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Risk Characterization, Assessment, and Management of Organic Pollutants in Beneficially Used Residual Products

Gregory B. Kester,* Robert B. Brobst, Andrew Carpenter, Rufus L. Chaney, Alan B. Rubin, Rosalind A. Schoof, and David S. Taylor

ABSTRACT

A wide array of organic chemicals occur in biosolids and other residuals recycled to land. The extent of our knowledge about the chemicals and the impact on recycling programs varies from high to very low. Two significant challenges in regulating these materials are to accurately determine the concentrations of the organic compounds in residuals and to appropriately estimate the risk that the chemicals present from land application or public distribution. This paper examines both challenges and offers strategies for assessing the risks related to the occurrence of organic compounds in residuals used as soil amendments. Important attributes that must be understood to appropriately characterize and manage the potential risks for organic chemicals in biosolids include toxicity and dose response, transport potential, chemical structure and environmental stability, analytical capability in the matrix of interest, concentrations and persistence in waste streams, plant uptake, availability from surface application versus incorporation, solubility factors, and environmental fate. This information is complete for only a few chemicals. Questions persist about the far greater number of chemicals for which toxicity and environmental behavior are less well understood. This paper provides a synopsis of analytical issues, risk assessment methodologies, and risk management screening alternatives for organic constituents in biosolids. Examples from experience in Wisconsin are emphasized but can be extrapolated for broader application.

Biosolids are complex materials, rich in naturally occurring organic and inorganic compounds, but also containing trace levels of synthetic organic compounds. Thousands of chemical compounds are used in commerce in today's modern industrialized world that may wind up in wastewater effluents or biosolids. While many compounds made by man perform intended functions with benign consequences, some can cause unintentional adverse effects in other ecosystems or in humans (Sonnenschein and Soto, 1998).

The presence of organic compounds in biosolids largely mirrors the organic compounds that we are exposed to daily. The majority are proteins, lignin, cellulose, hemicellulose, and other organic materials that make up living plant and animal matter (Li et al., 2001). Additionally, some volatile organic compounds (VOCs) occasionally found in biosolids, such as acetone and methyl ethyl ketone, are microbially generated during the decomposition of biosolids under anaerobic conditions (Rosenfeld et al., 2001). On the other hand, synthetic organic compounds used in food production, personal care products, plastics manufacturing, and other industrial processes may be found in biosolids, though typically at low concentrations (see below). For compounds used in food production, personal care products, and other commonly used materials, human exposure to the compounds is probably much lower from the indirect exposure presented by the use of biosolids as a soil amendment than would be expected from the primary exposure in eating or using the product that contains these compounds. Metabolites of synthetic organic chemicals to which people are exposed on a daily basis (e.g., surfactants) may also be present (LaGuardia et al., 2001). Additionally, ubiquitous persistent organic compounds, including some congeners of dioxin and polychlorinated biphenyls (PCBs), are routinely detected at low concentrations in laboratory analysis of biosolids (Cambridge Environmental, 2001; USEPA, 2002a).

Scientists and regulators are faced with the challenge of evaluating potential effects associated with an activity and determining whether regulatory action is necessary to mitigate resultant risks. The best predictor of risk is an assessment based on scientific research that estimates the increased risk from an activity to a defined population more susceptible to adverse effects than the general population. Important attributes that must be understood to appropriately characterize and manage the potential risks for organic chemicals in biosolids include toxicity and dose response, transport potential, chemical structure and environmental stability, analytical capability in the matrix of interest, concentrations and persistence in waste streams, plant uptake, availability from surface application versus incorporation, solubility factors, and environmental fate. This information is robust for only a few chemicals. Polychlorinated biphenyls and dioxin are examples of such chemicals, and models for conducting a quantitative risk assessment using both deterministic and probabilistic approaches are presented in this paper. Deterministic approaches rely on single-point estimates for each of the attributes listed above as well as other characteristics such as food and soil

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Abbreviations: HEI, highly exposed individual; LOD, limit of detection; PCB, polychlorinated biphenyl; PRA, probabilistic risk assessment; RME, reasonable maximum exposure; TEQ, toxic equivalent basis; WDNR, Wisconsin Department of Natural Resources; WSLH, Wisconsin State Lab of Hygiene.

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Table 1. Select volatile (VOCs) and semivolatile organic compounds (SVOCs) commonly found in biosolids.

	New Hampshire, USA†		British Columbia, Canada‡		Canada§	
	Mean	Maximum	Mean	Maximum	Median	Maximum
Year of sampling	2002		1999		1993–1994	
Number of samples	52		36		210	
Number of wastewater treatment plants (WWTPs)	17		5		12	
	mg kg^{-1} dry wt.					
Toluene	2.7	737	0.39	1.8	1.1	42
1,4-Dichlorobenzene	5.3	12.0	0.12	40.6	0.52	2.6
m,p-Xylene	1.0	2.0	0.16	1.2	1.5	5.1
Bis(2-ethylhexyl)phthalate	19.7	130	2.7	11	160	244
Phenol	54.7	220	12	43	2	9.4
4-Methylphenol	55.3	420	140	940	NR¶	NR
Benzo(*a*)pyrene	BDL#	BDL	0.31	1.1	0.33	6.8
Fluoranthene	1.5	2.0	1.6	4	1.04	5
Pyrene	1.5	1.9	1.7	3.7	1.2	14

† New Hampshire Department of Environmental Services, unpublished data (2002).
‡ Bright and Healey (2003).
§ Webber et al. (1996).
¶ Not reported.
# Below detection limit.

consumption by the target population. A common criticism of this method is that selection of single-point estimates are subjective and profoundly affect the prediction of risk. In addition, information on the challenges associated with analytical methods for organic constituents is presented.

