(S, S)-Ethlenediaminedisuccinic Acid (free acid)

Crop Production

Identification of Petitioned Substance

| Chemical Name: | Ethylenediamine-N,N'-disuccinic acid |
| Trade Names: |

| IUPAC name: | 2-[2-(1,2-dicarboxyethylamino)ethylamino]butanedioic acid |
| CAS Number: | 20846-91-7 |

| Other Names: | EDDS, EDSS, Ethylenediamine-N,N'-disuccinic acid, N,N'-ethylenedi-L-aspartic acid, N,N'-Ethylenediamine disuccinic acid, N,N'-Ethylenediaspartic acid |
| Other Codes: |

Characterization of Petitioned Substance

Note: Chelation is a process in which free metal ions combine with ligands (chelators, chelating agents) to form metal complexes. With respect to free metal ions, metal ions in complexes are less reactive, less subject to precipitation processes, and remain water-soluble for a longer time. Nutrient metals stay water-soluble for a longer time so that plants/animals assimilate more. Toxic metals also stay water-soluble for a longer period of time and cause more damage such as suppressing plant growth. Previously precipitated/adsorbed metal ions form complexes with available chelating agents, are released back to water-soluble, and cause different effects (such as being transported to underground water or to different geographical locations). Some basic concepts and issues related to chelation such as complex stability, ligand stability, reversible processes, competition processes, etc, are presented in Appendix A: Chelation and related issues.

Composition of the Substance:

Ethylenediamine-N,N'-disuccinic acid (EDDS) is one of the aminopolycarboxylic acids (APCAs). One commercial product is tri-sodium salt (Na$_3$-EDDS) with a CAS number of 178949-82-1.

There are two chiral centers in the structure of EDDS (Fig. 1) and consequently there are two enantiomeric isomers: (R,R')-EDDS, and (S,S')-EDDS, and one meso isomer (R,S)-EDDS (Neal and Rose, 1968; Schowanek et al., 1997). These isomers have about the same efficiency, in terms of complex stability constants, in forming complexes with metal ions (Orama et al., 2002). As given below in the section of “Biodegradability,” (R,R')-EDDS and (R,S)-EDDS are partially or wholly un-biodegradable. Most literature is focused on (S,S')-EDDS. (S,S')-EDDS is denoted as EDDS hereafter, unless otherwise specifically noted.

Fig. 1: Structure of EDDS

![Structure of EDDS](image-url)
Properties of the Substance:

Basic Properties

The basic properties of EDDS are listed in Table 1: Physical and chemical properties of EDDS (P&G Environmental Science data; US EPA 40 CFR Part 180.920-Document 0002; Sigma MSDS).

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular formula</td>
<td>C_{10}H_{16}N_{2}O_{5}</td>
</tr>
<tr>
<td>Density</td>
<td>1.59 g/cm^3</td>
</tr>
<tr>
<td>Solubility in water</td>
<td>slightly soluble</td>
</tr>
<tr>
<td>Acidity (pKa)</td>
<td>2.4, 3.9, 6.8, 9.8</td>
</tr>
</tbody>
</table>

EDDS is a white granular solid without characteristic odor. One commercial product of tri-sodium salt is prepared in solution form. The flammability of EDDS is not high. The solubility of EDDS acid is 0.015 g/100 g at 20°C, but the solubility of tri-sodium salt (Na₃-EDDS) is > 1000 g/L at 20°C. These properties are very similar to the chelating agent EDTA (ethylenediaminetetraacetic acid). No other unique or special properties are available.

Biodegradability

Biodegradation is a biotic process in which a substance is decomposed to components by microorganisms (as a reference, for example, a photodegradation is an abiotic process in which a substance is decomposed under light exposure). EDDS is a chelating agent and specifically exists as a ligand (i.e. EDDS acid) or as a complex (i.e. EDDS complex). The stabilities of EDDS acid and EDDS complex are different and should be investigated respectively (Metsarinne et al., 2001; Vandevivere et al., 2001; Bucheli-Witschel & Egli, 2001; and Nowack, 2002).

