Leaching of Dioxins from Municipal Waste Combustor Residues

June 2004

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## Contents

1 Introduction .............................................................................................................3  
2 Dioxins and Furans ..............................................................................................5  
2.1 Nomenclature ..................................................................................................5  
2.2 Relevant basic properties ................................................................................7  
2.3 Analysis ............................................................................................................8  
3 Waste-To-Energy: Generation of Ash and PCDD/F Emissions ..............................9  
4 Leaching of Dioxins/Furans from Waste-To-Energy Ash ....................................12  
4.1 The CORRE Municipal Solid Waste Ash Study ..............................................12  
4.2 Woodburn/Marion County long-term leachate monitoring .............................13  
4.3 Other landfill studies ....................................................................................14  
4.4 Enhancement of PCDD/F leaching in the presence of organic materials  
   (laboratory tests) .............................................................................................16  
5 Summary and Conclusions ..................................................................................17  
6 References .........................................................................................................18
Abstract

This study was initiated to provide an overview of available information related to the leaching of dioxins and furans during the disposal of combustion residues from U.S. Waste-to-energy facilities. While in the past waste-to-energy was a high known source of dioxins/furans emissions in the U.S., the combination of improved combustion and operation controls with advanced air pollution control equipment enable modern facilities to prevent both the formation and emission of dioxins/furans.

Long-term leaching studies on leachate from a combined ash monofill reported very low levels of dioxins/furans in the leachate samples, in most cases levels were below detection limits. Analysis of leachates from a co-disposal site in the U.S. accepting municipal solid waste and combined ash showed that levels of dioxins/furans were below detection limits in the leachate. Also, Japanese studies document low levels in leachate from ash landfill sites and a mass balance study indicated that over a period of eight years, less than 20 millionths of the dioxins/furans had been extracted from the disposed waste-to-energy ash.

Laboratory test procedures designed to examine enhanced leaching of dioxins/furans from ash in the presence of organic solvents resulted in the extraction of less than 1% of the total dioxins/furans present in the ash even under the most aggressive conditions. These results are consistent with the fact that dioxins and furans have low solubility.

No evidence has been found that under normal conditions of ash disposal, either in designated monofills or co-disposal landfills, significant leaching of dioxins and furans should be expected.

Acknowledgements

The Integrated Waste Services Association (IWSA) commissioned this work. Dr. Richard Anderson was the project coordinator. A previous study by Patrick H. Dyke provided tremendous help and his preliminary assessment of available data is the foundation of this report. The valuable input of IWSA members, the work of Mr. Dyke, and the valuable review by Dr. Anderson are gratefully acknowledged.
1 Introduction

Waste-to-energy facilities produce clean, renewable energy through the combustion of municipal solid waste in specially designed power plants equipped with the most modern pollution control systems to clean emissions. Trash volume is reduced by 90% and the remaining residue is regularly tested and consistently meets strict U.S. Environmental Protection Agency (EPA) standards allowing reuse or disposal in landfills. In 2002, there were 98 waste-to-energy plants operating in 29 states managing approximately 28.5 million tons or 7.7% of the 370 million tons municipal solid waste (MSW) in the U.S. (Kaufman 2004.) The solid residues, 25-30% by weight of the MSW, are produced in form of bottom and fly ash, which are combined at most U.S. facilities. Waste-to-energy plants generate about 2,800 megawatts of electricity to meet the power needs of nearly 2.4 million homes and serve the trash disposal needs of more than 36 million people.

America’s waste-to-energy facilities meet some of the most stringent environmental standards in the world and employ the most advanced emissions control equipment available. The U.S. EPA promulgated the Maximum Achievable Control Technology (MACT) standards as part of the Clean Air Act in 1995 that led to significant reductions in emissions from large waste-to-energy facilities. U.S. EPA data demonstrate that dioxins/furans emissions have decreased by more than 99% in the past ten years, and represent less than one percent of the national dioxin inventory (Stevenson 2002.) It is important to notice that the pollution control equipment now required for waste-to-energy facilities have reduced both the formation and emission of polychlorinated dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDF.)

The U.S. EPA announced that America’s waste-to-energy industry has achieved “dramatic decreases” in air emissions, an “outstanding performance”, and produce electricity “with less environmental impact than almost any other source of electricity” (Horinko 2003.) The success of the measures implemented to reduce emissions of PCDD/F is illustrated by the data reported by the U.S. EPA including year 2000 compliance test reports from all MWC facilities. The data documented a reduction from 4,260 g I-TEQ per year in 1990 to 12.0 g I-TEQ per year in 2000 for large MWC units (Stevenson 2002.)