Questions persist about the far greater number of chemicals for which toxicity and environmental behavior are less understood. Despite limited data, these chemicals must be evaluated to ensure public safety and environmental protection. Loss models based on chemical, biological, and physical properties, to develop recommended management practices, is one approach considered. Regulators determine the need and the structure of regulatory response based on an assessment. This paper serves to provide a basic understanding of analytical issues, risk assessment methodologies, and risk management screening alternatives for organic constituents in biosolids. Examples from experience in Wisconsin with respect to analytical issues and risk assessment are emphasized but can be extrapolated for broader application.

ORGANIC COMPOUND CONCENTRATIONS IN BIOSOLIDS

Summaries of three studies documenting concentrations of some frequently detected organic compounds in biosolids are given in Table 1 (New Hampshire Department of Environmental Services, unpublished data, 2002; Bright and Healey, 2003; Webber et al., 1996). Most of the nine commonly detected volatile (VOC) and semivolatile organic compounds (SVOC) are included in the priority pollutant scans used in the United States to characterize the organic compound concentrations in solid and hazardous wastes. The results presented are based on a number of samples in three studies in which up to 150 different compounds were analyzed. The other 141 compounds were not routinely detected. While some of the nine compounds shown are cited as compounds of concern they generally have very short half-lives in soils (Anderson et al., 1991; Mackay et al., 1992; Peterson et al., 2003).

Table 2 (New Hampshire Department of Environmental Services, unpublished data, 2002; Cambridge Envi-

Table 2. Dioxin-like compound concentrations in biosolids.†

	New Hampshire, USA‡			USA§			USA¶			British Columbia, Canada#		
	Mean	Maximum	95th percentile	Mean	Maximum	95th percentile	Mean	Maximum	95th percentile	Mean	Maximum	95th percentile
Year of sampling	2002			2000–2001			2001			1999		
Number of samples	52			200			94			36		
Number of wastewater treatment plants (WWTPs)	17			171			94			5		
	ng kg^{-1} dry wt.											
Polychlorinated dibenzodioxins and dibenzofurans (PCDD/Fs) (total TEQ††)	12.5	61.2	33.5	34.5	3578	49.1	21.7	682	33.3	40	250	120
Polychlorinated biphenyls (PCBs) with dioxin-like toxicity (total TEQ)	NT‡‡	NT	NT	8.3	229	18.8	5.22	58.3	13.1	NT	NT	NT

† In all cases, nondetects were calculated to equal zero.
‡ New Hampshire Department of Environmental Services, unpublished data (2002).
§ Cambridge Environmental (2001).
¶ USEPA (2002a).
# Bright and Healey (2003).
†† Toxic equivalent basis.
‡‡ Not tested.

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Table 3. Concentrations of three common organic compounds.

	USA†		Denmark‡		Sweden§		Sweden¶	
	Mean	Maximum	Mean	Maximum	Mean	Maximum	Median	Maximum
Year of sampling	1999–2000		1995		2003		1999	
Number of samples	11		20		NR#		10–14	
Number of wastewater treatment plants (WWTPs)	11		NR		NR		10–14	
	mg kg^{-1} dry wt.							
Nonylphenol	491	887	8	67	3.9	NR	NT††	NT
Linear alkylbenzene sulfonates (LAS)	NT	NT	530	16 100	252	NR	NT	NT
Sum of penta brominated diphenyl ethers	1.56	2.29	NT	NT	NT	NT	0.062	0.129

† LaGuardia et al. (2002).
‡ Torslov et al. (1997).
§ Swedish Environmental Protection Agency (2003).
¶ Hellstrom (2000).
# Not reported.
†† Not tested.

ronmental, 2001; USEPA, 2002a; Bright and Healey, 2003) lists the concentrations of compounds with dioxin-like toxicity and analytical results for dioxin and dioxin-like compounds on a toxic equivalent basis (TEQ). The USEPA used the results obtained in its survey as part of the dioxin risk assessment process (USEPA, 2002a). Note that 95th percentile values are similar in each survey (though the British Columbia results are slightly greater) and not much greater than the average values. This would indicate that it is likely that the maximum values were outliers.

Table 3 (LaGuardia et al., 2002; Swedish Environmental Protection Agency, 2003; Torslov et al., 1997; Hellstrom, 2000) lists three organic compounds detected frequently when analyzed in biosolids.

It is important to note that there are various sources of organic compounds to which humans and animals are exposed. The USDA (Fries et al., 2002) found that pentachlorophenol (PCP)-treated wood consumed at animal production facilities increased the animal body burden of dioxin and furans. A well-correlated relationship between PCP-treated wood and certain dioxin congeners was established and represents the dioxin congeners most prevalent in meat tissue samples. Different dioxin congeners, formed through combustion processes and prone to atmospheric deposition (Meharg and Killham, 2003), were not as prevalent in the meat tissue.

ANALYTICAL ISSUES

The organic matter–rich nature of biosolids and similar residuals complicates organic compound analysis relative to the analysis of other environmental media, such as soil or water. Accurate analysis thus requires many precautions and extra analytical steps during sample collection, preservation, extraction, and analysis.

In the laboratory, the primary steps necessary for organic analysis include extraction, cleanup, and the analysis of the sample. Each cleanup step is intended to eliminate interfering compounds by using physical or chemical properties that differ between interfering compounds and the analyte of interest.

The analytical methods currently used for the determination of organic compound concentrations in biosolids leave many decisions to the discretion of the lab analyst and do not specify the extraction method or the necessary cleanup steps. Without modifications to conventional analytical procedures to establish minimum requirements, distinguishing organic compounds of concern from the plethora of beneficial or benign organic compounds found in biosolids is extremely difficult.

Many laboratory analysts that perform organic compound analysis in biosolids are not familiar with the intricacies of analysis related to this complex media (when compared with soil or water analysis), and many of the critical analytical decisions, including appropriate cleanup steps, may be missed. Unless analysts have extensive experience specific to the determination of organic compound concentrations in biosolids, the reported levels of organic compounds in biosolids should be considered suspect.

