Appendix G. Chemical-specific Soil Half-life

G.1   Algorithm for Estimating Chemical-specific Soil Half-life

The average concentration of a substance in soil (Csoil) is a function of several different variables, including deposition rate, accumulation period, mixing depth, soil bulk density, and the chemical-specific half-life, as shown in equation G-1 below:

$$Csoil = [GLC \cdot (Dep\text{-}rate) \cdot (86,400) \cdot (X)] / [Ks \cdot (SD) \cdot (BD) \cdot (Tt)]$$ **(Eq. G-1)**

where: Csoil = average soil concentration at a specific receptor location over the evaluation period (µg/kg)

GLC = ground level concentration from the air dispersion modeling (µg/m^3)

Dep-rate = vertical rate of deposition (m/sec) (see Chapter 2 for values)

86,400 = seconds per day conversion factor

X = integral function accounting for soil half-life

Ks = soil elimination time constant = 0.693/T1/2

SD = soil mixing depth = 1 cm for dermal scenario

BD = bulk density of soil = 1333 kg/m^3

Tt = total averaging time = 70 years = 25,550 days

The soil half-life is part of the integral function X determined as below:

$$X = [\{Exp(-Ks \times Tf) - Exp(-Ks \times To)\} / Ks] + Tt$$ **(Eq. G-2)**

where: EXP = Exponent base e = 2.72

Ks = soil elimination constant = 0.693/ T1/2

T1/2 = chemical-specific soil half-life

Tf = end of exposure duration (days); 25,500 for a 70-year exposure

T0 = beginning of exposure duration (days) = 0 days

Tt = total days of exposure period = Tf - T0 (days)

Estimating toxicant soil concentration is necessary for estimating dose from incidental soil ingestion by home raised meat, home raised produce, and dermal absorption via contact with contaminated soil.

Since the chemicals that the Hot Spots program is concerned with are emitted into the air and then subject to deposition to the soil, there are only two classes of chemicals considered.   These classes are the semivolatilve organic chemicals, such as PAHs, PCBs and dioxins, and toxic metals such as hexavalent chromium, cadmium, lead,

arsenic, and beryllium. Other programs that consider hazardous waste sites may be concerned with other classes of chemicals such as volatile organic solvents.

Soil extraction studies were often used to estimate soil half-life by using rigorous extraction techniques with an organic solvent (e.g., dichloromethane) to release as much of the remaining chemical from soil as possible. The amount of chemical extracted from soil is considered the fraction that is bioaccessible for uptake. The bioaccessible fraction of a pollutant in soil, which is reduced over time by various processes, is used to estimate the soil half-life of chemicals.

An extraction procedure that mimics or parallels bioavailability is preferable for assessing exposure and risk than one whose sole virtue is the removal of the largest percentage of the compound from soil (Kelsey, 1997; Reid, 2000; Tang, 1999). These investigations suggest that mild, selective extractants may prove more useful as predictors of exposure than the methods currently used for regulatory purposes in some programs. The solvent needed for predictive purposes may vary with the pollutant and the species of concern.

Another common method to determine soil half-life of organic compounds is through mineralization, or ultimate degradation, studies. Instead of measuring the parent organic compound remaining in soil through extraction methods, mineralization studies add the radiolabeled chemical to soil, and measure the release of $^{14}CO_2$ from soil resulting from "ultimate" breakdown of the compound by microbial degradation.

Mineralization studies may be quite useful for determining the soil half-life of organic chemicals, if abiotic loss processes are minor, and if mineralization of the chemical occurs quickly once primary degradation (and presumably loss of toxicity) of the chemical takes place.

G.2   Metals and Other Inorganic Compounds

Biodegradation as such is not expected to occur with metals and other elements because of their elemental nature. However, once a metal is deposited to soil, leaching or weathering may eventually result in movement of the metal out of the system. The valence and charge of the metal in soil affects its sorption, solubility, and retention in soil. Additionally, soil pH and availability of charged sites on soil surfaces are the primary factors controlling formation of the ionic species, charged metal complexes or precipitates (US EPA, 2003).

Soil with predominately negatively charged sites is more plentiful in the United States; less than 5% of the total available charge on the soil surface is positively charged (US EPA, 2003; Fairbrother et al., 2007). For the metals that largely exist as cations in soil (beryllium, cadmium, lead, inorganic mercury and nickel), there is a greater propensity to be sorbed to soil particles. This makes them less bioavailable, but it also results in greater loading of metals into the soil because of reduced mobility and leaching.

