

Office of Environmental Health Hazard Assessment



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Secretary for Environmental Protection

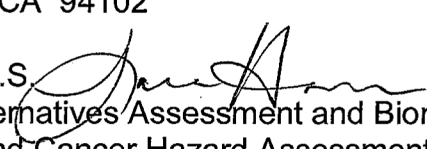
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MEMORANDUM

TO: Sushma Dhulipala Bhatia
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FROM: Sara Hoover, M.S. 
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DATE: March 22, 2010

SUBJECT: COMMENTS ON HUMAN HEALTH AND ENVIRONMENTAL HAZARDS
FOR DRY CLEANING SOLVENTS INCLUDED IN SF ENVIRONMENT'S
ALTERNATIVES ASSESSMENT

Under a service order with the San Francisco Department of the Environment (SF Environment), the Office of Environmental Health Hazard Assessment (OEHHA) is providing comments on the human health and environmental hazards for the solvents included in SF Environment's alternatives assessment of garment cleaning technologies (http://www.sfenvironment.org/downloads/library/alternatives_assessment_table_en_fin_al.pdf). As part of this service order, OEHHA has also conducted some analyses of the persistence, bioaccumulation and aquatic toxicity of selected dry cleaning solvents using predictive software.

This memorandum provides the final results of our work under the service order. The comments on the solvent decamethylcyclopentasiloxane (D5) that OEHHA previously provided to SF Environment are also incorporated (OEHHA, 2009).

If you have any questions, please feel free to contact me at 510-622-3224.

California Environmental Protection Agency

The energy challenge facing California is real. Every Californian needs to take immediate action to reduce energy consumption.

Technical Notes

In developing the comments below, OEHHA consulted readily available summary documents on the selected dry cleaning solvents. In some cases, we also consulted Material Safety Data Sheets (MSDSs) (links to the specific MSDSs are provided). MSDSs are known to have inaccuracies, so the information was checked against other available sources. For solvents with very little information in summary documents (e.g., Rynex, DF-2000), literature searches were also conducted.

PBT Profiler (available at: <http://www.pbtprofiler.net/>) was used to predict persistence, bioaccumulation and aquatic toxicity for the selected solvents. The PBT Profiler flags chemicals as “red” or “orange” for these categories, if certain criteria established by the US Environmental Protection Agency (US EPA) are exceeded. The criteria for the “orange” and “red” levels of concern are summarized in Table 1 below.

Table 1. Criteria used by PBT Profiler

PBT Profiler Category	“Orange” level of concern	“Red” level of concern
Persistence: Half-life in most relevant medium is compared to criteria	Half-life in relevant medium ≥ 2 months but < 6 months	Half-life in relevant medium ≥ 6 months
Bioaccumulation: Bioconcentration factor (BCF) for fatty tissue of fish compared to criteria	BCF ≥ 1000 but < 5000	BCF ≥ 5000
Toxicity: Based on the fish chronic toxicity value (Fish ChV) generated using the ECOSAR program ¹ .	Fish ChV 0.1 to 10 mg/L	Fish ChV <0.1 mg/L

1. ECOSAR is the Ecological Structure Activity Relationships program. More information on the program is available here: <http://www.epa.gov/oppt/newchems/tools/21ecosar.htm>.

The predictions from the PBT Profiler are for screening purposes only. Actual studies, if available, are preferred for evaluating persistence, bioaccumulation and aquatic toxicity.

Stoddard solvent, 1-propyl bromide and perchloroethylene are widely agreed to pose human health and environmental hazards. OEHHA provides only brief comments on the relevant hazards for these well known hazardous solvents. Comments on D5 are more extensive than the other solvents because of the amount of information available, including the previous memorandum prepared by OEHHA on D5.

The comments below are organized in the order that the solvents are listed in SF Environment’s alternatives assessment. The headings generally follow the health and

environmental concerns highlighted by SF Environment; however, persistence, bioaccumulation and aquatic toxicity are discussed for each solvent.

Hydrocarbon Solvents: DF-2000™, EcoSolv®, SHELLSOL™, PureDry®

Chemical identity

DF-2000, EcoSolv, SHELLSOL and PureDry are complex mixtures of primarily hydrocarbons, with some other minor ingredients (e.g., preservatives). A brief summary of chemical composition is provided for each solvent below.

DF-2000

In a 2007 MSDS (available here: <http://www.msds.exxonmobil.com/psims/psims.aspx>), Exxon Mobil Chemical describes DF-2000 as an isoparaffinic hydrocarbon with the CASRN of 64742-48-9. The chemical name is given as “naphtha (petroleum), hydrotreated heavy,” which is consistent with the chemical name specified by the Chemical Abstracts Services for that CASRN. In an earlier MSDS (see for example the 2005 MSDS available here: <http://www.nortonsupply.com/v/msds/Streets/DF-2000fluid.pdf>), DF-2000 was described as a “synthetic aliphatic hydrocarbon, hydrotreated,” though the same CASRN of 64742-48-9 was given. This inconsistency between CASRN and chemical name has been corrected in the most recent MSDS. Earlier MSDSs had also reported that BHT was used as preservative in DF-2000. In the 2007 MSDS, the composition is given as 100% hydrocarbon with no preservative listed.