Based on the result of Schowanek et al. (1997), out of the three isomers of EDDS, (S,S)-EDDS was biodegradable, while (R,R)-EDDS and (R,S)-EDDS were partially or wholly un-biodegradable. In that research, those three types of EDDS compounds were labeled with radioactive $^{14}$C isotope and added to a simulated sewage system. After these compounds were degraded, organic carbon was decomposed to inorganic carbon (i.e. CO₂ gas). By collecting CO₂ gas above the sewage system, measuring its $^{14}$C radioactivity, and comparing the measured activity with the originally added $^{14}$C activity, the percentages of degraded EDDS compounds were calculated. Close to 96% of (S,S)-EDDS was found mineralized (degraded) within one month. Similar conclusion was also made by Takahashi et al. (1997).

Vandevivere et al. (2001) investigated the stability of EDDS complex in a sewage/sludge treatment simulation test. It was found that the biodegradability (or the stability) of EDDS complex was metal ion dependent. For example, the concentrations of some EDDS complex (Cr, Cd, Mg, and Pb) decreased to less than 20% of original concentrations within 5-10 days in the test, while the concentrations of other EDDS complex (Cu, Co and Ni) remained virtually unchanged for more than 15 days.

The following is directly quoted from US EPA 40 CFR Part 180.920-Document 0002:

IV. Environmental Fate and Drinking Water Considerations

(S,S)-EDDS is a chelating agent. Several studies of (S,S)-EDDS describe it as a naturally occurring compound from strains of bacteria (Bucheli-Witschel, 2001; Goodfellow, 1997; Witschel, 1998). (S,S)-EDDS was “isolated from culture filtrate of the actinomycete Amycolatopsis orientalis” during an antibiotic screening program (Bucheli-Witschel, 2001). In examining environmental fate and biodegradation, studies describe (S,S)-EDDS as degrading rapidly (Witschel, 1998; Bucheli-Witschel, 2001). The rapid biodegradation properties of (S,S)-EDDS will greatly reduce the amount that could occur in run-off into drinking water. Therefore, the Agency has determined that contributions of concern to drinking water are not expected from the use of this chemical as an inert ingredient in pesticide formulations applied to growing crops.

The paper of Bucheli-Witschel (2001), cited above, actually is Bucheli-Witschel and Egli (2001). This paper is a 38-page long review article titled “Environmental fate and microbial degradation of aminopolycarboxylic acids,” extensively focused on NTA (nitritoltriacetate) and EDTA. Merely ¼ page on page 84 of the paper was devoted for
“Biodegradation of EDDS.” The discussion was totally based on the works of Takahashi et al. (1997) and Schowanek et al. (1997). The paper of Witschel (1998) actually is Witschel and Egli (1998). This paper is titled “Purification and characterization of a lyase from the EDTA-degrading bacterial strain DSM 9103 that catalyzes the splitting of [S,S]-ethylenediaminedisuccinate, a structural isomer of EDTA,” and is not specifically about the rate at which EDDS is biodegraded.

Bucheli-Witschel and Egli (2001) and Nowack (2002) indicated that the literature about the environmental chemistry of several aminopolycarboxylates including EDDS was very sparse. Vandevivere et al. (2001) stated that the biodegradability of metal-EDDS complex was not well established. The research by Takahashi et al. (1997) and Schowanek et al. (1997) were mainly about the biodegradation of EDDS acid in simulated sewage systems. The biodegradability of EDDS in soil was investigated (Hauser et al., 2005; Meers et al., 2005; Tandy et al., 2006; and Meers et al., 2008). A general conclusion was that EDDS was biodegradable in soil. However, more research might still be needed, as discussed in Appendix B: Biodegradation of EDDS.