POLYCHLORINATED BIPHENYL ANALYTICAL ISSUE CASE EXAMPLE

The following case study from Wisconsin further illustrates some of the challenges with the analytical process to accurately identify and quantify organic constituents in biosolids.

The Wisconsin Department of Natural Resources (WDNR) has required analyses for PCBs in biosolids by a state-certified laboratory since the late 1970s. No standard method for this analysis in biosolids is specified. Recent efforts to establish risk-based soil concentration limits resulted in a complete review by the WDNR of the PCB data collected over the years. That review identified several concerns related to data quality, and led the WDNR to conclude that the bulk of the data submitted was unreliable for decision-making or risk assessment. Some of the reasons for reaching this conclusion are as follows:

- Commercial labs are state certified for conducting PCB analyses based on their analysts' ability to perform the analysis in distilled water. The biosolids matrix is entirely different, and the ability to perform the analysis in water does not automatically transfer to biosolids.
- No extraction method or cleanup steps are mandated in USEPA methods or in Wisconsin rules.
- There was no requirement imposed to conduct a minimum detection limit (MDL) study for the ma-

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trix of interest (biosolids) nor was any target limit of detection (LOD) specified until 1995. Even in 1995, the LOD required in Wisconsin Pollutant Discharge Elimination System permits was 10 mg kg^{-1}, which fails to identify the lower concentrations actually present in biosolids.

To correct these problems, establish necessary analytical protocol, and obtain more reliable data, the WDNR cooperated with the Wisconsin State Lab of Hygiene (WSLH) in a survey of biosolids from 50 publicly owned treatment works (POTWs) in 2000. Samples were collected by WDNR staff from each POTW and sent to the WSLH. To ensure accurate and reliable data, a complete minimum detection limit study was undertaken as well as an assessment of necessary extraction, cleanup steps, and quantification methods. The methodology described below is the consensus recommendation of the WDNR as a result of the work done by the WSLH (Wisconsin State Lab of Hygiene, unpublished data, 2002).

RECOMMENDED METHODOLOGY

Method Manual SW 846 includes USEPA Method 8082A, which can be used for either an Aroclor or a congener-specific PCB analysis. If a congener-specific analysis is performed, the list of congeners tested should include (but is not limited to) numbers 5, 18, 31, 44, 52, 66, 87, 101, 110, 138, 141, 151, 153, 170, 180, 183, 187, and 206. Whether the new USEPA Method 1668A or 8082A is used, the sample should be extracted using the Soxhlet extraction (USEPA Method 3540C) (or the Soxhlet Dean–Stark modification) or the pressurized fluid extraction (USEPA Method 3545A). The sonication method should not be used. Cleanup steps of the extract are required to remove interferences and to achieve the lowest detection limit possible. Work done by the WSLH, and WDNR experience with these methods, suggest that a LOD of 0.11 mg kg^{-1} can be anticipated for Aroclor analysis in most cases. If congener-specific analysis is done using USEPA Method 8082A, a LOD of 0.003 mg kg^{-1} for each congener can be anticipated in most cases. If the anticipated LOD cannot be achieved following cleanup techniques, a reporting limit that is achievable for the sample should be determined. This reporting limit should be reported and qualified by indicating the presence of an interference. The WDNR concluded that the following cleanup steps (USEPA, 2004) are necessary and should be mandated for biosolids:

- USEPA Method 3620C, Florisil;
- USEPA Method 3640A, gel permeation;
- USEPA Method 3630C, silica gel; and
- USEPA Method 3660B, sulfur cleanup (note that copper shot must be used instead of copper powder).

The following additional cleanup steps can be used as necessary at the analysts' discretion:

- USEPA Method 3611B, alumina; and
- USEPA Method 3665A, sulfuric acid cleanup.

The chromatogram in Fig. 1 illustrates the value of the various cleanup steps when compared with a standard for Aroclor 1254. Copper shot was already used for sulfur cleanup in the boiling flask during the Soxhlet extraction process. The alumina cleanup step did not appreciably reduce interferences, but the other steps did.

A similar study was undertaken for paper mill sludge by the WSLH (Wisconsin State Lab of Hygiene, unpublished data, 2003). The recommended extraction and cleanup steps are the same as for biosolids, except that the gel permeation cleanup step is not mandatory for paper mill sludge, but can be used at the discretion of the analyst. The following example from that study further illustrates these analytical issues.

A paper mill sludge sample was collected and split between a certified commercial lab and the WSLH. The WSLH performed the Soxhlet extraction and all successive cleanup steps to determine which were necessary. The commercial lab performed the sonication extraction and only the sulfuric acid and the silica gel cleanup steps. The WSLH analysis produced textbook chromatograms of Aroclor 1242 at a concentration of 5.5 mg kg^{-1} on a dry-weight basis (Fig. 2).

The commercial lab reported a result of <0.118 mg kg^{-1} on a dry-weight basis. Each lab was then sent remaining portions of the original sample for re-analysis and the commercial lab was requested to use the Soxhlet extraction, and the sulfur, Florisil, and silica gel cleanup steps as would be used by the WSLH. This analysis produced essentially identical results for the WSLH of 5.2, 5.4, and 5.6 mg kg^{-1} dry wt. with triplicate analysis. The commercial lab reported 2.65 mg kg^{-1} dry wt. A subsequent meeting identified several issues that explained the discrepancy. One was that the commercial lab's reported result was on a wet-weight basis. Once corrected, the result was 3.65 mg kg^{-1}. The remaining difference was due to their use of copper powder and very poor recovery (17%) rather than the use of copper shot. Once the corrections were made, the two labs using the same procedure yielded very similar results. The WDNR concluded that extraction, cleanup, and matrix-specific minimum detection limits should be specified in regulation to obtain reliable analytical results. The extraction and cleanup steps are also necessary for USEPA Method 1668A.