OEHHA (2003) described DF-2000 as containing C11 to C13 aliphatic hydrocarbons, with ~90% paraffins and ~10% cycloparaffins (naphthenes). The boiling range of 185-211°C given by OEHHA (2003) for DF-2000 matches the 2007 MSDS, suggesting that OEHHA’s description is still accurate for the current formulation of DF-2000.

EcoSolv

The 2008 MSDS (see http://www.cpchem.com/enu/msds_unsecured/Import_711230_MSDS_O_ENGLISH_A_ENGLISH_A_N.pdf) for EcoSolv describes the solvent as being >99% C10-C13 isoalkanes. The CASRN for this major ingredient is given as 68551-17-7. The remainder of the product is listed as being <1% additives. The identity of the additive is not provided in the 2008 MSDS. The California Air Resources Board (CARB, 2006) reported that “the manufacturer formulated this product [EcoSolv] by adding butylated hydroxytoluene at 10 parts per million (ppm) to act as an oxygen stabilizer.”

SHELLSOL

Shell Chemicals produces a range of SHELLSOL solvents, such as D40, D60, D80, D90, D100, 140HT, with varying properties designed to fit particular needs. The product data sheet for SHELLSOL D40 (see http://www.scdynamiccontent.shell.com/Files%5Caliphaticmineralspirits_shellsold40_americas.pdf) explicitly mentions dry cleaning as a use for this solvent: "SHELLSOL D40 is used in many applications where its low odour is of value, e.g. low odor alkyd resin, architectural coatings, printing inks, cosmetics, metal degreasing, adhesives, wood preservatives, household products, car dewaxing and dry cleaning."

Shell assigns a CASRN of 64742-48-9 for D40, which is the same CASRN given by Exxon to DF-2000 (see above). The MSDS summarizes the composition as "Naphtha (petroleum), hydrotreated heavy" (MSDS produced for Great Britain available here: http://www.ccl.shell.com/MSDS/DownloadRtf?downloadUrl=http://www.chemicals.shell.com/GSAPEHS/MSDS/00000000883_GB_EN.pdf). Shell describes the chemical composition of D40 in more detail on the product data sheet (cited above) as follows: "SHELLSOL D40 is derived from Low Aromatic White Spirit which has been highly refined and reacted with hydrogen to convert aromatics to cycloparaffins. This deep hydrogenation results in products of controlled composition with very low aromatic contents, negligible reactive impurities and a low, sweet odour. SHELLSOL D40 consists predominantly of C-9 to C-11 paraffins and naphthenics."

CARB (2006) identified SHELLSOL 140 HT as a dry cleaning solvent as well. OEHHA did not identify a current product data sheet or MSDS for SHELLSOL 140 HT on the Shell Chemicals web site (http://www.shell.com/home/content/chemicals/products_services/our_products/).

PureDry

A current MSDS was not located for PureDry. OEHHA (2003) summarized the chemical composition of PureDry as follows:

- "PureDry contains by weight 95% odorless mineral spirits (OMS). The odorless mineral spirits are a mixture of aliphatic hydrocarbons. Pure Dry also contains 3.6% HFE-7200 (a mixture of ethyl perfluoroisobutyl ether and ethyl perfluorobutyl ether), 0.9% FC-43 (perfluoro compounds of primarily 12 carbons), 0.3% PF-5070 (perfluoro compounds of primarily seven carbons) and 0.2% PF5060 (perfluoro compounds of primarily six carbons)."
- "PureDry is an alternative to Stoddard Solvent and does not contain aromatic hydrocarbons (including benzene, a known human carcinogen). ShellSol®, the brand of mineral spirits in PureDry, contains naphtha petroleum, and heavy alkylates and is described in the MSDS as a complex stream of predominantly C₉ to C₁₂ hydrocarbons."

Neurotoxicity, eye, skin, and respiratory irritation

Neurotoxicity and eye, skin and respiratory irritation are common effects associated with high exposures to hydrocarbon solvents (OEHHA, 2003). Further details on these effects for the hydrocarbon solvents DF-2000, SHELLSOL D40 and Ecosolv are provided below. PureDry is approximately 95% mineral spirits and is expected to induce effects similar to those described above for the other hydrocarbon mixtures. For more information on the toxicity of PureDry, including its minor ingredient HFE-7200, please refer to OEHHA (2003).

DF-2000 and SHELLSOL D40 (CASRN 64742-48-9)

The MSDS for DF-2000 states that “Vapor/aerosol concentrations above recommended exposure levels are irritating to the eyes and respiratory tract, may cause headaches, dizziness, anesthesia, drowsiness, unconsciousness and other central nervous system effects including death. Prolonged and/or repeated skin contact with low viscosity materials may defat the skin resulting in possible irritation and dermatitis.”

The MSDS for SHELLSOL D40 indicates that exposure to high vapor concentrations “may cause central nervous system depression resulting in dizziness, light-headedness, headache, nausea and loss of coordination.” Vapors “may be irritating to the eye,” causing “a burning sensation, redness, swelling, and/or blurred vision.” Contact with skin may cause “moderate irritation, a burning sensation, redness, swelling and/or blisters.” SHELLSOL D40 is “slightly irritating to respiratory system,” and may cause “temporary burning sensation of the nose and throat, coughing and/or difficulty breathing.” Continued inhalation of vapors “may result in unconsciousness and death.”