Under most relevant scenarios, arsenic, chromium, fluoride and selenium deposition to soil typically results in an anion or formations of anionic complexes with oxygen (US EPA, 2003; Fairbrother et al., 2007). The most common forms of arsenic are arsenate (As(V)) and arsenite (As(III)), which are present in soil solution in the form of AsO_4^{3-} and AsO_3^{3-}, respectively. Similarly, selenium can be present as selenates (SeO_4^{2-}) and selenites (SeO_3^{2-}). Hexavalent chromium (Cr(VI)) can exist as chromate (CrO_4^{2-}) which is usually considered more soluble, mobile, and bioavailable than the sparingly soluble chromite (Cr(III)), which is normally present in soil as the precipitate $Cr(OH)_3$. Anionic metals generally move into pore water where they can leach out of the system faster, but are also more bioavailable.

As a default estimate, the metal content of soil is assumed to decay with a half-life of 10^8 days unless site-specific information is presented showing that soil conditions will result in the loss of soil metal content, i.e., soil aging or leaching. The 10^8 default means that significant loss or removal is not occurring within the risk assessment time frame of interest.

Some fraction of chromium (VI) will undergo reduction to the less toxic chromite (CrIII) species when deposited to soil (Bartlett, 1991; Fendorf, 2004; Stewart et al., 2003). However, oxidation reactions of chromium (III) to chromium (VI) can also occur at the same time in soil. Characterizing the reduction of chromium (VI) to chromium (III) is complex and "it is not possible to predict how chromium compounds will behave in soil until the soil environment has been adequately characterized" (Cohen et al., 1994a, citing Gochfeld and Whitmer, 1991). Several tests have been suggested for evaluating the reducing capacity of soils and may be considered in the development of site-specific information (Cohen et al., 1994a, citing Bartlett and James, 1988; Walkley and Black, 1934). These tests are described as follows:

> "(1) Total Cr(VI) Reducing Capacity. Use the Walkley-Black (1934) soil organic matter determination in which carbon oxidizable by $K_2Cr_2O_7$ is measured by titrating the Cr(VI) not reduced by a soil sample (in suspension with concentrated H_2SO_4) with $Fe(NH_4)_2(SO_4)_2$.
>
> (2) Available Reducing Capacity. Shake 2.5 cm^3 of moist soil 18 hours with 25 mL of 0.1 to 10mM chromium as $K_2Cr_2O_7$ in 10mM H_3PO_4, filter or centrifuge, and determine Cr(VI) not reduced in the extract by the s-diphenylcarbazide method.
>
> (3) Reducing Intensity. The procedure is the same as that used in (2) above except that 10mM KH_2PO_4 should be used in the matrix solution in place of H_3PO_4."

In the absence of site-specific data, the public health protective assumption is to assume that hexavalent chromium remains in the hexavalent form in the soil. In most instances this will lead to an over prediction of hexavalent chromium concentration from airborne deposition.

G.3   Organics

Organic compounds deposited in soil are subject to degradation or loss by both biotic and abiotic processes. Biotic processes include degradation by soil microorganisms. Abiotic loss of organic compounds in soil includes such processes as photochemical reactions (if on the surface of the soil) or volatilization from the soil.

For some persistent organic chemicals, such as PAHs, soil aging is the abiotic process causing the most loss. Aging is associated with a continuous diffusion and retention of compound molecules into remote and inaccessible regions within the soil matrix over time, often on the order of weeks or months, thereby occluding the compounds from abiotic and biotic processes (Northcott and Jones, 2001).

Many earlier soil half-life studies assumed that decreased soil extractability and bioavailability of chemicals with time was due to biodegradation by soil microorganisms, when, in fact, soil aging is a significant or dominant factor. Soil aging represents an abiotic loss process in which chemicals in soil become inaccessible for microbial degradation. Soil half-life of an organic compound can vary to a large extent depending on pre-treatment of soils before or after addition of the chemical to soil, the methodology used for soil extraction of the compound, and soil organic content. Other variables that can influence a soil half-life include vegetation coverage, weather and climate, and the presence of co-contaminants.