While the above example illustrates the difficulties with PCB analysis, the results and analytical methodology may be even worse for constituents not typically measured in biosolids. As with any analysis, reliability comes with repetition. Analyses for organic constituents in biosolids are not routine for most commercial labs so experience is typically lacking. This inexperience, combined with the lack of method specificity in regulation, yields results that must be considered suspect.

Analytical shortcomings provide perhaps the most critical limitation in performing meaningful risk assessment. The USEPA required a new sludge survey for dioxin to perform the probabilistic risk assessment used for their Round 2 decision-making. The USEPA initially proposed a regulatory approach for dioxin (USEPA, 1999b) based on a deterministic risk assessment con-

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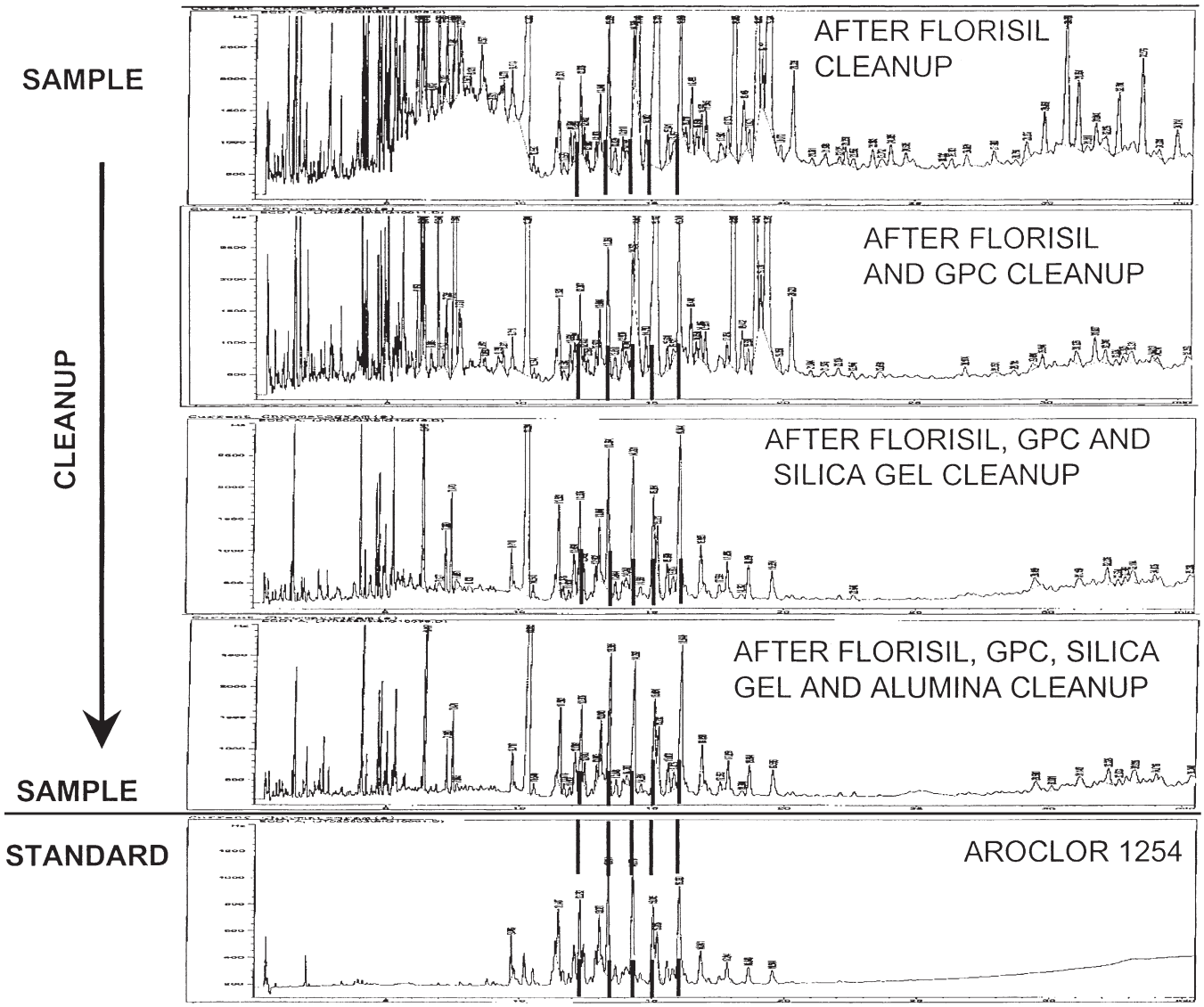

Fig. 1. Chromatograms illustrating effects of various cleanup steps in analysis for Aroclor 1254 (Wisconsin State Lab of Hygiene, unpublished data, 2002).

ducted using concentration information from the 1989 National Sewage Sludge Survey (USEPA, 1990). Many comments were received urging an update to the database on dioxin concentrations. In response, the USEPA conducted a new National Sewage Sludge Survey in 2001 to determine current concentrations of dioxin and dioxin-like compounds in biosolids (USEPA, 2002b). The analyses were conducted by a contract laboratory using high resolution mass spectrometry methods (USEPA Method 1613A [USEPA, 1994] for dioxins and furans, and USEPA Method 1668A for PCBs [USEPA, 1999a]), which can delineate specific congeners at very low detection limits. Reliable concentration data is a critical need for regulatory and implementation decision-making. Unfortunately, there are currently only a handful of laboratories throughout North America that have the capability to execute these methods.