Hass et al. (2001) studied dearomatized white spirits by exposing rats to 800 ppm of “Exxsol D 40, CAS no. 64742–48–9,” with a concurrent control group exposed to 0 ppm. The authors found that “exposure of rats to 800 ppm white spirit during pregnancy caused long-lasting impairment of learning and memory functions in the offspring. Although decreased maternal weight gain during pregnancy was recorded, it seems most plausible that the effect is related to a direct effect on the developing brain.” Hass et al. also reference earlier studies with related finding in adult rats: “In another study, long-lasting changes in brain evoked potentials and activity level were registered after exposure to dearomatized white spirit (Lund et al. 1996). Recently we have shown that dearomatized white spirit induced region-dependent increases and decreases of glial fibrillary acid protein after few weeks of exposure of adult rats to 400 or 800 ppm (Lam et al. 2000).”

The German Federal Environmental Protection Agency identified neurotoxicity, developmental toxicity and reproductive toxicity as the critical endpoints for

“dearomatized hydrocarbon solvents/white spirits (DAWS--CAS-No. 64742-47-8, 64742-48-9, 64742-88-7, 64741-65-7).” The risk assessment for DAWS was described in an English abstract (Sagunski and Mangelsdorf, 2005) as follows: “For risk evaluation the Hass et al. (2001) study was used as the pivotal study. Based on effects at 4680 mg DAWS/m³ for the endpoint developmental toxicity, the lowest adverse effect level for chronic exposure is assessed as 400 mg DAWS/m³. By applying an interspecies factor of 10, an intraspecies factor of 10 and an additional factor 2 referring to the special physiology of children (higher breath rate compared to adults) a so-called health hazard value of 2 mg DAWS/m³ indoor air and a so-called health prevention value of 0.2 mg DAWS/m³ are obtained.” The interim chronic reference exposure level of 1.2 mg/m³ derived by OEHHA (2003) for hydrocarbon mixtures based on body weight, kidney and erythrocyte count changes is comparable to the health hazard value derived by the German Federal Environmental Protection Agency.

EcoSolv

The MSDS states that “Prolonged or repeated skin contact may cause drying or defatting of the skin. Symptoms may include pain, itching, discoloration, swelling and blistering.” According to the MSDS, “breathing of high vapor concentrations may cause dizziness, light-headedness, headache, nausea and loss of coordination. Continued inhalation may result in unconsciousness.”

Persistence, bioaccumulation and aquatic toxicity

In reviewing the dry cleaning solvents, CARB (2006) found that “Most information is lacking on the environmental persistence of these and other hydrocarbon mixtures, however the manufacturer of DF-2000 indicated that their solvent can exhibit moderate rates of biodegradation (ExxonMobil, 2003). The manufacturer of EcoSolv indicated their solvent can exhibit moderate to rapid rates of biodegradation (Chevron Phillips, 2005).”

DF-2000 and SHELLSOL D40 (CASRN 64742-48-9)

The current MSDS for DF-2000 does not provide specific data on the potential persistence or aquatic toxicity for DF-2000. The MSDS indicates that DF-2000 is expected to be “readily biodegradable” and is “expected to readily degrade in air.” In terms of aquatic toxicity, the MSDS states that DF-2000 is “not expected to be harmful to aquatic organisms” and is “not expected to demonstrate chronic toxicity to aquatic organisms.” However, the MSDS also notes the following precaution: “Prevent entry into waterways, sewers, basements or confined areas.” No information on bioaccumulation is provided.

The MSDS for SHELLSOL D40 also reports low toxicity to fish, aquatic invertebrates and algae, but notes that SHELLSOL D40 is “expected to be toxic” to aquatic microorganisms.

In a screening evaluation, Canada (see http://www.ec.gc.ca/CEPARRegistry/subs_list/dsl/DSLsearch.cfm) concluded the following for the CASRN of 64742-48-9:

- Persistent?: “Yes”
- Bioaccumulative?: “Yes”
- Inherently toxic to aquatic organisms: “Yes”

The PBT Profiler did not locate CASRN 64742-48-9 in its lookup database. Because it is a complex mixture, this CASRN does not have a specific structure or SMILES (Simplified Molecular Input Line Entry Specification) notation and so was not analyzed.

EcoSolv (CAS No. 68551-17-7)

The PBT Profiler found that EPA’s criteria for persistence, bioaccumulation and toxicity (based on chronic toxicity to aquatic organisms) are all exceeded for EcoSolv, with results summarized as follows:

- Persistence - “orange” level of concern
- Bioaccumulation - “orange” level of concern
- Toxicity - “red” level of concern for chronic toxicity to fish

The PBT profiler uses a single representative structure for the C10-C13 isoalkane mixture [SMILES notation of CC(CCCCCC)C], however, which may not capture the true nature of the EcoSolv mixture.