Studies have confirmed the presence of PCDD/F in waste-to-energy residues. However, it is important to note that PCDD/F are widespread in the environment, for example, in soils, sediments, and municipal and other wastes. Therefore, data indicating the presence
of PCDD/F in residues have to be evaluated together with information on existing background levels. Public policy and its supporting research have focused on minimizing the exposure of the population and the environment to potentially harmful levels of these compounds. Concerns have been expressed that the co-disposal of waste-to-energy ash and municipal solid waste or the use of ash as a daily cover material in landfills could increase the potential for leaching of dioxins/furans to higher levels than expected at designated monocells or monofills that exclusively handle ash. The International Ash Working Group (IAWG) suggested in their review of waste-to-energy ash characteristics that significant amounts of certain organic compounds in MSW could enhance solubility of the PCDD/F (IAWG 1994.) This study discusses whether dioxins/furans can be expected to leach from waste-to-energy ash disposed under controlled conditions either in combination with untreated municipal solid waste (co-disposal landfill) or in a monofill.

Section 1 of this report outlines the background and objectives for this work. Section 2 provides an overview of general information about dioxins and furans including testing and research methods. It also considers the available data on regulatory levels for dioxins and furans in water as well as the analysis of leachate samples. Section 3 addresses the formation of PCDD/F during the combustion of MSW and the management of waste-to-energy ash in the U.S. Section 4 discusses the findings of previous studies on the leaching of dioxins and furans from combustion ash disposal sites. Summary and conclusions are presented in Section 5. The project is based on a review of scientific literature supplemented by technical reports and data from operating landfill and waste-to-energy facilities in the U.S. Data from field tests on actual leachate from operating co-fills were considered the most relevant. Overseas studies, laboratory trials and analysis of leachate from monofills were examined to provide supporting information.
2 Dioxins and Furans

2.1 Nomenclature

The term “dioxin” has become a catchphrase of the ongoing debate on the environmental sustainability of waste-to-energy processes. It is often used as a generic term beyond its technical denotation and usually includes the following two chemical groups:

- Polychlorinated dibenzo-p-dioxins (also referred to as dioxins, PCDD or CDD);
- Polychlorinated dibenzo furans (also referred to as furans, PCDF or CDF.)

The PCDDs include 75 individual compounds; PCDFs include 135 different compounds. These individual compounds are referred to technically as congeners. In total, there are 210 individual chemicals that make up the group “PCDD/F”, a term used for both, PCDDs and PCDFs. Throughout this report, the terms “dioxins/furans” and “PCDD/F” will refer to mixtures of the various congeners. However, only 7 of the 75 congeners of PCDDs are thought to have dioxin-like toxicity; these are ones with chlorine substitutions in, at a minimum, the 2, 3, 7, and 8 positions (Figure 1, left.) Only 10 of the 135 possible congeners of PCDFs are thought to have dioxin-like toxicity; these also are ones with substitutions in the 2, 3, 7, and 8 positions (Figure 1, right.) In sum, 17 individual PCDDs/PCDFs exhibit dioxin-like toxicity.

Figure 1. 2,3,7,8-Tetrachlorodibenzo-p-dioxin (left) and 2,3,7,8-Tetrachlorodibenzo furan (right)

A subset of chemicals called “dioxin-like” includes polybrominated dibenzo-p-dioxins (PBDDs), polybrominated dibenzofurans (PBDFs), and polychlorinated biphenyls (PCBs). Dioxin-like refers to the fact that these compounds have similar chemical structure (Figure 1), similar physical-chemical properties, and invoke a common battery of toxic responses. Only 13 of the 209 PCB congeners are thought to have dioxin-like toxicity; these are PCBs with four or more lateral chlorines with one or no substitution in
the ortho position (coplanar PCBs). In this report, PCBs are not included in the definition of any generic or specific terms used.

Analytical data may be grouped by homologue (compounds with the same number of chlorine atoms such as pentachlorodioxin – PeCDD with five chlorine atoms) or described as “total”. In most cases and in this report, the term “total” would refer to the sum of compounds that have substitutions with four to eight chlorine atoms (teta to octa). Total PCDD/F measurements are one indicator of the dioxin concentration in waste-to-energy ash. In addition to homologue and total data, quantification systems have been devised to indicate the relative toxicity of mixtures of the 210 individual dioxin and furan congeners.