The organic carbon content of soil is often a major factor influencing the half-life of an organic compound. Increasing the organic carbon content of soils will increase sequestration and decrease bioavailability of organic chemicals. The amount of organic material in the soil is expressed as either organic carbon or organic matter. A conversion factor of 1.724 can be used to approximate the OC content of a soil that is expressed as OM (Northcott and Jones, 2001). The OC or organic matter (OM) contents of the soils used are identified in the summaries below if included in the study methodology. The OC content of the contaminated soil at a particular site can be taken into consideration if enough data are present to show that the OC content is a significant factor for the soil half-life of an individual chemical. A default assumption is available for the Hot Spots program, in which the fraction organic carbon in soil is 10%.

Considerable differences between field and laboratory half-life estimates have also been found for some organic chemicals such as PAHs (Doick et al., 2005). Pollutant fate studies are frequently performed under laboratory conditions and over short time periods. Field studies under realistic environmental conditions and protracted time frames probably represent a better estimate of the soil half-life and, therefore, carry more weight for estimating the soil half-life.

G.3.1 Creosotes

Creosotes are of concern primarily because of the polycyclic aromatic hydrocarbon content, which represent 85-90% of creosote constituents (Cerniglia, 1992). Therefore, in terms of soil half-life of this complex mixture, OEHHA recommends using the PAH half-life of 429 days for creosotes (see below).

G.3.2 Diethylhexylphthalate

Phthalates share the same basic structure of an esterified benzenedicarboxylic acid with two alkyl chains, and are chemically stable in the environment (Cartwright et al., 2000; Staples et al., 1997). Thus, the general absence of high concentrations of phthalates in the environment indicates the importance of biodegradative processes, specifically those mediated by microorganisms because higher organisms are unable to cleave phthalate's aromatic ring.

Metabolism of DEHP often results in the formation of the MEHP and phthalic acid. These metabolites retain some toxicological properties but are metabolized at a much faster rate than DEHP. Therefore, mineralization (i.e., ultimate degradation) of DEHP represents a reasonable and health protective indicator of the destruction of the phthalate's toxicological potential (Maag and Lokke, 1990). The very high Koc and Kow values for DEHP relative to other phthalates promote slower degradation in soil because a major fraction of this compound can eventually become strongly sorbed to soil organic material (i.e., soil aging) and therefore becomes much less bioavailable to soil microorganisms (Gejlsbjerg et al., 2001; Madsen et al., 1999).

Numerous microbial DEHP degradation studies are available in the literature, many of which measured degradation in unadulterated agricultural/garden soil. Only two studies were located in which DEHP soil degradation was investigated outdoors. In one study, DEHP-polluted sandy soil was mixed with compost topsoil and fertilizer, and then layered over a grass-covered plot (Maag and Lokke, 1990). White clover and grass were sown into the plot with four soil samples collected for analysis over 192 days. The depletion of extracted parent compound from soil roughly followed first-order kinetics with a half-life of 73 days.

In the other outdoor study, [^{14}C]DEHP was applied to sandy soil (pH 6.8, organic matter 0.3%) and potatoes planted the first year, followed by planting of barley during the second year (Schmitzer et al., 1988). Only 6.9% of the applied radiocarbon, mainly as DEHP, was recovered after 111 days when the potatoes were harvested. Nearly all the remaining activity, at least 92.3%, was lost to the atmosphere as ^{14}CO$_2$. After 446 days when the barley was harvested, only 1.7% of the radiocarbon was found in the soil. A half-life was not determined, although assuming first order kinetics, the half-life would roughly be 30 days over the first four months of the study.

In a highly detailed laboratory study, Madsen et al. (1999) revealed that there are actually two phases in the mineralization of [^{14}C]DEHP in a sandy loam soil (pH 5.9, OC 2.5%) over a 130 day exposure - an initial phase during the first 30-60 days described

well by first-order kinetics, and a late phase in which mineralization activity was much lower. This second phase was thought to represent mineralization that was increasingly regulated by strong sorption to organic matter, resulting in decreased bioavailability to soil microbes. The researchers also observed mineralization was strongly regulated by temperature, with the rate of mineralization increasing with increasing temperature. To account for diurnal swings in temperature that would occur in the field, the mean half-life over the temperature range examined (5, 10 and 20 °C) was 99 days during the initial phase and 161 days during the late phase.

A similar two-phase degradation rate for [^{14}C]DEHP was observed by Roslev et al. (1998) in a sludge-amended soil (DEHP is a common contaminant in sludge). The half-life for mineralization in a sandy loam soil (pH 5.9, organic matter 2.5%) was found to increase 2.5-fold in the late phase from 58 to 147 days.