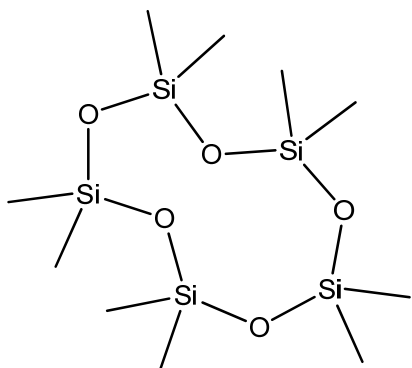
In a screening level evaluation, Canada reported the following results for EcoSolv:

- Persistent?: “No”
- Bioaccumulative?: “No”
- Inherently toxic to aquatic organisms: “Yes”

GreenEarth® (D5 as primary ingredient)

Chemical identity

The primary ingredient of GreenEarth® is decamethylcyclopentasiloxane (or D5; CASRN 541-02-6). The structure is shown below.



decamethylcyclopentasiloxane

Potential carcinogenicity

OEHHA (2007, 2008a) concluded that concerns for potential carcinogenicity relevant to humans cannot be ruled out for D5. A rat-specific mechanism for the uterine tumors induced by D5 has been proposed by Dow Corning and the Silicones Environmental Health and Safety Council (SEHSC). OEHHA found this mechanism, which hypothesizes dopamine agonism by D5, plausible but still uncertain (see OEHHA, 2007 and 2008a for a full discussion). OEHHA has found no new information that would alter our earlier findings. Concerns for the potential carcinogenicity of D5 remain.

Excerpts related to potential carcinogenicity

OEHHA (2007):

- “Concerns for possible toxic effects of D5 were raised following the discovery that D5 exposure causes uterine cancer in female rats.”
- “A statistically significant increase in a malignant tumor (uterine adenocarcinoma) due to D5, a chemical that may be bioconcentrated and is a candidate to replace perchloroethylene in dry cleaning, indicates a potential hazard for workers in the dry cleaning industry and perhaps for the general public.”
- “Dow Corning has proposed that the tumors in rats are due to a mechanism not applicable to humans (Environ, 2006). Dow Corning postulates that D5 acts as a dopamine agonist, i.e., D5 mimics the effects of dopamine by binding to

dopamine receptors in the body and causing effects like dopamine...This hypothesized mode of action for D5 rat uterine carcinogenicity is plausible, but a substantial amount of uncertainty remains due to contradictions and information gaps in the available data.”

OEHHA (2008a):

- “However, OEHHA has concluded that 1.) current data are insufficient to definitively determine that the proposed mode of action (MOA) for tumorigenesis, namely endocrine action in the rodent through dopamine agonism, is in fact the MOA, and 2.) there is still a concern for potential carcinogenicity relevant to humans. In making this determination, OEHHA is consistent with the judgment of U.S. EPA’s scientists, who reported a similar conclusion to SEHSC [Silicones Environmental Health and Safety Council] in December 2006.”

Effects on the reproductive system

OEHHA (2007, 2008a) found some evidence of potential effects of D5 on the reproductive system. D5 may affect reproductive hormones and one study of D5 observed a significant increase on male pup anogenital distance.

Excerpts for reproductive effects

OEHHA (2007):

- “Siddiqui et al. (2007) observed a significant increase in male pup anogenital distance [AGD]. This may indicate an anti-estrogenic or androgenic effect...OEHHA considers the statistically significant increase in AGD at 160 ppm an effect of concern, possibly reflecting an anti-estrogenic (female hormone) or androgenic (male hormone) property of D5.”
- “Hormonal effects are of interest and concern because of the finding of malignant tumors (adenocarcinomas) due to chronic D5 exposure in a hormone sensitive organ, the rat uterus.”
- “Dopamine acts on the endocrine system by inhibiting prolactin release (Ben-Jonathan and Hnasko, 2001). In humans prolactin induces and maintains the secretion of milk (lactation) and during lactation decreases reproductive function and suppresses sexual drive in the mother. Drugs used to treat hyperprolactinemia, such as cabergoline and bromocriptine, are dopamine receptor agonists.” (This effect would depend on D5 being a dopamine agonist, which is still uncertain; see OEHHA, 2007 and 2008a for a full discussion of this issue.)

OEHHA (2008a):

- “...OEHHA staff noted a statistically significant increase in the anogenital distance in Sprague-Dawley rat F1 males exposed to 160 ppm D5 in the Siddiqui

et al. (2007) study. OEHHA staff was concerned that this might be a hormonal effect of D5.”

- “OEHHA agrees that [increased anogenital distance] is [a] sensitive endpoint for female reproductive toxicity... Given the existence of multiple studies indicating that chemicals which mimic the action of estradiol in the body could alter the AGD in male animals of several species, OEHHA believes that the concern expressed over the apparent effect of D5 on AGD in male rats in the study by Siddiqui et al. (2007) is still valid.”

Effects on the liver, nervous system, and immune system

There are indications that D5 has effects on the liver and immune and nervous systems, based on evidence from experimental studies and/or D5's proposed effects on the hormone prolactin and its hypothesized potential for dopamine agonism. There are contradictions and data gaps in the available information on the potential dopamine agonism of D5 (see OEHHA, 2007 for a detailed discussion of this issue). If D5 is truly a dopamine agonist, this could have effects on the nervous system as well as many other physiological processes. OEHHA's principal concern with a dopaminergic mode of action is the possibility of functional and developmental neurological or neuroendocrinological effects. Relevant excerpts on a range of potential effects of D5 are given below.