Chelating Capacity

Aminopolycarboxylic acids (APCAs) form strong and water-soluble complexes with metal ions (Bucheli-Witschel and Egli, 2001; Nowack, 2002). EDDS, one of the APCAs, forms stable hexadentate (six binding sites, see Appendix A) chelates with metals such as copper, zinc and lead. The stability constants are metal dependent. For example, the constants are, expressed as log (k) where k is a stability constant, 22.0, 18.4, 13.4 and 8.57, respectively for Fe(III), Cu(II), Zn(II) and Mn(II) (Orama et al., 2002). Stability constants are not always available from experimental data and frequently estimated from some basic thermodynamic properties. The constants of some metals and radionuclides are listed in Jones and Williams (2001), Vandevivere et al. (2001), and Bucheli-Witschel and Egli (2001).

Both of EDDS and EDTA are aminopolycarboxylic acids with similar structures (Fig. 2 Structure of EDTA). The six-member rings of EDDS function effectively as chelating agents (Fig. 3. Metal-EDDS complex). The chelating capacity of EDDS is compared to that of EDTA, in terms of complex stability constant. One example is shown below.

<table>
<thead>
<tr>
<th>Formation Reaction</th>
<th>Formation Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Fe(H₂O)₆]³⁺ + (S,S)-EDDS⁺ → Fe[(S,S)-EDDS] + 6 H₂O</td>
<td>k_EDDS = 10^{20.6}</td>
</tr>
<tr>
<td>[Fe(H₂O)₆]³⁺ + EDTA⁺ → Fe(EDTA)⁺ + 6 H₂O</td>
<td>k_EDTA = 10^{25.1}</td>
</tr>
</tbody>
</table>

In the work of Jones & Williams (2001), stability constants of the EDDS and EDTA complexes were estimated for these ions: Sb, Co, Mn, Ce, Ru, Eu, Pu, Am, UO₂, NpO₂, Fe, Cr, Ni, Mg, Zn, Mo, Nd, and Gd, respectively. The ratio of (log k_EDDS)/(log k_EDTA) was 0.76±0.13. Based on this, the ETDA complex is generally more stable than EDDS complex.

The estimated formation and stability of a complex, based on the stability constants, is a “thermodynamic approach” and is a “possibility.” The actual formation and stability of a complex is determined by the kinetics in which the complex is formed (Nortemann, 1999; Nowack, 2002; and Bucheli-Witschel and Egli, 2001). In a specific case, the stability constant alone might be insufficient to predict the biodegradability or stability of a metal complex.
Chelating agents are used in soil washing and phytoextraction. There was sufficient evidence to suggest that copper and zinc were more stable with EDDS than with EDTA, while lead and cadmium were less stable with EDDS than with EDTA (Kos & Lestan, 2003; Luo et al., 2005; Meers et al., 2005; and Ko et al., 2010).

Toxicity

The following toxicity values are directly quoted from Table 2 of US EPA 40 CFR Part 180.920-Document 0002.

"Table 2. Acute Toxicity"

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Toxicity Value</th>
<th>MRID</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oral LD50 - rats</td>
<td>&gt; 2,700 mg/kg</td>
<td>46323201</td>
</tr>
<tr>
<td>Dermal LD50 – rat</td>
<td>&gt; 2,000 mg/kg</td>
<td>46309104</td>
</tr>
<tr>
<td>Inhalation LC50 - rat</td>
<td>&gt; 1.49 mg/L</td>
<td>46323203</td>
</tr>
<tr>
<td>Eye irritation - rabbit</td>
<td>Mild irritant</td>
<td>46309107</td>
</tr>
<tr>
<td>Dermal irritation - rabbit</td>
<td>Not an irritant</td>
<td>46323205</td>
</tr>
<tr>
<td>Dermal sensitization – guinea pig</td>
<td>Not a sensitizer</td>
<td>46309110</td>
</tr>
</tbody>
</table>

The following statements are directly quoted from US EPA 40 CFR Part 180.920-Document 0002.