PCDDs, PCDFs, and PCBs are commonly found as complex mixtures when detected in environmental media and biological tissues, or when measured as environmental releases from specific sources. Humans are likely to be exposed to variable distributions of PCDD/PCDF and dioxin-like PCB congeners that differ by source and pathway of exposures. This complicates the human health risk assessment that may be associated with exposures to variable mixtures of dioxin-like compounds. In order to address this problem, toxic equivalency factors (TEFs) have been developed for each congener. TEFs take into account chemical structure, persistence, resistance to metabolism, risks, and uncertainties to quantify the relative toxicity of individual compounds. In this sense, they can be described as “public health conservative” values. 2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD) is assigned a TEF of 1.0 and the other congeners have TEF values ranging from 1.0 to 0.00001 (orders of magnitudes.) To apply this concept, the TEF of each individual congener is multiplied by the respective mass concentration and the products are summed to represent the Toxic Equivalence (TEQ) of the mixture, as:

$$\text{TEQ} = \sum_{i=1}^{n} (\text{Congener}_i \times \text{TEF}_i)$$

with \( n = \text{number of congeners} \)

The TEF values for PCDDs and PCDFs were originally adopted by international convention. Subsequent to the introduction of the first international TEFs, these values were further reviewed and/or revised. Thus, it is necessary to clarify which TEF sets were used to estimate the TEQ. Commonly, there are two main schemes in use:

1. I-TEQ: the international TEF scheme (adopted by the U.S. EPA)
2. WHO-TEQ: TEF scheme by the World Health Organization as an extension of the I-TEF scheme to include 13 dioxin-like PCBs
Values of PCDD/F concentration are reported in this document as toxic equivalents using the international toxic equivalency scheme (I-TEQ) unless otherwise stated. The I-TEQ refers to all the 17 2,3,7,8-substituted congeners of PCDD/F (Table 1.) If toxic equivalents are calculated using the WHO scheme, this will be specifically indicated in this document as WHO-TEQ. Note that only the PCDD/F congeners have been included herein, following the I-TEQ scheme, and the PCBs are not included (Table1.)

Table 1: Toxic equivalency factors for PCDD/F (McKay 2002)

<table>
<thead>
<tr>
<th>Dioxin (D) Congener</th>
<th>I-TEF</th>
<th>WHO-TEF</th>
<th>Furan (F) Congener</th>
<th>I-TEF</th>
<th>WHO-TEF</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,3,7,8-TCDD</td>
<td>1.0</td>
<td>1.0</td>
<td>2,3,7,8-TCDF</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>1,2,3,7,8-PeCDD</td>
<td>0.5</td>
<td>1.0</td>
<td>1,2,3,7,8-PeCDF</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>1,2,3,4,7,8-HxCDD</td>
<td>0.1</td>
<td>0.1</td>
<td>2,3,4,7,8-PeCDF</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>1,2,3,6,7,8-HxCDD</td>
<td>0.1</td>
<td>0.1</td>
<td>1,2,3,4,7,8-HxCDF</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>1,2,3,7,8,9-HxCDD</td>
<td>0.1</td>
<td>0.1</td>
<td>1,2,3,6,7,8-HxCDF</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>1,2,3,4,6,7,8-HpCDD</td>
<td>0.01</td>
<td>0.01</td>
<td>1,2,3,7,8,9-HxCDF</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>OCDD</td>
<td>0.001</td>
<td>0.0001</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,2,3,4,6,7,8-HpCDF</td>
<td></td>
<td></td>
<td>1,2,3,4,6,7,8-HxCDF</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>OCDF</td>
<td>0.001</td>
<td>0.0001</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2.2 Relevant basic properties

Dioxins and furans form a group of related compounds found at low concentrations in the environment. They are produced during a wide range of industrial and non-industrial processes including waste-to-energy combustion. Because of their hydrophobic nature and resistance towards metabolism, these chemicals persist and bioaccumulate in fatty tissues of animals and humans. Relevant properties when considering the potential leaching of dioxins and furans from ash include:

- strong tendency to associate with carbonaceous materials
- affinity to bind to solid materials;
- tendency to dissolve in organic solvents and fatty materials;
- very low solubility in water (< 5×10^{-4} mg/L).

