal complexes < 0.45 µm

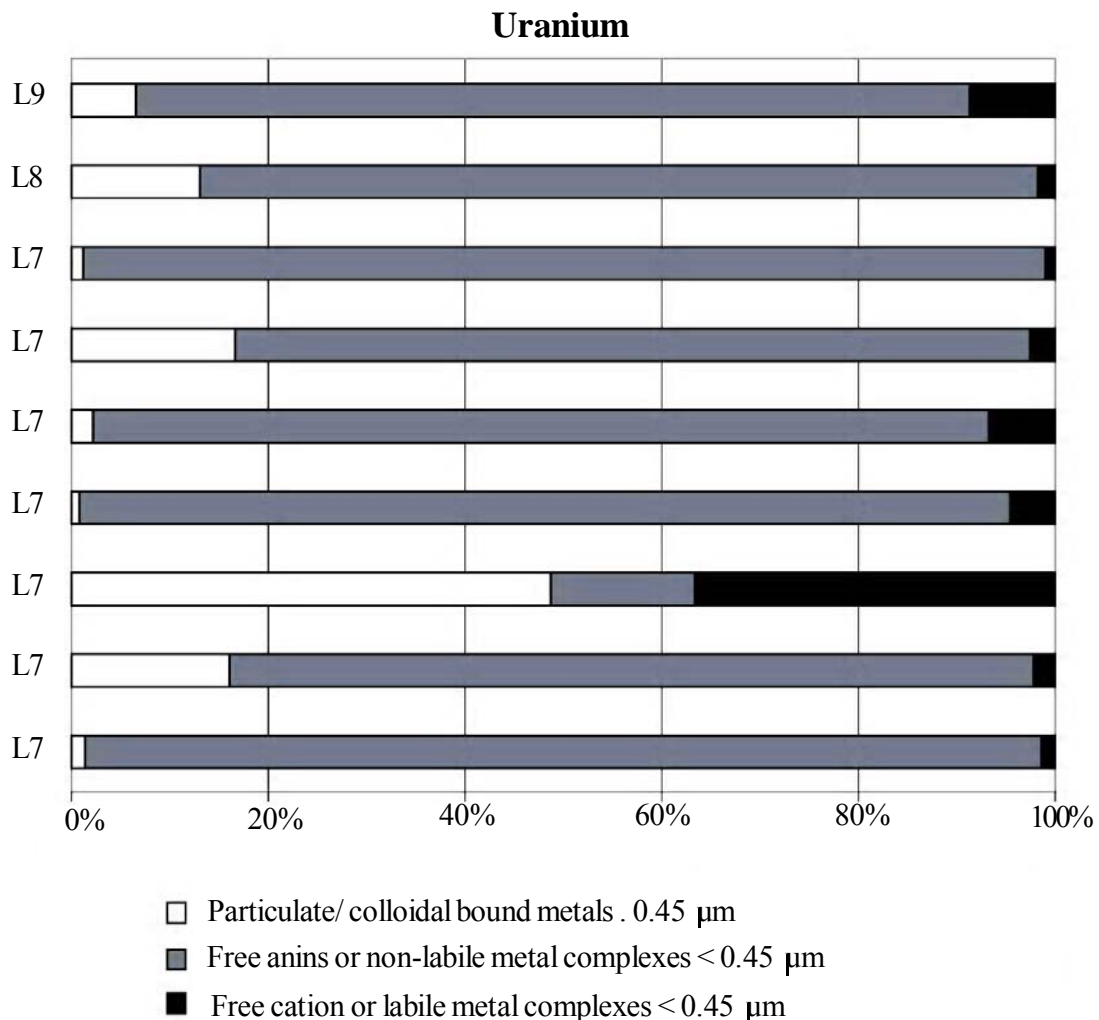Free cation or labile metal complexes < 0.45 µm

Fig. 2. Distribution of U present in fresh leachate from 9 landfills. Data for the various U species shown as percentage relative to total concentration

Table 3. Concentration of uranium and other heavy metals in landfill sediments (n=1)

Landfill	Uranium	Cadmium	Lead	Copper	Zinc	Nickel	Chromium
L2	0.88	1.1	49	220	1300	26	91
L3	0.33	1.3	96	130	2800	48	57
L4	0.94	1.1	13	34	4300	64	56
L6	0.28	0.23	47	300	370	15	70
L7	2.0	4.8	22	19	490	9	15
L8	0.79	0.35	37	130	500	15	50
L9	0.92	1.9	30	83	1200	37	77
L10	0.88	0.50	18	67	410	47	31

All concentrations present as mg/Kg

in this experiment consisted of U bound to organic matter. However, since landfill leachate generally has a high carbonate content, U could also be present as anionic carbonate complexes. Further work needs to be carried out in order to determine which of these is dominant.

The U concentrations in leachate sediments from some of the investigated landfills are presented in Table 3. Heavy metals, such as Pb, Cu, Cd, and Zn, are generally found to be present to a large degree as particulate or colloidal matter in leachate, and thus accumulate in leachate sediments (Øygard *et al*., 2007). In aquatic systems, sediments are known to act as sinks for uranium (Cadee, 1985; Klinkhammer and Palmer, 1991; Ribera *et al*., 1996). Naturally occurring Japanese lake sediments had a concentration range of 0.5 – 3.9 mg/kg (Nagao *et al*., 2002), while marine sediments (from the North Pacific Ocean) had a concentration range from 1.3 – 5.8 mg/kg (Klinkhammer and Palmer, 1991). The U concentrations in the landfill leachate sediments are in the lower part of these natural concentration ranges, suggesting that the leachate sediments do not pose a particular U pollution risk. Uranium occurs in the earth's crust at concentrations of 3-4 mg/kg (Kabata and Kembias, 1984; Bosshard *et al*., 1992), and the sampled sediments are all below the average soil concentrations.

It can be seen from (Table 3) that Zn, Cu, Pb and Cd were present proportionally in much higher concentrations in the sediments compared to the leachates from the same landfills than were Ni, Cr, and U. Considering that U is present in leachate mainly in the < 0.45 µm fraction, it can be assumed that U will sediment out of the leachate more slowly than Zn, Cu, Pb and Cd, as these metals are present to a much greater degree as particulate matter > 0.45 µm (Øygard *et al*., 2007).

CONCLUSION

The U concentrations in sampled landfill leachates were low, and in accordance with naturally occurring water in other regions of the world. Sampling and analysis of groundwater at six of the landfills suggested that at only one of these landfills could groundwater infiltration potentially be a significant source of U. The U concentrations in leachate sediments were similar to those reported in lake sediments around the world. Size charge fractionation of U in freshly sampled leachate showed that U was present mainly as either non-labile dissolved complexes or free anions. Since these species could not be separated in this work, it is possible that U is present either as non-labile organic matter complexes, which have intermediate mobility and toxicity, or anionic carbonate complexes, which are highly mobile and eco-toxic. Based on the results of the investigations, it can be concluded that the presence of U is not a major concern in MSW and MSWI bottom ash landfills. Though it is likely that the U in the leachates is present as species which may be highly mobile and eco-toxic (worst case scenario), the concentrations are low both in the leachate and in the sediments, making the presence of the metal a minor environmental problem.

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