"The available studies show (S,S)-EDDS is poorly absorbed and rapidly excreted from the body, and it has low toxicity in acute, repeat dose, and developmental studies. The results of the (S,S)-EDDS studies indicate developmental toxicity is present only at high dosage levels (limit dose) and only in the presence of maternal toxicity (limit dose). Based on this information, there is low concern, at this time, for increased sensitivity to infants and children to (S,S)-EDDS when used as an inert ingredient in pesticide formulations. For the same reason, a safety factor analysis has not been used to assess risk and, therefore, the additional ten-fold safety factor for the protection of infants and children is also unnecessary."

"Considering the low toxicity, poor absorption, and rapid biodegradation properties of (S,S)-EDDS, residues of concern are not anticipated from dietary exposures (food and drinking water) or from residential exposures (inhalation and dermal). Utilizing a highly conservative aggregate exposure assessment, EPA has concluded that aggregate exposures to (S,S)-EDDS are more than three orders of magnitude less than the dose at which no adverse effects were seen in the most sensitive animal study and are therefore below the level of concern. In addition, this highly conservative exposure assessment is protective of any possible non-occupational exposures to (S,S)-EDDS as it results in exposure estimates orders of magnitude greater than the high-end exposure estimates for residential uses of pesticides routinely used by the Office of Pesticide Programs."

"Taking into consideration all available information on (S,S)-EDDS, it has been determined that there is a reasonable certainty that no harm to any population subgroup, including infants and children, will result from aggregate exposure to this chemical when used as an inert ingredient in pesticide products when considering dietary exposure and all other nonoccupational sources of pesticide exposure for which there is reliable information. Therefore, the exemption from the requirement of a tolerance for residues of (S,S)-EDDS under 40 CFR 180.920 can be considered safe under section 408(q) of the FFDCA."

Specific Uses of the Substance:

EDDS is mainly used as a chelating agent (e.g. Grcman et al., 2003; Tandy et al., 2004; Hauser et al., 2005; Duquene et al., 2009; and Ko et al., 2010). Metal ions such as iron, manganese, copper, cadmium and lead cause various kinds
of interferences and problems in different application areas such as industry, agriculture, consumer products, etc. Chelating agents combine with metal ions to form complexes and keep these ions water-soluble.

The following is directly quoted from the petition (page 4 of the petition).

“The proposed substance ([S,S]-EDDS free acid, CAS # 20846-91-7, trade name Enviomet C265), is intended to be used as an inert ingredient in multiple pesticide formulations. It is intended to be a substitute for other, less readily biodegradable synthetic chelating agents currently used in these pesticides. The pesticide formulations containing EDDS are intended to be sold to kill pests of many types. These pesticides are registered for use on and around nearly all crop types (fruits, vegetables, fruit trees, outdoor ornamentals, lawns, greenhouses, field crops, nurseries, etc.) in both the homeowner and commercial agricultural markets.”

Based on the majority of literature, EDDS is used as a chelating agent but not as other specific uses.

Approved Legal Uses of the Substance:

U.S. Environmental Protection Agency:

The U.S. Environmental Protection Agency (EPA) established the exemption from the requirement of a tolerance for residues of (S,S)-EDDS when used as an inert ingredient sequestrant or chelating agent in pesticide formulations applied to growing crops only under 40 CFR Part 180.920 (EPA-HQ-OPP-2008-0250; FRL-8362-4; effective November 14, 2008).

The following is directly quoted from US EPA’s Document 0001 (US EPA 40 CFR Part 180.920).

“SUMMARY: This regulation establishes an exemption from the requirement of a tolerance for residues of (S,S)-Ethylenediaminedisuccinic acid (CAS Reg. No. 20846–91–7) ([S,S]-EDDS) when used as an inert ingredient sequestrant or chelating agent in pesticide formulations applied to growing crops only under 40 CFR Part 180.920. Associated Octel Company, Limited, submitted a petition to EPA under the Federal Food, Drug, and Cosmetic Act (FFDCA), as amended by the Food Quality Protection Act of 1996 (FQPA), requesting an exemption from the requirement of a tolerance. This regulation eliminates the need to establish a maximum permissible level for residues of (S,S)-Ethylenediaminedisuccinic acid.