Summary statements on a range of potential noncancer effects

OEHHA (2007):

- “Furthermore, additional non-carcinogenic effects, associated with altered dopamine and prolactin levels, have been reported in humans and animals. Systems affected include the nervous system, fat tissue, the liver (bile formation), and the immune system.”

OEHHA (2008b):

- “D5 also has adverse health effects on the reproductive system, adipose tissue, bile production, and the immune system through its effects on prolactin, and it has the potential to cause adverse effects on the nervous system because of its influence on the neurotransmitter dopamine (OEHHA, 2007).”

Excerpts on liver effects

OEHHA (2007):

- “There were several minor changes observed in clinical biochemistry parameters; the most notable was an increase in gamma glutamyl transferase (gamma-GT) in both sexes at the high dose (Table 3). In females, this effect was dose-related between 46 and 224 ppm and did not return to control levels upon cessation of

exposure. Additionally, there was a decrease in serum lactate dehydrogenase (LDH) observed in females at 86 and 224 ppm, which did not resolve during recovery. There was an increase in absolute and/or relative liver weight in rats of both sexes. Taken together, these data suggest that the female rat is more sensitive to the actions of D5 on the liver.

- "...in F0 females the 10% increase in liver weight at 160 ppm was significantly different from controls" (from Siddiqui et al., 2007)

OEHHA (2008a):

- "...OEHHA noted that there were effects in rat liver after 3 months of D5 exposure, including increased liver weight and increased levels in serum of the liver enzyme gamma-glutamyl transferase (Burns-Naas et al., 1998). These are not always adaptive responses but rather indicators of cellular toxicity. In the 2-year chronic study (Dow Corning, 2005b) there were some sporadic increases of enzymes in the serum. In female rats exposed to 160 ppm D5 there was a 37% increase in GGT activity at 3 months and a 132.8% increase at 12 months."
- "We are not aware of data on the effect(s) of D5 on human liver, but such effects cannot be ruled out."

Excerpts on nervous system effects

OEHHA (2007):

- "...there is still concern that D5 could be a dopamine agonist and result in other adverse effects in humans...Dopamine is a major neurotransmitter, involved in many brain functions and downstream physiological processes. Dopamine has been demonstrated to affect brain neural architecture during development (Todd, 1992; Swarzenski et al., 1994; Song et al., 2002)."
- "...the proposed mode of action of D5 involves central dopamine agonism. Thus production of tumors at 160 ppm indicates dopamine agonism at this dose level."
- "Data described above indicate that brain levels of D5 in rats exposed to 160 ppm D5 were approximately twice as high as corresponding blood levels. This raises the possibility that *in utero* exposure to D5 could result in adverse effects on brain neural development. Dopamine D2 receptors, with which D5 interacts, have a role in neurological disorders and mental illness (Ben-Jonathan and Hnasko, 2001; Seeman et al., 2006)."

Excerpts on immune system effects

OEHHA (2007):

- Immune effects observed in lung studies :
 - "...in the two year study a statistically significant effect was increased lung foci, presumably sites of macrophage accumulation, in 13% of the females (8/60) at 160 ppm after 24 months (controls = 0%)."

- "In a two-generation reproduction study of D5 by inhalation, Siddiqui et al. (2007) reported increased alveolar histiocytosis (minimal) in the F0 and F1 rats....The increase was statistically significant in F0 and F1 females exposed to 160 ppm D5."
- Immune and other effects via dopamine effects: "Dopamine can activate dopaminergic receptors in normal human T-cells, and trigger the selective secretion of IL-10 and/or TNF α (Besser *et al.*, 2005). Assuming D5 has dopamine agonist properties, this could have detrimental consequences in various immunological diseases, injuries and cancers."
- Immune and other effects via prolactin effects: "Prolactin has been reported to affect a variety of other cells including human adipocytes (Asai-Sato et al., 2006; Nilsson et al., 2005), mouse adipocytes (Flint et al., 2006) rat cholangiocytes (Bogorad et al., 2006a, b), rat chondrocytes (Zermeno et al., 2006), human natural killer (NK) cells (Sun et al., 2004), developing human thymocytes (Carreno et al., 2005), and rat pancreatic islet cells (Amaral et al., 2004)."

Persistence, bioaccumulation and aquatic toxicity

Canada recently concluded that D5 is persistent in the environment, consistent with OEHHA's evaluations (OEHHA, 2007; 2008a; 2008b). While there is some conflicting information on bioaccumulation, D5 has been detected in fish and other aquatic species. This provides empirical evidence for D5's potential accumulation in living organisms. After evaluating OEHHA's reports as well as submissions from SEHSC, the Scientific Guidance Panel for the California Environmental Contaminant Biomonitoring Program recommended it as a priority chemical for biomonitoring in California.