Slow degradation of DEHP has been observed in other laboratory studies. Cartwright et al. (2000) observed that only 10% of DEHP added to a sandy clay loam soil (pH 6.25, OC 3.78%) was removed by indigenous microbes by day 70. Gejlsbjerg et al. (2001) observed an average mineralization of [^{14}C]DEHP in three Danish agricultural soils (pH 6.0-6.6, OC 2.2-3.0) to be only 13% (range = 8.46 to 21.8%) over two months. In both studies, strong sorption to soil organic matter was assumed to be the reason for slow microbial degradation.

On the other hand, rapid soil degradation of DEHP has also been observed. Kirchmann et al. (1991) determined a half-life of 20-80 days for loss of parent DEHP extracted from soil (pH 7.3, OC 1.77%), although the data suggested more of a linear disappearance of DEHP with time, rather than a first order disappearance. Shanker et al. (1985) observed a half-life of 15 days for loss of parent DEHP extracted from garden soil (pH 8.2) under a relatively high incubation temperature (30 °C).

The soil half-life of DEHP can vary greatly depending on the soil conditions, with a significant amount of the parent compound eventually being sorbed to soil organic matter for long periods and becoming recalcitrant to breakdown by soil microbes. The soil half-life of 73 days based on the field study by Maag and Lokke (1990) is used here as the default soil half-life for DEHP. Similar results were obtained in comprehensive soil mineralization studies by Madsen et al. (1999) and Roslev et al. (1998), although first order kinetics were not strictly followed over the full length of the studies.

G.3.3 Hexachlorobenzene

Hexachlorobenzene is a persistent soil contaminant that does not appear to be significantly degraded in soils by either abiotic or biodegradation processes (Isensee et al., 1976; Beall, 1976). In a simulated field experiment conducted in a greenhouse, HCB applied to soil almost completely volatilized from the first two cm of soil after 19 months. However, only about 20% of the HCB was lost at a soil depth of 2-4 cm over 19 months. Only the parent compound was found in soil throughout the experiment suggesting HCB could be quite stable and persistent in a plowed field. It should be

noted that this study used a single addition of HCB to the soil and the distribution of HCB with long-term low level (deposition) is likely to be different.

A soil half-life estimate for HCB was obtained from a controlled laboratory experiment conducted in plastic-covered pots over a period of 600 days (Beck and Hansen, 1974; Bro-Rasmussen et al., 1970). Analysis for parent compound following soil extraction showed a soil half-life for disappearance of HCB to be 969-2089 days with a mean of 4.2 years. In a similar experiment, Isensee et al. (1976) observed no loss of HCB from soil in covered beakers over a one-year period.

The data show loss of HCB from soil to be primarily by volatilization with essentially no loss due to microbial degradation. It is recommended that as a default estimate, the deposition of HCB to soil in particle form be assumed to decay with a half-life of 10^8 days, similar to the metals.

HCB accumulation in the soil from airborne sources has been shown to occur in field studies. There are a couple of mechanisms that could account for this observation. HCB could partition and bind tightly onto airborne particulate matter and then be subject to deposition. Alternatively, tight binding of gaseous HCB to soil could effectively make the soil a sink for gaseous airborne hexachlorobenzene. The studies in which hexachlorobenzene is added directly to soil establish that hexachlorobenzene below a certain depth remains in the soil, presumably bound.

G.3.3 Hexachlorocyclohexanes

The α- and γ-forms of the HCHs are the most common isomers in technical grade HCH, while the β-isomer is generally the most environmentally persistent. Similar to HCB, loss of HCH deposited on soil is expected to be primarily from volatilization, although some microbial degradation has been shown to occur with the HCHs (Spencer et al., 1988; Jury et al., 1987). HCH tilled into soil will adsorb to soil organic matter significantly reducing the potential for volatilization. HCHs can undergo dehydrochlorination by soil microbes in moist, acidic-to-neutral soils (Yule et al., 1967). Anaerobic soil conditions tend to favor faster degradation over aerobic conditions (MacRae et al., 1984).

No recent soil half-life studies for HCHs conducted in the U.S. could be located. Early field studies in the U.S. suggested a soil half-life for Lindane (γ-HCH) to be on the order of months to years (Lichtenstein and Schultz, 1959; Lichtenstein and Polivka, 1959). However, the method of detection used also included detection of relatively non-toxic degradation products of Lindane. It was also unclear if offsite atmospheric deposition of HCHs onto the field plots was occurring, which can dramatically increase the apparent half-life of HCHs if not taken into account (Meijer et al., 2001).

Table G.1   Soil half-lives (days) for HCHs in subtropical environments of India.