RISK ASSESSMENT

Assessing potential risk is an evolving dynamic process. When the USEPA developed the federal biosolids regulations (40 CFR part 503; USEPA, 1993), a then state-of-the-art process was used. The deterministic assessment used discrete, single-point input values based on assumed exposure scenarios, bioavailability factors, uptake slopes, dose–response relationships, characteristics of the target population, and other variables to calculate risks for a highly exposed individual (HEI) (USEPA, 1995; Chaney et al., 1996). A recently refined alternative risk assessment approach relies on probabilistic methods, and uses an array of mathematical simulation models and a wide distribution of input variables. The final decision on the second round of the biosolids regulations (USEPA, 2003) used the probabilistic risk assessment methodology and predicted the risk approached zero for the potentially exposed population. Based on the outcome of this risk assessment, the USEPA declined to further regulate dioxin and dioxin-like compounds (7 dioxin, 10 furan, and 12 coplanar PCB congeners expressed on a total toxicity equivalence [TEQ] basis), in biosolids.

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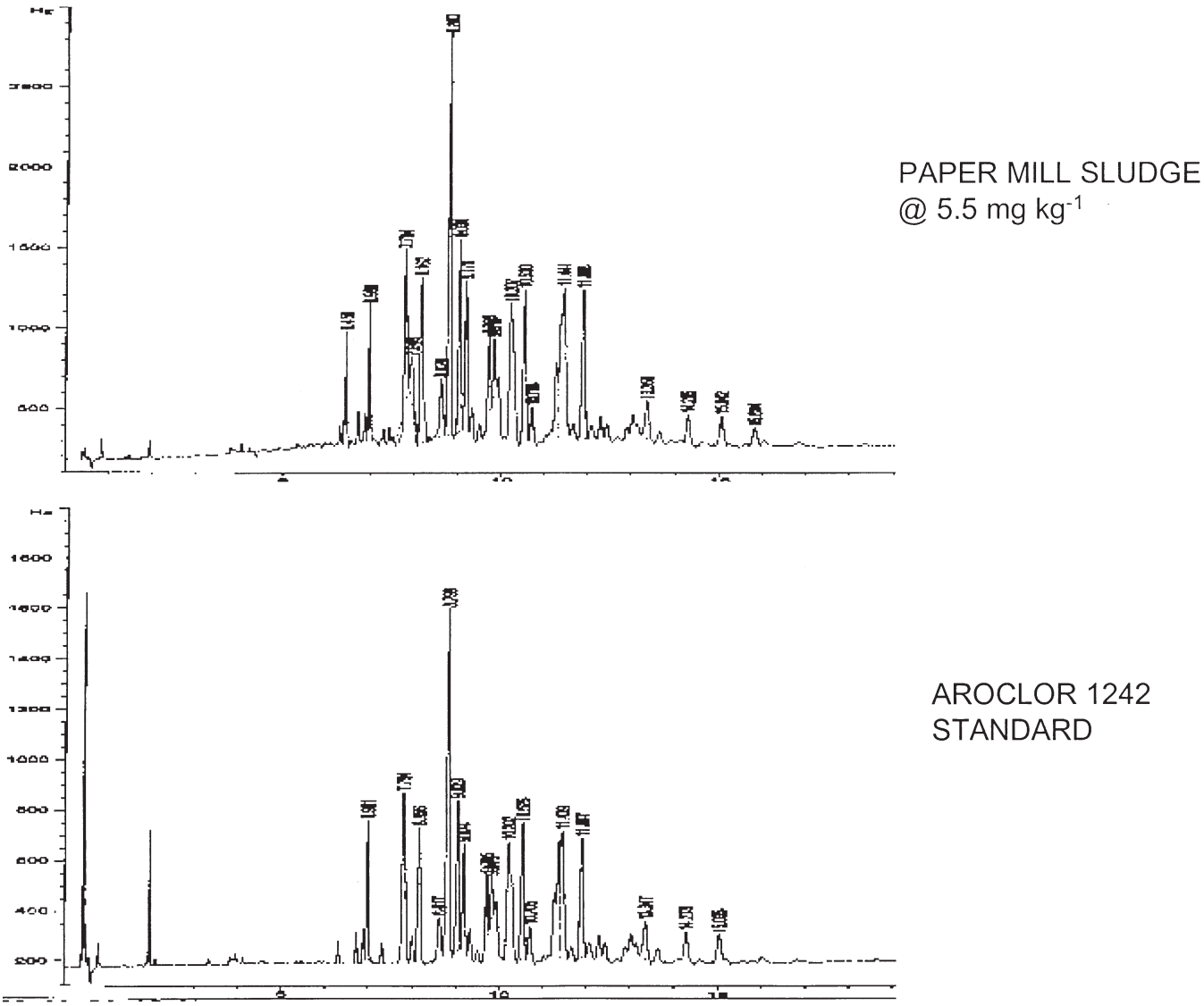

Fig. 2. Chromatograms illustrating actual sample with approximately 5.5 mg kg^{-1} Aroclor 1242 versus the standard chromatogram for Aroclor 1242 (Wisconsin State Lab of Hygiene, unpublished data, 2003).

DETERMINISTIC RISK ASSESSMENT

As described above deterministic risk assessments rely on single-point estimates of multiple input parameters to define exposure. Current risk assessments use a mixture of average and upper bound assumptions to identify a reasonable maximum exposure (RME) receptor (e.g., humans, plant, or animals). The assessment supporting the Round 1 Part 503 regulation assessed risks to an HEI. Both state and federal regulators have historically embraced the use of conservative assumptions to minimize the potential for underestimating risk and to ensure protection of human health or environmental quality. The appropriate level of conservatism in risk assessments is the subject of continued debate in setting regulatory policy.