DATES: This regulation is effective November 14, 2008.”

U.S. Food and Drug Administration:

The U.S. Food and Drug Administration (FDA) approved Food Contact Notification (US FDA FCN 000799). In this FCN, Innospec requested that the tri-sodium salt of EDDS (a close chemical relative of EDDS) be allowed as a chelating agent in the manufacture of food-contact paper and paperboard. FDA approved that request on February 6, 2008 (FDA FCN 000799).

The following is directly quoted from FDA Memo “FCN No. 799 – [S,S]-ethylenediaminedisuccinic acid, trisodium salt, as a chelating agent in the manufacture of paper and paperboard” (US FDA FCN 000799).

“Finding of No Significant Impact:

A food contact notification (FCN No. 799), submitted by Innospec Limited, to provide for the safe use of (S,S)-ethylenediaminedisuccinic acid, trisodium salt, as a chelating agent in the manufacture of paper and paperboard.

The Environmental Review Team has determined that allowing this notification to become effective will not significantly affect the quality of the human environment and, therefore, will not require the preparation of an environmental impact statement. This finding is based on information, submitted by the notifier, in the notification, which includes an environmental assessment, dated December 24, 2007.”
No other major approved uses of EDDS were found.

**Action of the Substance:**

EDDS combines with metal ions to form metal complexes. The process and the product depend on the metal ions and other parameters such as pH (e.g. Nowack, 2002; Orama et al., 2002; Wu et al., 2007; Yip et al., 2009).

For example, the stability constants of several metal-EDDS complexes, as summarized in Tandy et al. (2006), are $10^{0.34}$, $10^{7.77}$, $10^{12.7}$, $10^{14.46}$, $10^{20.46}$ and $10^{23.68}$ for Ca$^{2+}$, Mg$^{2+}$, Cd$^{2+}$, Pb$^{2+}$, Cu$^{2+}$ and Fe$^{3+}$-EDDS complexes, respectively. EDDS preferentially combines with transition metals and/or heavy metals such as Cd, Pb, Cu and Fe over alkaline elements such as Ca and Mg. By using this differential action, EDDS was used for the preferential removal of heavy metals from contaminated soil (Grcman et al., 2003; Tandy et al., 2004).

**Status**

**U.S. Environmental Protection Agency:**

See above in “Approved legal uses of the substance.”

**U.S. Food and Drug Administration:**

See above in “Approved legal uses of the substance.”

**Association of American Feed Control Officials, Inc.**

No specific items were found.

**International:**

No specific items were found.

**Evaluation Questions for Substances to be used in Organic Crop or Livestock Production**

**Evaluation Question #1: Is the petitioned substance formulated or manufactured by a chemical process? (From 7 U.S.C. § 6502 (21).)**

As proposed in the petition, EDDS is produced by mixing two major chemicals and several other supporting chemicals (calcium hydroxide, sodium hydroxide, and hydrochloric acid) in a heated and pressurized reactor to react chemically under pre-specified conditions for a duration of about half a day. The reaction product is crystallized after acidification and then is separated, as solid material, from other byproducts with physical processes.

As a reference, (S,S)-EDDS was produced chemically starting from the chemicals of L-aspartic acid, sodium hydroxide, and 1,2-dibromoethane at a laboratory experimental scale (Neal and Rose, 1968). L-aspartic acid was reacted with sodium hydroxide at low temperature (ice-bath) to form sodium L-aspartate salt. Other chemicals (sodium carbonate and ethanol) were added and the mixture was heated to reflux. The other major chemical, 1,2-dibromoethane, was added slowly to the heated mixture. The reaction was given about one day to finish. The reaction product was cooled, acidified, and separated physically from other by-products.
(S,S)-EDDS was produced when L-aspartic acid was reacted to 1,2-dibromoethane. (R,R)-EDDS was produced when D-aspartic acid was reacted to 1,2-dibromoethane, and the mixture of 25% (S,S)-EDDS, 50% (R,S)/(S,R)-EDDS and 25% (R,R)-EDDS was produced when maleic anhydride was reacted to ethylene diamine (Neal and Rose, 1968; Schowanek et al., 1997).