In general, PCDD/F are found tightly bound to soils and sediments in the environment and are primarily transported in water by the motion of solid materials rather than by dissolving into water. Therefore during the analysis of leachates, it has to be carefully distinguished between the association of PCDD/F with fine particulate matter in
suspension and true concentrations in the extraction fluid. Dioxins/furans belong to a special group of chemicals known as persistent organic pollutants. After entering a certain environment or body, these substances stay there for a long time, due to their ability to dissolve in fats and chemical stability. For example, the half-life of dioxins/furans in the human body is about seven years.

2.3 Analysis

The chemical analysis of dioxins and furans has advanced considerably over the past 20 years resulting in extremely sensitive techniques capable to detect dioxins and furans down to levels of parts per quadrillion or pg/kg in aqueous matrices. The evolution in chemical analysis requires researchers to consider that tests conducted many years ago may have indicated that dioxins and furans were undetectable, and that a modern analysis on the same sample may well yield measurable levels of dioxins and furans. Care must therefore be taken in interpreting data spanning many years to avoid the potentially misleading conclusion that the detection of PCDD/F in more recent tests suggests an increase in actual concentration. The perception of an increase in concentrations may simply reflect the improved sensitivity of analytical instruments to detect dioxins/furans.

The concentration of PCDD/F in leachate can be determined by direct measurements on collected leachates. Testing of the total concentration of PCDD/F in waste-to-energy ash would also be necessary in order to quantify how much PCDD/F leached relative to the total concentration (or potential.) As noted above, the science of dioxins/furans has evolved rapidly over the past decades with great advances in analytical techniques and understanding of formation, control and behavior of PCDD/F. Consequently, different protocols for testing parameters such as leaching rates from residues may have been used in different studies or cases. In reviewing data in the literature, this slight inconsistency has to be taken into account.
3 Waste-To-Energy: Generation of Ash and PCDD/F Emissions

Waste-to-energy residues can be divided in the following groups (Wiles 1996):

1. Bottom ash as discharged from the bottom of the furnace (mainly the grate) and fallen through the furnace grates;
2. Heat recovery ash (HRA) as collected in the heat recovery system including boiler, economizer, and superheater. HRA is frequently discharged into the bottom ash stream and thus often included in a broader definition of bottom ash;
3. Fly ash as carried over from the furnace and removed before sorbents are injected to clean the flue gas;
4. Air pollution control (APC) residues as collected in the APC equipment (e.g., scrubbers, electrostatic precipitators, and baghouses) including fly ash, sorbents, condensates, and reaction products;
5. Combined ash as a mixture of the above categories. In the U.S., the majorities of waste-to-energy facilities combine their ashes to one residue stream.

While the above definitions detail the various ash streams, for practical reasons, it is often only differentiated between bottom and fly ash. The bottom ash consists largely of incombustible residue passing through the combustion system. Fly ash consists mainly of particulate matter entrained in the flue gases and removed by the flue gas treatment system. In many plants, reagents are injected into the flue gas stream to control emissions of acid gases, volatile metals and organic pollutants. The products of the reactions are collected with the fly ash in emission control systems for particulate matter such as fabric filters (also known as baghouses) or electrostatic precipitators. The combustion of MSW in a modern massburn waste-to-energy facility generates approximately 85% (by weight) bottom ash and 15% fly ash. Ferrous metal is often removed from the ash stream and sent for reprocessing. However, this report does not consider the ferrous metal stream.

The disposal of ash is subject to regulatory control under authority of the Resource Conservation and Recovery Act (RCRA) and subsequent amendments. The combined ash may be disposed in specially designated monocells, as part of a “normal” landfill, or monofills that only accept ash. The ash may also be co-disposed in combination with untreated MSW or non-hazardous industrial waste in a landfill. In both cases, the typical landfill is lined and equipped with leachate collection to ensure groundwater protection. Collected leachates are then handled, treated and disposed in accordance with the applicable regulations.
After authorities worldwide promulgated new regulations for waste-to-energy facilities to control their emissions, advanced operating and pollution control systems were installed. It is important to note that with the upgrade air emissions of PCDD/F decreased drastically, as noted above reductions of more than 99% were achieved in the U.S., but also the overall formation of PCDD/F decreased.