Excerpts on persistence and bioaccumulation

OEHHA (2007):

- "Concerns exist for the environmental persistence of D5, which is highly lipophilic, has been measured in aquatic species in a number of environments, and has a long half-life in human tissues."
- "D5 has been detected in human adipose tissue and breast milk, and in fish. Animal experiments have also shown that siloxane residues, including unchanged D5, are persistent in a variety of tissues for extended periods after exposure. Based on the log K_{ow} , BCF, detection in biota and experimental data showing residues, OEHHA considers D5 to be a persistent substance."
- "...in the Rhine River in Germany, D5 has been detected in fish up to 1 mg/kg (1 ppm) and in eels up to 2.6 mg/kg (Mait, 2005). D5 was also detected in aquatic organisms in the Nordic siloxane screening study (Norden, 2005). D5 was the predominant cyclosiloxane found in both fish livers and marine mammals. D5 concentrations in freshwater and marine fish from urban areas and near STPs ranged from < 5 - 84 ng/g wet weight (ww). One sample of cod liver (9 pooled livers) collected near a Norwegian city center had a D5 concentration of 2,200

ng/g ww. D5 was also detected in the blubber of seals and pilot whales at concentrations ranging from <5 - 24 ng/g ww. Environment Canada (2007) concluded that since concentrations of D5 in Nordic waters were <5 µg/L, except for STP influents, the detection of D5 in biota indicated that D5 has the potential to bioaccumulate.”

OEHHA (2008a):

- “D5 theoretically has significant bioaccumulative potential based on its high bioconcentration factor (BCF). In the environment, D5 has been measured in several aquatic species at ppm concentrations. Its half-life in humans is measured in weeks, not in hours. Pharmacokinetic model results predict that it may take a year to reach steady state in fat tissue. Thus, D5 persistence in the environment and in animal and human tissues is a concern.”
- “OEHHA’s concern about D5 as an environmental contaminant is based primarily on environmental sampling which has indicated accumulation in wildlife, including fish (Mait, 2005; Norden, 2005). More widespread and intensive use of D5 could therefore result in human exposure via the consumption of fish. This concern persists regardless of any experimental data, which may or may not help understand the details of the environmental fate and transport of D5.”

Environment Canada and Health Canada (2008):

- Persistence: “Therefore, D5 has been determined to meet the persistence criterion as set out in the *Persistence and Bioaccumulation Regulations*.”
 - Air: “...atmospheric half-lives of more than 3 days. D5 has the potential to be transported over long-distances in the atmosphere.”
 - Water: “The hydrolysis half-lives for D5 under Canadian water conditions ranged from 1 to 733 days, indicating the substance is persistent under certain Canadian water conditions, especially in cooler and neutral water (5-10°C).”
 - Sediment: “D5 is also judged to be persistent in sediment, with half-lives of 49 to 588 days estimated under realistic Canadian sediment conditions (temperature of 5-25°C) based on information to structurally similar analogue, D4, indicating the substance may be persistent in sediment.”
 - Soil: “D5 is not considered persistent in soil, based on evidence of clay-catalysed degradation, with dimethylsilanediol being the stable hydrolysis product.”
- Bioaccumulation: “Therefore, while D5 has the potential to accumulate in biota, it is not possible to conclude at this time that D5 meets the criterion for bioaccumulation as set out in the *Persistence and Bioaccumulation Regulations* based on consideration of the conflicting evidence from laboratory studies and predictive models.”
 - “The empirical bioconcentration factor and modelled bioaccumulation factor are both above 5000, indicating D5 may have a high potential to

accumulate in aquatic organisms. However, data from a biomagnification study in fish and a biota-sediment accumulation study in invertebrates suggest that the bioaccumulation potential of D5 may be lower, possibly due to reduced bioavailability.

- Concluding statement on aquatic organisms: “Considering the persistence of D5 under colder Canadian water conditions and its potential to bioaccumulate in biota, long-term environmental exposure to D5 may potentially cause adverse effects to aquatic organisms in certain Canadian environments.”

United Kingdom Environment Agency (2009):

- "D5 meets the screening criteria for very persistent and very bioaccumulative (vPvB substances), but some mitigating factors and uncertainties need to be considered further. In particular, the substance is expected to be lost from water by volatilization to the air, where subsequent degradation occurs."

Predictions from PBT Profiler – “orange” or “red” designations indicate that specific U.S. Environmental Protection Agency criteria have been exceeded as described above. Results for D5 are given below:

- Persistence - “red” level of concern
- Bioaccumulation - “orange” level of concern
- Toxicity - “red” level of concern for chronic toxicity to fish

Rynex™

Chemical identity

The original formulation of Rynex™ was propylene glycol mono-t-butyl ether, but this carcinogenic compound is no longer used as a dry cleaning solvent. The 2005 MSDS for Rynex (available at: <http://www.rynex.com/main/msds/MSDS%20printable.pdf>) withholds the chemical identity of the solvent as a trade secret, describing it only as “aliphatic propylene glycol ethers.” A Danish study (Glensvig and Mortensen, 2003) determined that Rynex 2 was more than 95% dipropylene glycol t-butyl ether and referenced the CASRN of 132739-31-2. More recently, CARB (2008) reported that “Rynex 3 represents the current formulation for Rynex™, which does not contain PGtBE but instead contains dipropylene glycol tert-butyl ether (DPTB). Currently, there is limited toxicity data available for DPTB.”