A major concern regarding the level of conservatism in multipathway risk assessments is the cumulative effect of conservative assumptions used to define transfer and transport coefficients and other exposure parameters. Such conservatism can result in exposure and risks being significantly overestimated, oftentimes by several orders of magnitude (Finley and Paustenbach, 1994). This can have significant implications on subsequent regulation development. Overestimating exposure and resultant risk can lead regulators to unnecessarily ban or severely restrict practices, resulting in significant financial, policy, and risk implications. An example where this occurred was the first draft of the Round 1 proposed 40 CFR 503 regulation. A member of the defined population that the USEPA sought to protect would have consumed all foods at the maximum rate for that food group for their entire life (e.g., the individual would consume grain, potatoes, root vegetables, dairy, and dairy fat at the rate of the teenage male [14–16 yr] for each year of a 70-yr life). Commenters concluded that the target population or the maximally exposed individual (MEI), as defined in the 1989 draft, did not exist (W-170 Cooperative State Research Service Technical Committee, 1989). The USEPA responded with a revised deterministic risk assessment that averaged con-

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sumption rates across sex and age. That and other changes resulted in the definition of a much more plausible HEI population. With both deterministic and probabilistic risk assessments, a policy choice must also be made regarding the level of acceptable risk. The acceptable cancer risk for regulatory purposes is typically in the range of one in ten thousand to one in one million additional cases. A case study from the State of Wisconsin illustrates the effect of multiple conservative assumptions in a deterministic risk assessment. Many of the same conservative assumptions used were the same as those the USEPA used in that first round of proposed Part 503 regulations.

Case Study: State of Wisconsin Effort to Regulate Polychlorinated Biphenyl Concentrations in Soil from Land-Applied Organic Amendments (e.g., Biosolids, Paper Mill Sludge, Compost, Sediment)

This case study is intended to illustrate the subjective nature and other issues associated with the incorporation of multiple conservative assumptions in deterministic risk assessment. It is not intended to judge the validity of the assumptions.

In 1998, the State of Wisconsin began developing baseline PCB soil criteria protective of human and ecological health that could translate into regulations for the land application of materials that could contain PCBs (Wisconsin Department of Health and Family Services, unpublished data, 2002). The state sought to evaluate the public health implications associated with application of PCB-containing material to agricultural land and to identify the maximum acceptable soil concentration protective of public health and the environment. The effort examined total PCBs rather than only the coplanar congeners.

A multipathway exposure assessment was conducted with an ultimate recommendation to limit the risk from these pathways to an incremental cancer risk of 1×10^{-7} (1:10 000 000) for the target population. Concerns over cumulative exposure from fish consumption precipitated an order-of-magnitude greater protection than any other risk-based level of protection currently in place in Wisconsin. Seven specific pathways were evaluated:

soil → air → humans (occupational inhalation)
soil → air → humans (residential inhalation)
soil → humans (dermal exposure-absorption)
soil → humans (direct soil ingestion)
soil → plants → humans (ingestion: vegetable consumption)
soil → plants→ animals → humans (ingestion: meat and dairy consumption)
soil → animals → humans (ingestion: meat and dairy consumption)

The risk-based approach used by Wisconsin identified target populations and used a series of assumptions regarding diet, etc., to quantify exposure to those populations. Two target populations were identified: (i) Wisconsin farm operators who use biosolids or other material that contain PCBs as soil amendments and fertilizers on pasture or crop lands, and others who reside on these farms; and (ii) Wisconsin residents who ingest food produced on these farms. While the specific exposure assumptions used are not detailed in this paper, the target population defined had *all* of the following cumulative characteristics:

- Consumes fish consistent with the levels used to derive the fish consumption advisory for Great Lakes sport fish for a 70-yr period. The fish advisory levels are based on a protected risk level of one in ten thousand additional cancer cases. It is not assumed that PCBs in fish originate from land application of contaminated residuals unlike all other exposure assumptions.
- Consumes vegetables at the 95th percentile consumption level as specified in the USEPA Exposure Assessment Handbook (USEPA, 1997), for the home gardener year-round each year for a 70-yr period. One-hundred percent of these vegetables were assumed to be grown on fields where biosolids, or other material containing PCBs, were applied. Conservative values were used for plant uptake coefficients.
- Consumes beef fat and dairy fat at the 95th percentile consumption levels specified in the Exposure Assessment Handbook (USEPA, 1997) each year for a 70-yr period. All the animal products were assumed to come from animals that either grazed on fields where biosolids or other material containing PCBs were applied or were fed crops grown on these fields. Grazing animals were conservatively assumed to consume 6% of the daily dry matter intake as soil. Animals consuming crops grown on amended fields were additionally assumed to ingest 0.6% of the daily dry matter intake as soil adhered to the crops. Conservative values were used for plant uptake coefficients as well as for bioaccumulation factors (BAFs) in beef and dairy fat.
- Is occupationally exposed to dust containing PCBs, with the dust level corresponding to the occupational exposure limit for particulate matter recommended by the American Conference of Governmental Industrial Hygienists. Exposure occurs 8 h d^{-1}, 90 d yr^{-1} for a 70-yr period.
- Is exposed to residential dust containing PCBs for all remaining hours for a 70-yr period.
- Is exposed daily, through dermal contact, to soil amended with biosolids or other material that contain PCBs.
- Ingests 50 mg d^{-1} of soil amended with biosolids or other material that contain PCBs (adults) or 200 mg d^{-1} of such soil (children from years 1 to 6).

Wisconsin relied on single-point estimates (e.g., a deterministic approach) to define exposure to the target populations. The approach used to characterize exposure could be claimed to define a population of maximally exposed individuals. The USEPA restructured their HEI assumptions to define exposure in Round 1 of the 40 CFR Part 503 Rule, with the Clean Water

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Act–mandated objective of protecting the HEI from "reasonably anticipated adverse health effects." A recently published National Academy of Sciences report (National Research Council, 2002) noted the problems associated with using an HEI approach. Specifically, the report stated that the "general practice has changed from using the HEI as the receptor of concern, because such an individual is unlikely to exist, to using an individual with reasonable maximum exposure (RME). An RME individual is a hypothetical individual who experiences the maximum exposure that is reasonably expected to occur (i.e., an upper-bound exposure estimate)."