Although the combustion of municipal solid waste was in the past a major source of anthropogenic dioxins/furans, incineration is the best available technology for the destruction of PCDD/F although other methods have been investigated (WHO 1999.) The process requires high temperatures over 850° C (1560 F), which are maintained in modern waste-to-energy facilities. The amount of dioxins/furans in municipal solid waste has been measured between 20 to 70ng I-TEQ PCDD/F per kg waste (Vehlow 2003.) Old combustors with obsolete control technology were measured to emit PCDD/F in excess of 500% compared to the amounts of dioxins/furans in the incoming municipal solid waste (IAWG 1994.) In contrast, modern waste-to-energy facilities are net PCDD/F reducers. A study by the IAWG (1994) concluded that that modern facilities destroy about 66% of dioxins/furans measured in the solid waste. Assuming 50ng I-TEQ PCDD/F per kg of incoming MSW (100%), about 17ng I-TEQ or 34% of the dioxins/furans remain after combustion. Of those 34%, 13% are emitted through air and 21% through the combined residues stream (MacKay 2002.)

Table 2 summarizes PCDD/F levels found in combustion residues from various countries. Values are comparably low because facilities comply with very stringent regulations. The reported decrease in dioxins/furans emissions before and after a retrofit with modern air pollution control equipment waste-to-energy plant in Spain is summarized in Table 3. The combined emissions (air, bottom ash, fly ash) was reduced by 97%, which indicates that the upgrade resulted in less PCDD/F formation (Abad 2003.)

**Table 2:** Maximum total dioxins/furans concentration in ash samples

<table>
<thead>
<tr>
<th>Country (Reference)</th>
<th>Type of ash</th>
<th>PCDD/F concentrations in ng/g (ppb)</th>
<th>PCDD/F concentrations in pg/g I-TEQ (ppt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Canada (IWSA 1997)</td>
<td>bottom</td>
<td>&lt; 0.6</td>
<td>NR</td>
</tr>
<tr>
<td>Germany (IWSA 1997)</td>
<td>bottom</td>
<td>0.142</td>
<td>2</td>
</tr>
<tr>
<td>Germany (Zwahr 2004)</td>
<td>bottom</td>
<td>NR</td>
<td>5.34 (in 2003)</td>
</tr>
<tr>
<td>Sweden (RVF 2003)</td>
<td>fly</td>
<td>NR</td>
<td>1,800</td>
</tr>
<tr>
<td>U.S. (IWSA 1997)</td>
<td>bottom</td>
<td>0.81</td>
<td>NR</td>
</tr>
<tr>
<td>U.S. (CORRE 1990)</td>
<td>combined</td>
<td>NR</td>
<td>211</td>
</tr>
</tbody>
</table>

Note: NR – not reported
Table 3: Annual emissions before and after upgrading the air pollution control system of a waste-to-energy facility in Barcelona, Spain (Abad 2003)

<table>
<thead>
<tr>
<th></th>
<th>Unit</th>
<th>Before</th>
<th>After</th>
<th>Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Air emissions</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flue gas volume</td>
<td>N m(^3)</td>
<td>360 million</td>
<td>360 million</td>
<td></td>
</tr>
<tr>
<td>PCDD/F concentration</td>
<td>ng I-TEQ/N m(^3)</td>
<td>111.39</td>
<td>0.016</td>
<td></td>
</tr>
<tr>
<td>Annual PCDD/F formation</td>
<td>g I-TEQ</td>
<td>40.1</td>
<td>0.006</td>
<td>99.98%</td>
</tr>
<tr>
<td><strong>Fly ash</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fly ash generation</td>
<td>Mg</td>
<td>1,300</td>
<td>1,300</td>
<td></td>
</tr>
<tr>
<td>PCDD/F concentration</td>
<td>ng I-TEQ/g</td>
<td>16.3</td>
<td>1.07</td>
<td></td>
</tr>
<tr>
<td>Annual PCDD/F formation</td>
<td>g I-TEQ</td>
<td>21.19</td>
<td>1.39</td>
<td>93.44%</td>
</tr>
<tr>
<td><strong>Bottom ash</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bottom ash generation</td>
<td>Mg</td>
<td>10,500</td>
<td>10,500</td>
<td></td>
</tr>
<tr>
<td>PCDD/F concentration</td>
<td>ng I-TEQ/g</td>
<td>0.025</td>
<td>0.025</td>
<td></td>
</tr>
<tr>
<td>Annual PCDD/F formation</td>
<td>g I-TEQ</td>
<td>0.26</td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total PCDD/F emissions</td>
<td>g I-TEQ</td>
<td>61.55</td>
<td>1.66</td>
<td>97.30%</td>
</tr>
</tbody>
</table>
4 Leaching of Dioxins/Furans from Waste-To-Energy Ash