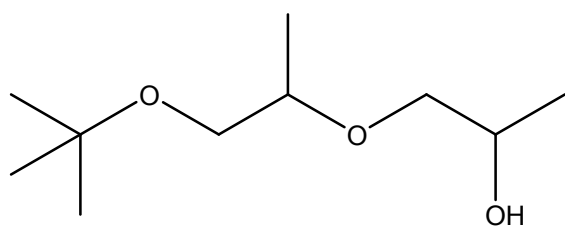
The Chemical Abstract Services (CAS) describes the CASRN of 132739-31-2 as an “incompletely defined substance,” although the chemical name is given as dipropylene

glycol mono-tert-butyl ether. This CASRN appears to represent mixed isomers of the chemical.

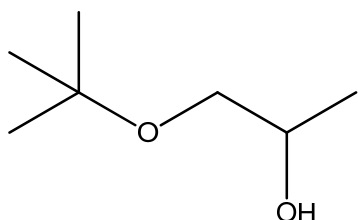
Entering the chemical name “dipropylene glycol t-butyl ether” into ChemDraw Ultra version 11 produced the structure shown in the next section below. The CASRN for the chemical with the defined structure shown below is 58797-58-3. The name given by CAS for the chemical shown below is 1-[2-(1,1-dimethylethoxy)-1-methylethoxy]-2-propanol. The European Chemical Substances Information System (ESIS; available at: <http://ecb.jrc.ec.europa.eu/esis/>) gives “Rynex Dry Cleaning Solution” as one of the trade names for the CASRN 58797-58-3. The other CASRN (132739-31-2) was not found in ESIS.

Structural features

The structure of dipropylene glycol t-butyl ether is similar to propylene glycol mono-t-butyl ether, a Proposition 65 carcinogen. Both structures are shown below. Propylene glycol mono-t-butyl ether was listed as known to the state of California to cause cancer after the National Toxicology Program (NTP, 2004) found clear evidence of carcinogenicity in male and female mice. In addition, any chemical with a t-butyl ether group might be expected to degrade in the environment to t-butanol. NTP (1995) found some evidence of carcinogenicity in male rats and female mice exposed to t-butanol. OEHHA did not locate carcinogenicity studies in which dipropylene glycol t-butyl ether itself was administered to animals.



dipropylene glycol t-butyl ether



propylene glycol t-butyl ether

Persistence, bioaccumulation, aquatic toxicity and other environmental concerns

The PBT Profiler was able to analyze dipropylene glycol t-butyl ether based on the above structure and produced the following results:

- Persistence - “orange” level of concern (US EPA criteria exceeded)
- Bioaccumulation – “green”
- Toxicity – “green”

These results indicate that Rynex may be a concern for environmental persistence.

The MSDS for Rynex does not comment on its potential environmental persistence. The MSDS indicates that the substance is biodegradable and is “expected to be non-hazardous to aquatic species.”

Stoddard Solvent

As indicated in “Technical Notes” above, the comments given for Stoddard solvent, a well known hazardous solvent, are brief.

Chemical identity

Stoddard solvent is a mixture of 48% C9 to C12 straight and branched chain hydrocarbons, 38% naphthalenes (cycloparaffins such as cyclohexane), and 14% aromatic hydrocarbons including benzene (OEHHA, 2003). Benzene is a known human carcinogen. Stoddard solvent is also referred to as mineral spirits type I or white spirits. The CASRN 8052-41-3 is commonly used for Stoddard solvent.

Neurotoxicity, eye, skin, and respiratory irritation

OEHHA (2003) noted that “The occupational hazards of mineral spirits in the dry cleaning industry are known....Neurotoxicity, eye irritation and respiratory irritation at high levels of exposure are common effects of solvents.”

The MSDS for Stoddard solvent (available at: http://www.sciencelab.com/xMSDS-Stoddard_solvent-9927610) indicates that the solvent is “hazardous in case of skin contact (irritant), of eye contact (irritant), of inhalation.” The MSDS further notes that “the substance is toxic to lungs, the nervous system, mucous membranes” and “repeated or prolonged exposure to the substance can produce target organs damage.”

Persistence, bioaccumulation and aquatic toxicity

In a screening evaluation, Canada concluded the following for the CASRN 8052-41-3:

- Persistent?: “No”
- Bioaccumulative?: “Yes”
- Inherently toxic to aquatic organisms: “Yes”

A Canadian MSDS (available here:

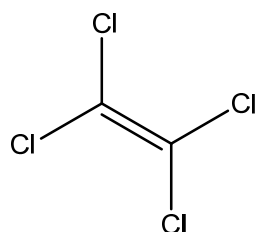
http://msds.univarcanda.com/wercswv/wercswv.asp?A=putHTM%00&RID=F_PDF%27EN%27%27RENS%27%27LA4817%27%27MTR%27%27ANSI%27%7bts+%272004-06-10+14%3A13%3A09%27%7d) asserts that ecotoxicity information is “not available,” but also notes that Stoddard solvent “may be harmful to aquatic life.” The MSDS indicates that Stoddard solvent “biodegrades easily in water.”