	Singh et al., 1991[a]	Kaushik, 1989[a]	Srivastava & Yadav, 1977
α-HCH	55	-	-
γ-HCH	85	-	-
β-HCH	142	-	-
Technical HCH	-	23	44

[a] Half-lives are an average of cropped and uncropped soils

In an Indian field study, Kaushik (1989) monitored the loss of technical grade HCH sown into the top 15 cm of a field that remained fallow, and a field that contained plants and was watered regularly. The climate was characterized as subtropical, and the soil in both fields was sandy loam with a pH of 8.2 and an OC content of 0.8-1.0%. In the fallow field, the HCH half-life in the upper and lower 7.5-cm soil layers was 21 and 41 days, respectively, with a combined total half-life of 26 days. In the planted field, a total half-life of 20 days was recorded, with little difference in HCH loss observed between the upper and lower soil layers field.

In another Indian field study, Singh et al. (1991) determined the soil half-lives for several HCH isomers sown into the top 10 cm of cropped and uncropped sandy loam soil (pH 7.8; OC 0.63%) over a 1051 day period. Half-life values in the subtropical climate showed similar persistence in cropped and uncropped treatments. The longest half-life was observed for β-HCH (100 days cropped; 183 days uncropped) and the shortest half-life was observed for α-HCH (56.1 days cropped; 54.4 days uncropped). Another field study in India observed an average soil half-life of 44 days (range: 35 to 54 days) for a low concentration of technical grade HCH applied under cover of maize crop over three years of planting (Srivastava and Yadav, 1977).

Researchers have noted that the soil half-life for HCHs estimated in tropical climates likely underestimates the half-life for HCHs in cooler, temperate climates of the U.S. due to greater volatility, and probably higher microbial degradation, at warmer temperatures (Singh et al., 1990; Kaushik, 1989). Because temperate climate of California will tend toward lower volatility of HCHs from soil, the longer HCH half-lives determined by Singh et al. (1991) in Table G.1 are recommended for use in the "Hot Spots" program. If the HCH isomer profile in the soil is unknown, an average of the three isomer soil half-lives (94 days) can be used.

G.3.4 4,4'-Methylenedianiline

 Cowen et al. (1998) investigated biodegradation of 4,4'-methylenedianiline under aerobic and anaerobic conditions using ^{14}C labeled methylenedianiline. The data showed that, after 365 days of aerobic biodegradation in silt loam soil, 59.9% of 4,4'-methylenedianiline remained intact. Based on the aerobic biodegradation data from this study, using first-order kinetics default for dissipation of chemicals, OEHHA derived a soil half life of 455 days for 4,4'-methylenedianiline.

G.3.5 Polychlorinated Biphenyls (PCBs)

Polychlorinated biphenyls (PCBs) are a mixture of chlorinated biphenyl congeners that vary in the degree of chlorination. The degree of chlorination has a major impact on soil half-life. Several different mixtures were marketed and used widely before PCBs were banned because of their toxicity, environmental persistence and bioaccumulative properties. Small amounts are generated as combustion byproducts and these emissions are subject to the Hot Spots program. The toxicity of individual congeners varies widely. For these reasons, meaningful overall soil half-life for PCBs is difficult to ascertain for situations in which PCB emissions are not speciated and the cancer potency factor for the entire mixture is applied. A half-life of 940 days for Aroclor 1254 was derived by Hsieh et al. (1994). This value is used by the Department of Toxic Substances Control in CalTOX. In 2000, OEHHA proposed to use this value for all Aroclor mixtures and airborne emissions of unspeciated PCB mixtures generated from Hot Spots facilities.

Harner et al. (1995) studied four PCB congeners (28, 52, 138, 153) in air, herbage, and soil of the southern U.K. over the period 1942-1992 and observed soil half-lives ranging from 7 to 25 years (mean 18 years) (6570 days). Wania and Daly (2002) estimated soil half-lives of seven PCB congeners (8, 28, 52, 101, 153, 180, 194) ranging from 550 hours (23 days) to 1,700,000 hours (70,833 days).

Sinkkonen and Paasivirta (2000) suggested soil half-lives for eleven PCB congeners, ranging from 26,000 hours (1,083 days) to 330,000 hours (13,750 days), based on the work of Lake et al. (1992), Beurskens et al. (1993) and Brown et al. (1984).