The review of the available literature included some of the reports and papers below. One study documents measured levels of dioxins/furans in leachate from a co-disposal landfill in the U.S. taking combined waste-to-energy ash (CORRE 1990.) The Woodburn study (1988-2000) reports field measurements, including long-term data on levels of dioxins and furans in leachate from an ash monofill. The other studies provide data on leachate from ash disposal sites or laboratory tests in the U.S. and other countries. It is noteworthy that in most countries waste-to-energy ash disposal requires separate streams (at least, bottom ash and fly ash) rather than a combined stream as practiced in the U.S.

4.1 The CORRE Municipal Solid Waste Ash Study

The Coalition on Resource Recovery and the Environment (CORRE) and the Environmental Protection Agency (EPA) initialized a study on the leachability of contaminants from and the composition of waste-to-energy ash including field tests of leachate from different disposal sites taking combined waste-to-energy ash. Residues from five waste-to-energy plants, built between 1975 and 1987, were assessed. Characteristics of the five plants and the associated disposal sites were reported as follows (CORRE 1990):

1. MSW Mass Burn lime slurry injection and fabric filters; monofill with single clay liner and leachate collection.
2. MSW Mass Burn with dry lime injection and fabric filter (scrubber residue is treated with phosphoric acid and is agglomerated prior to mixing with bottom ash); monofill with double liner and leachate collection.
3. MSW Mass Burn with electrostatic precipitators; co-disposal lined landfill with leachate collection.
4. MSW Mass Burn with electrostatic precipitators; unlined monofill, where ash is placed on top of “old” MSW in place, no leachate collection.
5. MSW Mass Burn, lime slurry addition with electrostatic precipitators (fly ash is agglomerated with addition of water prior to mixing with bottom ash); monofill with double liner and leachate collection.
The authors of the CORRE study conclude that the dioxin and furan compounds do not readily leach in real landfill situations. The PCDD/F detected from site 1) were likely associated with fine particulate because the samples were not filtered or centrifuged. Laboratory testing also showed low leaching of dioxins/furans in a single composite test on each ash using the monofill waste extraction procedure SW-924 that provides information on reasonable levels of contaminants in leachate from industrial wastes monofilled under controlled conditions. The SW-924 employs a four-step sequential batch extraction with a liquid-to-solid ratio of 10:1 and determines the maximum release under mildly acidic conditions.

Table 4:  

<table>
<thead>
<tr>
<th></th>
<th>Ash leachate (max.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pg/g I-TEQ (ppt)</td>
</tr>
<tr>
<td>1 (monofill)</td>
<td>75</td>
</tr>
<tr>
<td>2 (monofill)</td>
<td>211</td>
</tr>
<tr>
<td>3 (co-disposal landfill)</td>
<td>119</td>
</tr>
<tr>
<td>4 (monofill)</td>
<td>189</td>
</tr>
<tr>
<td>5 (monofill)</td>
<td>64</td>
</tr>
</tbody>
</table>

Note: ND – not detected or below detection limit

4.2 Woodburn/Marion County long-term leachate monitoring

The Woodburn study was initiated by the U.S. EPA Office of Solid Waste and provided a time series of data on pollutants present in an ash monofill, in the leachates and surrounding environment. Marion County has (co-) sponsored the sampling and analysis since 1988 – the baseline year – concluding with the latest report being published in April 2002 (Roffman Associates 2002.) Combined ash (bottom ash mixed with fly ash from a combustor fitted with lime slurry injection and bag filters) was landfilled in a separate part of the landfill from other wastes (monocell.) The “interim ash landfill” was constructed with a liner and leachate collection.

In summary, all sampling and analysis in leachates from the ash disposal site of the 13-year long Woodburn study showed very low levels of dioxins/furans (Table 5.) The majority of analysis has not shown any congeners at a detectable level. Only the higher chlorinated HpCDD, HpCDF and OCDD have been detected in some of the samples and
these results have been correlated with particulate in the sample rather than the aqueous phase of the leachate as the source of PCDD/F. Analytical techniques have improved over thirteen years and detection limits have been lowered to the parts per trillion level (See also Section 2.3.) The last report includes a reference to a drinking water standard of 30 ppt I-TEQ for 2,3,7,8-TCDD, which is above the detected concentrations for all samples of the Woodburn study (Roffman Associates 2002.)