Perchloroethylene (or tetrachloroethylene)

As indicated in “Technical Notes” above, the comments given for perchloroethylene, a well known hazardous solvent, are brief.

Chemical identity

Perchloroethylene and tetrachloroethylene are the commonly used names for the chemical tetrachlorethene (CASRN 127-18-4). The structure of the chemical is shown below:



perchloroethylene

Carcinogenicity

Perchloroethylene was listed as known to the state of California to cause cancer under Proposition 65 in 1988.

Noncancer effects

OEHHA (2008c) identified the nervous system, eyes and respiratory system as the key targets for the acute toxicity of perchloroethylene. Perchloroethylene is also irritating to the skin.

The key target organs for the chronic toxicity of perchloroethylene are the kidney and the liver (see <http://www.oehha.ca.gov/air/allrels.html>). There is also some evidence in animals of a chronic neurotoxic effect as well as possible neurodevelopmental effects from exposure to perchloroethylene. For more detailed discussions of the noncancer health effects of perchloroethylene, see the California Department of Health Services (CDHS, 1991) and OEHHA (2001).

Persistence, bioaccumulation and aquatic toxicity

The MSDS (<http://www.sciencelab.com/xMSDS-Tetrachloroethylene-9927293>) cites the European hazard statements for perchloroethylene as being “toxic to aquatic organisms” and that it “may cause long-term adverse effects in the aquatic environment.” The PBT Profiler was unable to estimate the aquatic toxicity for perchloroethylene using the quantitative structure activity equations from ECOSAR (see <http://www.pbtprofiler.net/methodology.asp> for more information).

CARB (1991) found that “Depending on atmospheric conditions, the half-life of perchloroethylene (as a result of its degradation by reactions with hydroxyl radicals) is estimated to be about 100 days. Therefore, perchloroethylene is sufficiently persistent to be transported throughout an air basin before it is degraded.” Screening assessments from the PBT Profiler and Canada also identify a concern for the persistence of perchloroethylene, as summarized below.

Predictions from the PBT Profiler:

- Persistence - “orange” level of concern
- Bioaccumulation - “green” level of concern
- Toxicity – not estimated

Canada’s screening assessment reported the following for perchloroethylene:

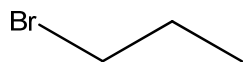
- Persistent?: Yes
- Bioaccumulative?: No
- Inherently toxic to aquatic organisms: No

1-Propyl Bromide (1-Bromopropane)

As indicated in “Technical Notes” above, the comments given for 1-propyl bromide, a well known hazardous solvent, are brief.

Chemical identity

1-Propyl bromide is also known as n-propyl bromide or 1-bromopropane (CASRN of 106-94-5). The structure is provided below.



1-propyl bromide

The dry cleaning solvent DrySolv™ contains more than 95% 1-propyl bromide (see MSDS at http://www.dctco.com/drysolv_msdms.pdf).

Reproductive and developmental toxicity

1-Propyl bromide is listed under Proposition 65 as known to the state of California to cause developmental toxicity and male and female reproductive toxicity. The listing is under the synonym 1-bromopropane.

Neurotoxicity, eye, skin, and respiratory irritation

OEHHA (2003) identified 1-propyl bromide as a neurotoxicant.

The MSDS for 1-propyl bromide (available here: http://www.sciencelab.com/xMSDS-1_Bromopropane-9923169) states that it causes both skin and eye irritation. A range of other human health toxicities, including neurotoxicity and respiratory effects, are highlighted as well: “It may cause respiratory tract and mucous membrane irritation and may affect respiration. Vapors may cause dizziness and suffocation. Inhalation of high concentrations may affect behavior/central nervous system (CNS depression) characterized by nausea, headache, dizziness, somnolence, unconsciousness and coma. It may also cause liver and kidney damage, lung injury, weight loss/anorexia, bone marrow changes, and blood abnormalities [sic].”

Persistence, bioaccumulation and aquatic toxicity

The MSDS for 1-propyl bromide provided no information on ecotoxicity, persistence or bioaccumulation. The MSDS for DrySolv provided the following ecological information for 1-propyl bromide (referred to as “nPB”): “nPB is less persistent in the environment than many solvents and would be of low to moderate concern for movement in soil. Based on the LC₅₀, the acute concentration at which 50% of tested animals die, nPB’s toxicity to aquatic life is moderate, being less than that for trichloroethylene, hexane, *d*-limonene, and possibly some aqueous cleaners...Based on its relatively low bioconcentration factor and log K_{OW} value, nPB is not prone to bioaccumulation.”

The PBT Profiler found a “green” level of concern for persistence and bioaccumulation. U.S. EPA criteria were exceeded for aquatic toxicity, resulting in an “orange” level of concern for 1-propyl bromide.

- Persistence – “green” level of concern
- Bioaccumulation – “green” level of concern
- Toxicity - “orange” level of concern for chronic toxicity to fish

Canada reported the following for 1-propyl bromide:

- Persistent?: Yes
- Bioaccumulative?: No
- Inherently toxic to aquatic organisms: No

The results for persistence and aquatic toxicity differ between the PBT Profiler and the Canadian screening assessment for 1-propyl bromide. OEHHA could not determine the origin of this discrepancy.

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