Doick et al. (2005) studied long-term fate of two PCBs in an agricultural soil in Germany. Their observation over 152 months concluded that the soil half-lives were 10.9 years (3979 days) for PCB 28 and 11.2 years (4088 days) for PCB 52. The authors attributed the much longer soil half-lives of PCBs than estimates in other studies to length of study, field study conditions, vegetation (type and coverage), weather and climate, the presence of co contaminants and, particularly, soil type -- a high silt, high clay content, "heavy" soil with reduced water infiltration, compared with higher porosity, sandy soils.

There is great variability in soil half-lives among the PCB congeners in the above studies. The OEHHA adopted Toxicity Equivalency Factors (TEF) for individual PCB congeners (WHO97-TEF) (OEHHA 2003a); thus, it is appropriate to apply the soil half-life data for these individual congeners where speciation of PCBs has been performed

on facility emissions. Based on the studies above, only the data for PCB congeners with a WHO TEF (IUPAC # 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, 189) were used for estimating soil half-lives in this document, unless only total PCBs are available (OEHHA 2003b).

Among the above studies, Lake et al. (1992) derived a half-life of 7.5 years for PCB 105 and 6.8 yrs for PCB 118, using the anaerobic dechlorination reaction in sediment of 15-17.5 cm deep from New Bedford Harbor, Connecticut. Beurskens et al. (1993) have estimated a half-life time of nine years for PCB 105, PCB 126, PCB 156 and PCB 169 in the anaerobic sediment. Brown et al. (1984) found the average elimination half-life for PCB 105 and PCB 118 in Hudson River sediments was 10 years. The OEHHA acknowledges that the degree of biodegradation in sediment would be different from that for a dry land scenario. Until studies in dry soil become available, the river sediment data appear to be the best choice.

Table G-2.   Soil half-lives (days) for PCBs (IUPAC #) relevant to the "Hot Spots" program

Study	105	118	126	156	169	Total PCBs
Lake et al. 1992	2738	2482				
Beurskens et al., 1993	3285		3285	3285	3285	
Brown et al. 1984	3650	3650				
Arithmetic mean half-lives	3224	3066	3285	3285	3285	3229

The arithmetic mean half-lives for each PCB are shown at the bottom of Table G-2, and a grand mean half-life including all studied PCBs is 3229 days. This overall half-life of 3229 days is recommended as the estimated soil half-life for PCBs.

G.3.6 Polycyclic Aromatic Hydrocarbons (PAHs)

There are a variety of polycyclic aromatic hydrocarbons emitted from combustion sources. The structures vary by number and placement of fused aromatic carbon rings and functional groups on those rings. In general, it has been observed that the soil half-life increases with the increasing number of fused rings on a PAH and is correlated directly with molecular weight and K_{ow} (Northcott and Jones, 2001; Wild and Jones, 1993). The PAHs currently of toxicological concern under the "Hot Spots" program consist almost entirely of four or more rings with the prototype PAH, benzo(a)pyrene, containing five fused benzene rings. Naphthalene is carcinogenic and only has two rings but it is too volatile to be a multipathway chemical subject to deposition. Therefore, OEHHA chose to base the soil PAH half-life on those compounds with greater than three rings to avoid underestimating the accumulation of the carcinogenic PAHs in the soil.

Studies where PAHs have been added to soil have noted that those PAHs with three
rings or less show significant volatilization from soil and microbial degradation, whereas
PAHs with greater than three rings show little or no volatilization and slower microbial
degradation (Wild and Jones, 1993; Cerniglia, 1992). In addition, a broad inverse
relationship has been observed between the rate of biodegradation and the organic
carbon (OC) content of the soil (Northcott and Jones, 2001; Wild and Jones, 1993). Soil
half-life estimates for PAHs that currently have a potency equivalency factor (PEF) were
given the greatest weight in determining a default soil half-life. Table G-3 shows the
PAH half-life results from the most comprehensive studies found in the literature and a
brief summary of the studies is given below.

Doick et al. (2005) conducted a field study and determined the long-term fate of ^{12}C and
^{14}C analogues of benzo[a]pyrene spiked in a cultivated agricultural soil subject to typical
agricultural practices. The soil had a pH=7.2 and an organic matter content of 2.2%.
Their observation over 152 months found that the soil half-life for benzo[a]pyrene was
2.7 years (982 days). These half-life values are much longer than estimates in other
studies and are thought to be a result of the soil type, length of the study, use of field
conditions rather than laboratory conditions, and vegetation (type and coverage).