Table 5: Reported PCDD/F concentration in leachates from the Woodburn ash disposal facility (Dow Environm. 1995, Roffman Associates 2000, 2002)

<table>
<thead>
<tr>
<th>Year</th>
<th>Detected congeners (max.)</th>
<th>Total TEQ</th>
</tr>
</thead>
<tbody>
<tr>
<td>1988 (five samples)</td>
<td>OCDD: 0.107  HpCDD: 0.222 HpCDF: 0.076</td>
<td>0.003</td>
</tr>
<tr>
<td>1989 (two samples)</td>
<td>OCDD: 0.049</td>
<td>0.5×10^-4</td>
</tr>
<tr>
<td>1990</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>1993</td>
<td>HpCDF: 0.022</td>
<td>2.2×10^-4</td>
</tr>
<tr>
<td>1998</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>2000</td>
<td>OCDD: 0.011</td>
<td>0.1×10^-4</td>
</tr>
</tbody>
</table>

Note: ND – not detected or below detection limit of 0.001 ppb (not reported prior to 1990)

4.3 Other landfill studies

Municipal solid waste management in Japan relies heavily on combustion, with landfilling of residuals. Concern over the presence of dioxins and furans in the residues led to a series of projects coordinated by the Japan Waste Research Foundation to evaluate the amounts of dioxins and furans present in ash, the compounds’ behavior in the landfill environment, and the effect of leachate treatment on levels of dioxins and furans released.

Yoshikawa and others (1999) report on results of an extensive survey of dioxins/furans levels in leachate samples from thirteen landfill sites. These landfills included several sites accepting ashes from a range of municipal waste combustors that showed highly variable air emissions of dioxins/furans (as high as 80 ng TEQ/Nm³.) Two landfill sites studied by Yoshikawa did not have any ash in them. Two landfill sites were ash monofills. One site separated ash and non-combustible wastes. The other landfills were co-disposal sites. Levels of PCDD/F in the raw leachate were below 16 pg TEQ/L (ppq).
More than half the sites showed concentrations under 1 pg TEQ/L. In most cases, the majority of the dioxins/furans were associated with particulate material in the leachate. The authors did not identify a pattern, which would allow the prediction of levels of dioxins/furans in the raw leachate based on the materials landfilled (Yoshikawa 1999.)

Nishikawa and others (1999) present levels of dioxins and furans in leachates from landfill sites used to dispose of incinerator residues in Japan. Details of the composition of the disposed wastes and ashes were not included. A review of other studies yielded total PCDD/F concentrations in 18 samples of leachate from ash disposal sites ranging from 23 to 15,900 pg/L. On a toxic equivalent basis, the maximum level reported was 50 pg TEQ/L (0.05 ppt) (Nishikawa 1999.)

Noma and others (1999) report findings of a mass balance study conducted on a lined landfill site accepting ash from three different municipal waste incinerators in Japan. An estimated 39.6 g TEQ of PCDD/F (2,863 g total) had been added to the landfill over a period of eight years, primarily by the disposal of waste-to-energy ash. More than 99% of the dioxin and furan was associated with the landfilled fly ash. Tests on raw leachate showed PCDD/F concentrations of 2.02 pg TEQ/L (0.002 ppt), mostly associated with the suspended solids. The authors calculated that over a period of eight years, a total of 0.00063% of the input dioxins/furans had been released from the landfill in the raw leachate. Further analysis at this landfill site showed that rainwater contained 0.80 pg TEQ/L (0.0008 ppt) of dioxins/furans and water in a nearby river less than 1.60 pg TEQ/L (0.0016 ppt.) Thus, the PCDD/F level in the raw leachate is very similar to that found in rainwater and river water near to this site. However, the patterns of congeners were completely different confirming that the leachate was not responsible for the background levels found in the rain and river water (Noma 1999.)