**Evaluation Question #2:** Is the petitioned substance formulated or manufactured by a process that chemically changes the substance extracted from naturally occurring plant, animal, or mineral sources? (From 7 U.S.C. § 6502 (21).)

EDDS was reported to be produced naturally by a number of microorganisms (Nishikiori et al., 1994; Zwicher et al., 1997; and Takahashi et al., 1999; Bucheli-Witschel and Egli, 2001). EDDS is a pure chemical compound with a relatively simple molecular structure but not a mixture of compounds or a substance with great structure complexity and/or component variations. No evidence is available to indicate that the manufactured EDDS would be different chemically from the naturally occurring EDDS.

**Evaluation Question #3:** Is the petitioned substance created by naturally occurring biological processes? (From 7 U.S.C. § 6502 (21))

EDDS was found to be produced by microorganisms in soil (Nishikiori et al., 1984).

In a laboratory fermentation experiment, EDDS was produced by bacteria *Amycolatopsis orientalis* (Zwicker et al., 1997). With feeding solutions of glycerol (carbon source), glutamic acid (phosphorus source) and urea (nitrogen source), the concentration of EDDS in fermentation medium reached to 20 g/L after about 42 days of fermentation time. The fermentation medium must be low in zinc content. In fact, the fermentation was carried out in glass containers only and the scale-up in larger (metal) tanks was not realized. The product EDDS was purified using a three-step process consisting of an acid precipitation, an ethanol washing, and a final crystallization step.

EDDS was produced by bacteria isolated from soil and sludge (Takahashi et al., 1999). In a reaction mixture composed of ethylenediamine (200 mmol/L) and fumaric acid (200 mmol/L) in 50 mmol/L phosphate buffer (pH7.5) at 30°C, the bacterium *Acidovorax* sp. (TNT149) produced 71 mmol/L (21 g/L) of EDDS in 24 hours. Other bacteria, *Sphingomonas, Brevundimonas, or Pseudomonas*, produced less than 1 g/L of EDDS in 24 hours.

**Evaluation Question #4:** Is there environmental contamination during the petitioned substance’s manufacture, use, misuse, or disposal? (From 7 U.S.C. § 6518 (m) (3).)

Publically available data are scarce about the environmental contamination during the EDDS’ manufacture, use, misuse or disposal. From the MSDS (material safety data sheet), EDDS is not considered as hazardous. EDDS is considered to be low-toxicity by US EPA and allowed to be used in food-contacting paper and paper board by US FDA. EDDS chemically functions like EDTA and provides strong chelating capabilities.

Two major chemicals are used for manufacturing the product of EDDS, as proposed in the petition. One chemical is L-aspartic acid with CAS # 56-84-8, and the other chemical is dibromoethane with CAS # 106-93-4.

Aspartic acid CAS # 56-84-8

![Aspartic acid](https://example.com/aspartic-acid.png)

Aspartic acid (L-aspartic acid, asparagic acid, or S-aminobutanedioic acid), one of the nonessential amino acids, occurs in animals and plants, especially in young sugar cane and in sugar beet molasses. Aspartic acid is allowed in the compounds for use in foods for infants and children, as listed in Codex Alimentarius (Codex – L aspartic acid).
Aspartic acid is colorless crystals with a low to medium solubility (0.45 g/100 mL). Dust explosion is possible if in powder or granular form, mixed with air. If dry, aspartic acid can be charged electrostatically by swirling, pneumatic transport, pouring, etc. Aspartic decomposes on burning producing toxic gases including nitrogen oxides. Aspartic acid reacts violently with oxidants. The substance can be absorbed into the body by ingestion. Other relevant risk evaluations are listed in “International chemical safety cards” (ICSC-aspartic acid) and in “National Institute for Occupational Safety and Health” (NIOSH-aspartic acid).