Sewage sludge containing PAHs was applied to two agricultural soils at five dose levels
(30 to 600 ton/ha) in field plots, followed by cultivation with annual crops or a perennial
(willow) for up to 54 months (Oleszczuk and Baran, 2005). It was unclear from the
description of the methodology if this work was an actual field study. Before addition of
the sewage sludge, the soil with the annual crops had a pH=4.3 and a total organic
carbon (OC) content of 1.12%. The soil with the perennials had a pH=5.8 and a total
OC content of 1.21%. Analysis of 16 PAHs showed longer half-lives in the soil with the
annual crops. However, the sewage sludge properties were considered as important as
the type of crop used. The investigators suggested that longer half-lives of PAHs
compared to other studies may have occurred due to the increased soil aging process
in a soil-sludge matrix.

In a climate-controlled greenhouse experiment, sewage sludge containing PAHs was
applied to four different soils to determine the soil half-life for a number of individual
PAHs (Wild and Jones, 1993). The four soils ranged from a sandy clay loam
agricultural soil (pH=6.6, organic carbon content, 6.04%) to a coniferous forest soil
(pH=2.9, organic carbon content, 58%). Although the half-lives among 12 PAHs
measured in the forest soil tended to be longest, the overall average of the sum of the
PAH half-lives was not considerably higher in forest soil ($t_{1/2}$=192 d) compared to the
overall average of the sum of the half-lives in the agricultural soils ($t_{1/2}$=146 d and 165 d)
and a roadside soil (177 d). The authors noted that the controlled environmental
conditions in the greenhouse optimize biodegradation compared to field conditions, and
likely results in more rapid losses of PAHs from the soil.

Two different sandy loam soils were spiked with 14 PAHs in incubation chambers and
their soil half-lives estimated over an exposure period of up to 196 days (Park et al.,
1990). One soil (Kidman sandy loam) had a pH=7.9 and an OC content of 0.5%, and
the other soil (McLaurin sandy loam) had a pH=4.8 and an OC content of 1.1%. The

half-lives for PAHs with PEF values ranged from 24 days to 391 days.   Although the organic content and pH of the two soils differed, the biological degradation rates of the PAH compounds were not statistically different between the two soils.

In another laboratory study, Coover and Sims (1987) spiked a sandy loam agricultural soil (pH=7.9; OC content, 0.5%) with 16 PAHs and estimated the soil half-lives over a 240 day incubation period. Increasing the soil temperature was observed to increase the apparent loss of low molecular weight PAHs but had little effect on loss of five- and six-ring PAHs.

Table G.3   Soil half-lives (days) for PAHs relevant to the "Hot Spots" program

Study	Ch	BaA	BaP	BbF	BkF	DahA	DaiP	Ind	DaA
Coover & Sims, 1987[a]	1000	430	290	610	1400	750		730	
Park et al., 1990[b]	379	212	269	253		391	297	289	24
Wild & Jones, 1993[c]	215	215	211	202	301				
Doick et al., 2005			982						
Arithmetic mean half-lives	531	286	438	355	851	571	297	510	24

Abbreviations: Ch, chrysene; BaA, benz[a]anthracene; BaP, benzo[a]pyrene; BbF, benzo[b]fluoranthene; BkF, benzo[k]fluoranthene; DahA, dibenz[a,h]anthracene; DaiP, dibenzo[a,i]pyrene; Ind, Indeno[1,2,3-c,d]pyrene; DaA, 7,12-Dimethylbenz [a] anthracene
[a] Environmental temperature held at 20C
[b] Average half-life values for two sandy loam soils
[c] Average half-life values for four different soils. Ch and BaA co-eluted; the $t_{1/2}$ is for both PAHs combined

The arithmetic mean half-lives for each PAH are shown at the bottom of Table G.3, and a grand mean half-life including all PAHs is 429 days. Greater differences in PAH half-lives are seen between studies rather than within studies. One possible reason is that longer half-lives are attained from field studies (Doick et al., 2005) compared to laboratory studies (Coover & Sims, 1987; Park et al., 1990; Wild & Jones, 1993).

However, the limited number of field studies makes it difficult to confirm this assumption. The overall PAH half-life of 429 days is recommended until further field studies are conducted.