In the U.K., a study focused on potential pathways of PCDD/F contamination through the release of dusts from landfilled air pollution control residues. None of the activities at the landfill sites was found to result in significant releases of dust. The predicted annual mean concentration of fine particulate matter (PM$_{10s}$) in airborne dust from the landfill at the nearest property was 1.8 µg/m$^3$, which is significantly lower than the Air Quality Strategy Objective of 40 µg/m$^3$ (U.K. Environment Agency 2002.) If windblown PM$_{10s}$ would exhibit the highest reported PCDD/F concentration of 5,800 ng/kg TEQ then this would still result in a negligible contribution to daily exposure for an adult through inhalation of 0.2 pg TEQ dioxins/furans. Also, a Swedish study on dioxins/furans associated with waste-to-energy concluded that dioxins/furans “are solidly fixed” and waste-to-energy “breaks the ecocycle of the dioxins in the waste” (RVF 2003.)
4.4 Enhancement of PCDD/F leaching in the presence of organic materials (laboratory tests)

Recent experiments by researchers in Japan and Korea examined the effect of dissolved humic matter on the leaching of dioxins and furans from fly ash. The experiments may have relevance to landflling of ash residues from municipal waste combustors with municipal waste. Humic-like materials make up a major part of the organic matter in landfill leachates where organic materials are decomposing (Paxeus 2000.) Kim and others (2002) examined some effects of humic acid on fly ash, and report test results using a long-term leaching test at various concentrations of humic acid. The results of these experiments showed that leaching increased in the presence of humic acid compared to pure water and highest leaching occurs in an alkaline environment. However, less than 0.2% of the dioxins/furans were mobilized in the tests (Kim 2002.)

Another series of experiments in Germany studied the potential enhancement of removal (leaching) of dioxins/furans by solutions containing water and organic solvents as a viable “cleaning technique” for contaminated materials such fly ash and soil (Schramm 1995a, 1995b, 1997.) In a column-leaching test, fly ash treated with a fire-extinguisher solution released about 30 ng/L PCDD/F (or 30ppt) (Schramm 1995a.) The research was extended to investigate leaching properties of fly ash and bottom ash from municipal waste combustors in landfill environments, focusing on the possible enhancement of leaching by co-solvents such as linear alkylbenzene sulphonate (LAS.) Replacing pure water with a solution of LAS at 1.5 g/L increased leaching considerably. However, the concentration of LAS was far above the “critical micelle concentration,” which may lead to enhanced solubility of organic non-polar compounds (Schramm 1995b.) Such a situation is unlikely to exist within a landfill. In further experiments using LAS at levels below the critical micelle concentration, less than 1% of the dioxins and furans on the fly ash were transferred to the aqueous phase (Schramm 1997.)
5 Summary and Conclusions

This report was written to address concerns that dioxins and furans might be released from waste-to-energy ash disposal sites including both monofills and co-disposal landfills. Analytical results from the reviewed studies showed that dioxins/furans were only present in the ashes at very low limits and leachates contained PCDD/F at concentrations below the allowable drinking water standards level at 30 ppt (Roffman Associates 2002.) Long-term testing on the leachates from an ash monofill site is available through the EPA’s efforts in monitoring leachate from the Woodburn monofill. The study also confirmed the low or non-detectable concentrations of dioxins/furans.

Tests in Japan on leachates from landfills, including ash co-disposal sites, showed dioxins and furans in raw leachate were below 16 ppq (parts per quadrillion.) A mass balance study conducted in Japan for dioxins and furans in an ash landfill showed only 0.00063% of the dioxins/furans (TEQ basis) present in the landfill had transferred into the raw leachate over a period of eight years. The used concept of mass balance of a trace constituent confirmed the low mobility of dioxins/furans in a landfill environment. Researchers have repeatedly stated in various studies that detected levels of dioxins/furans in landfill leachates or ash extracts are often associated with suspended solid materials or oily phases rather than the aqueous leachate. Organic solvents enhance the mobility of dioxins/furans to level of about 1% but the conditions during the laboratory tests do not compare to the environment in ash disposal sites.

In sum, the available data indicates that the total concentrations of dioxins/furans in waste-to-energy ash are very low and that leachates from ash disposal sites do not pose a public health threat regarding the catch phrase “dioxins” that is often used during the discussion about the environmental performance of waste-to-energy residues. Also, it has been reported that modern MSW combustors are net-reducers of dioxins/furans. Therefore, a shift from dioxins/furans release from air emissions to solid residues or leaching of dioxins/furans from ash disposal sites cannot be expected for modern waste-to-energy facilities.
6 References


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