Dibromoethane  CAS # 106-93-4

The other chemical is dibromoethane (or 1,2-dibromoethane, ethylene dibromide, ethylene bromide, EDB, and glycol bromide). The trade names are “Bromofume” and “Dowfume.” It is a colorless liquid with a melting point of 9-10°C.

Dibromoethane is reasonably anticipated to be a human carcinogen and has been banned by US EPA for most kinds of uses since 1984.

The following potential danger is directly quoted from “Agency for toxic substances and disease registry” (ATSDR-dibromoethan)

“SUMMARY:

Exposure to 1,2-dibromoethane can result from drinking groundwater or breathing air that is contaminated. This is most likely to occur in the workplace or from living near a hazardous waste site. 1,2-dibromoethane can affect the brain, damage skin, damage sperm in males, and even cause death if exposure is very high. This chemical has been found in at least 27 of 1,416 National Priorities List sites identified by the Environmental Protection Agency.”

The following environmental consequence is directly quoted from “Agency for toxic substances and disease registry” (ATSDR-dibromoethan)

“What happens to 1,2-dibromoethane when it enters the environment?

It moves into the environment from manufacturing use and leaks at waste sites.

When released, it quickly moves to air and will evaporate from surface water and soil to the air.

It dissolves in water and will move through soil into the groundwater.

Small amounts remain attached to soil particles.

It breaks down slowly in air (over 4-5 months), more quickly in surface water (2 months), and hardly at all in groundwater.

It is not expected to build up in plants or animals.”
The following regulations are directly quoted from the “11th Report on Carcinogens” by US Department of Health and Human Services (11th ROC)

“Regulations

DOT
1,2-Dibromoethane is considered a hazardous material and special requirements have been set for marking, labeling, and transporting this material.

EPA
Clean Air Act
NESHAP: Listed as a Hazardous Air Pollutant (HAP).
NSPS: Manufacture of substance is subject to certain provisions for the control of Volatile Organic Compound (VOC) emissions.
Urban Air Toxics Strategy: Identified as one of 33 HAPs that present the greatest threat to public health in urban areas.

Comprehensive Environmental Response, Compensation, and Liability Act
Reportable Quantity (RQ) = 1 lb.

Emergency Planning and Community Right-to-Know Act
Toxics Release Inventory: Listed substance subject to reporting requirements.

Federal Insecticide, Fungicide, and Rodenticide Act
Most registrations have been cancelled.

Resource Conservation and Recovery Act
Listed Hazardous Waste: Waste codes in which listing is based wholly or partly on substance - U067, K117, K118, K136.
Listed as a Hazardous Constituent of Waste.

Safe Drinking Water Act
Maximum Contaminant Level (MCL) = 0.00005 mg/L.

FDA
Action levels for 1,2-dibromoethane in food and in animal feed range from 0.01-150 ppb.
Maximum permissible level in bottled water = 0.00005 mg/L

OSHA
Acceptable Peak Exposure = 50 ppm (maximum duration = 5-minutes).
Ceiling Concentration = 30 ppm.
Permissible Exposure Limit (PEL) = 20 ppm.

Guidelines

NIOSH
Ceiling Recommended Exposure Limit = 0.13 ppm (15 minute exposure).
Immediately Dangerous to Life and Health (IDLH) = 100 ppm.
Recommended Exposure Limit (time-weighted-average workday) = 0.045 ppm.
Listed as a potential occupational carcinogen.”

The following use of dibromoethane is directly quoted from the “11th Report on Carcinogens” by US DHHS (11th ROC)

“Use
Historically, the primary use of 1,2-dibromoethane was as a lead scavenger in anti-knock mixtures added to gasolines. Lead scavenging agents transform the combustion products of lead alkyls to forms that are more likely to be vaporized from engine surfaces. In 1978, 90% of the 1,2-dibromoethane produced was used for this purpose. Annual consumption of 1,2-dibromoethane in the United States has decreased due to EPA regulations banning the use of lead in gasolines (IARC 1977, ATSDR 1992).