The problems associated with the exposed population as defined by Wisconsin were compounded by multiple factors. First, while Wisconsin reviewed the USEPA technical support documents for the Round 1 rule, some of the single-point estimates were even more conservative than those peer-reviewed values used by the USEPA. In addition, Wisconsin considered aggregate exposure (e.g., exposure from residuals containing PCBs was summed across all pathways). While the National Academy of Sciences report supports the use of aggregate exposure when such exposure can be reasonably anticipated, it is done so in the context of an RME approach.

The approach used by Wisconsin, combined with an aggregate risk assessment, compounded the effect of using conservative assumptions and resulted in a level of risk that was potentially several orders of magnitude more protective than the stated risk level of 1×10^{-7}. The draft soil PCB criteria recommended by Wisconsin were 0.1 μg kg^{-1} (dry-weight basis) if grazing was allowed or 0.3 μg kg^{-1} if grazing was never allowed. These criteria are less than the mean background soil PCB concentrations in never-amended Wisconsin soils (i.e., mean 0.48 μg kg^{-1} with a range of 0.14–1.33 μg kg^{-1}) (Wisconsin State Lab of Hygiene, unpublished data, 2002; AXYS Labs, unpublished 2002).

If implemented, the draft soil criteria would have had a profound effect on the beneficial reuse of biosolids (and other materials) in Wisconsin. Specifically, based on the PCB concentrations found in the WDNR 2000 biosolids survey, beneficial reuse would have been eliminated, with management practices shifting to either landfilling or incineration. The financial impact associated with a shift in management practices for biosolids alone was estimated to be in excess of $300 million for the capital construction costs and at least $40 million in increased annual operating costs (WDNR, unpublished fiscal analysis, 2002). The cost per potential cancer case avoided (assuming a 70-yr exposure) was estimated in excess of one trillion dollars. No estimate of population size was provided in the risk assessment, so no effective evaluation of public health benefits was possible for the input variables. In the authors' opinions the size of the target population that met all of the required criteria for this assessment would approach zero. Because background concentrations exceed the criteria, there would effectively be no public health benefit.

The criteria would have had a significant effect in other areas as well. Wisconsin would have been required to adopt major policy changes, including the elimination of the state's statutory mandate for encouraging the beneficial reuse of biosolids. The recommendations also may have (i) had a major effect on the ability to market agricultural commodities in Wisconsin, (ii) had a major effect on property transfer, and (iii) forced the WDNR (or other agencies) to regulate animal manures and/or commercial fertilizers that were land-applied.

The WDNR tentatively chose not to adopt the recommendations based on the risk assessment, but to impose risk management decisions that would limit annual loading of PCBs to allow the retention of current practices. Other general requirements would also have been imposed, but current beneficial use practices would not have been affected. However, when the USEPA decided not to further regulate dioxin and dioxin-like compounds in biosolids based on the low risk potential (USEPA, 2003), the WDNR likewise decided to suspend regulatory action for PCBs. That decision reflects a full acceptance of the probabilistic risk assessment conducted by the USEPA.

PROBABILISTIC RISK ASSESSMENT

The National Academy of Sciences report on biosolids (National Research Council, 2002) recognized that both the policy and science related to conducting risk assessments have evolved considerably. Improvements include the ability to more appropriately characterize exposure by substituting probability distributions for single-point estimates. This approach, often referred to as a probabilistic risk assessment (PRA), can minimize many of the concerns related to overestimating exposure and the compounding nature of conservative assumptions. In 2001, the USEPA issued guidance for conducting PRA for both human health and ecological risk assessments (USEPA, 2001). This guidance provides policies and guiding principles on the application of PRA methods to risk assessments specifically in the USEPA Superfund program; however, the guidance is broadly applicable across USEPA programs. The guidance focuses on Monte Carlo analysis as a method of quantifying variability and uncertainty in risk. A tiered approach to PRA is recommended for Superfund sites, beginning with a point-estimate analysis or deterministic risk assessment, progressing to PRA as needed to satisfy site-specific decision-making needs. In 2002, the USEPA issued a draft report using PRA to evaluate the potential human exposure and risk to dioxins from land-applied biosolids (USEPA, 2002b). As an analysis of national risk distributions, the USEPA determined early in the process that PRA would be needed to support regulatory decision-making.

In a PRA, distributions for each input parameter are combined to yield an overall exposure distribution. The main advantage of PRA is that the degree of conservatism can be more accurately determined. The USEPA guidance calls for using the exposure distribution to identify the RME, which is defined as risks corresponding to the 90th to 99.9th percentiles of the risk distribution. The definition of RME is consistent between deterministic and probabilistic risk assessment. The main

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difference in outcome is typically due to the ability of PRA approaches to avoid unintended compounding of conservative assumptions.

The USEPA dioxin PRA used the results of 2001 National Sewage Sludge Survey (USEPA, 2002b) to provide distributions of concentrations of dioxin and dibenzofuran congeners and coplanar PCBs. Receptors evaluated were based on the potential exposure and risk to farmers (and their families) who apply biosolids to their land and consume a high percentage of their own agricultural products. The USEPA's assumption that each receptor was exposed by all of the identified exposure pathways has been repeatedly criticized; however, as will be shown below, this may not be a significant factor affecting the USEPA's interpretation of the results.

Exposure point concentration distributions were determined using source partition modeling of constituent releases, fate and transport modeling, and food chain models. The distributions were combined with exposure factor distributions to yield dose distributions for various receptors. Risks were estimated using the then-current dioxin cancer slope factors, rather than selecting slope factors from the draft reassessment (USEPA, 2000) that is still undergoing peer review. Total multipathway risks were estimated to be 1×10^{-6} for both adults and children at the 50th percentile, and 2×10^{-5} and 1×10^{-5} for adults and children, respectively, at the 95th percentile. Most of the risk was attributable to beef and milk ingestion, with beef ingestion contributing slightly more than half the risk. The fact that two exposure pathways contributed the majority of the risk suggests that the effect of adding multiple exposure pathways together did not unduly influence the outcome of the risk assessment.