G.3.7 Polychlorinated Dibenzo-p-dioxins and Dibenzofurans (PCDD/F)

The prototype compound and most potent of the dioxin and furan family of compounds is 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD). The degree and placement of chlorination affects both the toxicity and soil half life of dioxins and furans. Sampling of 32 sites in Seveso, Italy, produced an initial calculated regression half-life of one year (365 days) (Di Domenico et al., 1980). Experimental application of TCDD to two different soil types (loamy sand and silty clay loam) for 350 days produced calculated half-life values ranging from 394 to 708 days (Kearney et al., 1972; Kearney et al., 1973). Soil half-life estimates ranging from 10 to 12 years (3650-4380 days) were reported based upon experimental measured soil concentrations of TCDD from a contaminated site at an Air Force base in Florida (Young, 1981). Soil half-life estimates of 10 to 100 years (3650-36500 days) were reported, depending on the depth of the contamination, with deeper soil having reduced biodegradation rates (Nauman and Schaum, 1987). An estimated soil half-life of 3609 days has also been reported (calculated from a soil reaction rate constant of 8×10^{-6} hr^{-1}) (Mackay et al., 1985).

Several other half-life estimates have also been identified and summarized (Cohen et al., 1994b). Soil samples showing loss of TCDD content by volatilization produced estimated half-lives of 7-24 days (Nash and Beall, 1980). TCDD measured in soils from the contaminated site in Seveso, Italy, produced a half-life estimate of 9.1 years (3322 days) (Cerlesi et al., 1989). A half-life estimate of 3 days was made based on loss of TCDD content from soil by both photodecomposition and volatilization (Di Domenico et al., 1982).

McLachlan et al. (1996) studied PCDD/F persistence in a sludge-amended soil sample with presence of PCDD/Fs from 1968 to 1990. Half-lives for these PCDD/Fs in the sludge-amended soil after 1972 were of the order of 20 years (7300 days).

The arithmetic mean of the suggested values from ten studies (6,986 days) cited above is recommended as the estimated soil half-life of PCDD/Fs if the facility is reporting emissions for all dioxins and furan congeners as total PCDD/Fs.

There is great variability in soil half-lives among the PCDD/F congeners among the above studies. Soil half-life estimates for PCDD/Fs that currently have a toxicity equivalency factor (TEF) were given the greatest weight in determining a default soil half-life, where speciation of PCDD/Fs has been performed on facility emissions, unless only total PCDD/Fs are available (OEHHA, 2003). Table G-4 shows the PCDD/F half-life results from the study (Kjeller and Rappe, 1995) found in the literature which speciated PCDD/F congeners in sediment.

Table G.4. Half-lives (days) for PCDD/Fs in sediment

Compound	TEF$_{WHO-97}$	Half-life (days) from Kjeller and Rappe (1995)
PCDDs		
2378-TCDD	1	37,500
12378-PeCDD	1	42,000
123478-HxCDD	0.1	100,000
123789-HxCDD	0.1	29,200
123678-HxCDD	0.1	23,000
1234678-HpCDD	0.01	37,500
12346789-OCDD	0.0001	54,200
PCDFs		
2378-TCDF	0.1	23,000
12378-PeCDF	0.05	18,750
23478-PeCDF	0.5	23,000
123478-HxCDF	0.1	25,000
123789-HxCDF	0.1	20,800
123678-HxCDF	0.1	29,200
234678-HxCDF	0.1	18,750
1234678-HpCDF	0.01	14,600
1234789-HpCDF	0.01	12,500
12346789-OCDF	0.0001	10,400
Arithmetic mean half-lives		30,600

G.3.8 Summary

The chemical-specific soil half-lives for each chemical are summarized as Table G-5 below.

Table G-5. Summary of Soil Half-life Values (Days).

Compound	Soil Half-life (days)
Arsenic	1.0 E+08
Beryllium	1.0 E+08
Cadmium	1.0 E+08
Chromium	1.0 E+08
Diethylhexylphthalate	1.5 E+01
Fluoride	1.0 E+08
Hexachlorobenzene	1.0 E+08
Hexachlorocyclohexanes	9.4 E+01
Lead	1.0 E+08
Mercury	1.0 E+08
4,4'-methylenedianiline	4.6 E+02
Pentachlorophenol	-[a]
PAHs	4.3 E+02
PCBs	3.2 E+03
PCDD/F	7.0 E+03
Selenium	1.0 E+08

[a] To be assessed for soil half-life

For a chemical with individual congeners, such as PCBs, PAHs, PCDD/Fs, only the grand average was presented in Table G-5. When speciation of these chemicals in soil has been performed on facility emissions, soil half-life data for individual congeners are summarized in Table G-2 (PCBs), and Table G-3 (PAHs).

G.4   References

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