The USEPA also evaluated the effect on risk estimates of assuming that biosolids exceeding cutoff limits for TEQ of dioxin was excluded from land application. Risk estimates did not change when either a 300 or 100 ng kg^{-1} TEQ cutoff was applied to the 2001 National Sewage Sludge Survey sample data, suggesting that regulation of dioxins in biosolids at either of those cutoffs would not reduce risks in the exposed population. For the theoretical highly exposed population, only 0.003 new cases of cancer could be expected each year or only 0.22 new cases of cancer over 70 yr. The risk to people in the general population of new cancer cases resulting from biosolids containing dioxin would be even smaller due to lower exposures to dioxin in land-applied biosolids than the highly exposed farm family that the USEPA modeled. The USEPA concluded that the information available on dioxin exposures, toxicity, and cancer risks supported a decision that no numeric limits or management practices were required to adequately protect human health and the environment from the adverse health effects of dioxins in land-applied biosolids.

The USEPA dioxin risk assessment provides a useful model for additional risk assessments of other organic chemicals. Application of the model to other chemicals will be limited by scant information on concentrations in biosolids, as well as by undeveloped data on fate and transport parameters and uptake into the food chain. However, sensitivity analysis of the dioxin risk assessment can help focus efforts on the most important fate and transport parameters and food chain pathways. Application will be limited to chemicals whose structure and behavior are similar.

Information needs for complex, multipathway risk assessments are substantial. For many organic compounds with the potential to be present in biosolids, data gaps in critical areas limit the accuracy of risk assessments. Risk assessments for PCBs and dioxin and dioxin-like compounds are expected to be more accurate because much is known regarding their fate and transport. Unfortunately, there are many compounds for which much less is known.

ORGANIC CHEMICALS AND SIMPLIFIED MODELS

Commonly, insufficient data exist for a detailed environmental risk assessment for a chemical of concern. Nevertheless, initial risk management decisions can be made for most organic chemicals, even with minimal chemical and environmental data. Mathematical models that examine organics being added to the soil environment have existed for more than 45 yr (Gardner and Brooks, 1957; Day and Forsythe, 1957). Model results are derived from limited input data, and can be used to make more informed decisions in the management of risk for the chemicals of concern. The complexity of the mathematical models depends on inputs but, in general, the more numerous the inputs or assumptions, the more complex the model and the more experienced the modeler must be. Models are only as good as the input data and the experience of the modeler interpreting the results. In general, models can be used to determine the likelihood that a contaminant leaches to ground water, runs off to surface water, or volatilizes into the atmosphere. Once that likelihood is known, management practice modifications can be made to minimize the potential loss.

Models have been classified into three categories based on intended use: management models, screening models, and simulation models (Wagenet, 1986). Management models provide basic qualitative or quantitative information to make decisions for practical situations. Screening models address transport and persistence of chemicals in soil under idealized conditions. The results can provide a comparison of organic chemicals, producing a relative comparison and/or description of the chemicals' environmental fate. Simulation models are complex and data intensive, but provide detailed predictions of chemical behavior in the environment.

Screening models of varying degrees of complexity exist. We describe in general terms a model developed by Jury et al. (1983). The model, and its uses as a screening tool, are described in a series of articles (Jury et al., 1983, 1984a, 1984b, 1984c). The model uses the basic principles of solute movement, persistence, degradation, and volatilization, and provides sufficient output to guide management decisions. Screening models are designed to compare the relative movement of one organic chemical to another organic chemical, under similar conditions.

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The Jury transport equations are derived from the basic flux equations and mass balance equations. The model assumes that chemicals undergo linear, reversible, equilibrium adsorption, and first-order biochemical decay while leaching at an average drainage rate.

Each chemical of concern needs to be characterized by two environmental factors: the organic carbon partition coefficient and the biochemical half-life. The chemical is also assumed to be applied uniformly in a single application. The soil characteristics needed, and assumed uniform throughout the soil area in question, are volumetric water content, soil bulk density, and the organic carbon fraction.

The derivation of the model is beyond the scope of this paper and can be found in many standard soil physics texts as well as the Jury articles mentioned above. The model can be run on desktop computers with publicly available programs such as HYDRUS 1-D (Simunek and Van Genuchten, 1998).

The models represent only the conditions specifically described, and screening models are only able to represent a specific uniform location. Heterogeneity of the soil and, therefore, soil properties is the rule rather the exception on a field or landscape scale. Models tend to use simplified assumptions, and field application of the models must consider heterogeneity issues. The land application of the organic chemical also tends to be random rather than uniform as assumed in the model. Several methods can be used to account for this heterogeneity. One example is to run the model under the range of conditions existing in the field, and then use the most conservative results for the organic chemical of concern. This provides a model result that, when used to make a risk management decision, is conservative. The more data used in the model, the more representative the model output can be of land application at field scales.

The intent of introducing this approach is to encourage all involved in sustainable land application to collect meaningful data for use in more complex models that provide more information. The use of these models is not intended to replace risk assessment but to provide data that the land applier can use in the interim until data are available and an improved risk management decision can be made.

CONCLUSIONS

Improved specificity of analytical methods is necessary to quantify organic pollutants in residuals. This includes a matrix-specific determination of the method detection limit, extraction methods, cleanup steps that must be used, and quantification methods. If sufficient information is known about a chemical of concern, a probabilistic risk assessment will generally yield a better indication of threat to human health or the environment than will a deterministic assessment. If insufficient information is available for a pollutant, data gaps should be identified and addressed in an effort to gain that information. In the latter cases, mathematical models can be used on an interim basis to determine loss potential of the pollutant via different paths, and management practices can be adjusted to minimize that loss potential.

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