Another major use of 1,2-dibromoethane in the past was as a pesticide and ingredient of soil and grain fumigant formulations. It was used for post-harvest application to a variety of vegetable, fruit, and grain crops. It was also used to kill fruit flies on citrus fruits and in the soil to protect
grasses in environments such as golf courses. By 1984, EPA regulations had eliminated most of the use of 1,2-dibromoethane as a pesticide in the United States (ATSDR 1992).

Currently, 1,2-dibromoethane is used as a chemical intermediate in synthesis and as a nonflammable solvent for resins, gums, and waxes. The major chemical made from 1,2-dibromoethane is vinyl bromide, which is used as a flame retardant in modacrylic fibers. It also has been used as an intermediate in the preparation of dyes and pharmaceuticals (ATSDR 1992).”

In the petition, no information was given whether dibromoethane, one of the two major chemicals for manufacturing (S,S)EDDS, would be completely converted to the end-product of (S,S)EDDS. If the conversion is not 100%, no information was given whether the un-reacted dibromoethane would be mixed with the end-product of (S,S)EDDS or mixed with by-products.

**Evaluation Question #5:** Is the petitioned substance harmful to the environment? (From 7 U.S.C. § 6517 (c) (1) (A) (i) and 7 U.S.C. § 6517 (c) (2) (A) (i.).)

US EPA exempted EDDS from the requirement of a tolerance when used as an inert ingredient sequestrant or chelating agent in pesticide formulations applied to growing crops (US EPA 40 CFR Part 180.920-Document 0001). In this document, US EPA did not specify conditions for use where concentrations are limited.

US FDA approved the use of (S,S')-EDDS in food-contacting paper or paperboard (US FDA FCN 000799).

As given in “Appendix B: Biodegradation of EDDS,” the use of and research on EDDS are recent events relatively, in the range of 5-10 years. Information about potential harmfulness of EDDS to the environment is still limited, relative to the information about EDTA’s effects to the environment (Nortemann, 1999; Vandevivere et al., 2001; Bucheli-Witschel and Egli, 2001; and Nowack, 2002). EDTA, as a chelator, has been used for 40-50 years. In a review article by Bucheli-Witschel and Egli (2001), 256 papers were cited to provide the base for the discussion of “environmental fate and microbial degradation of aminopolycarboxylic acids.” NTA and EDTA were the major APCAs discussed in the paper.

Quantity is one index relevant to a potential harmfulness of a substance to the environment. For example, EDTA was found in natural waters close to places where substantial use and discharge of EDTA occurred (Sillanpaa & Oikari, 1996; Bucheli-Witschel and Egli, 2001). EDDS is used in domestic products such as detergents, but the usage of EDDS, in quantity and in scale, is far less than that of EDTA. In 1981, the estimated world-wide usage of EDTA was $5.6 \times 10^3$ metric tons, while the usage of other APCAs was $5 \times 10^3$ metric tons (Bucheli-Witschel and Egli, 2001). Joanna et al. (1999) carried out environmental risk assessment on the use of EDDS in detergent applications. Based on the assessment, a “no immediate concern” at the anticipated usage level was proposed. Additional and other major researches about the effect of EDDS on environment are still very limited.

In Bucheli-Witschel and Egli (2001), four types of potential environmental risks caused by APCAs were listed: “(1) adverse effects on the operation of wastewater treatment plants, (2) toxic effects of APCAs on aquatic and mammalian organisms, (3) the contribution of nitrogen from APCAs to eutrophication, and (4) the potential to mobilise metals.” However, no words were mentioned about EDDS.

**Evaluation Question #6:** Is there potential for the petitioned substance to cause detrimental chemical interaction with other substances used in organic crop or livestock production? (From 7 U.S.C. § 6518 (m) (1.).)

The petitioned substance EDDS works as a strong chelating agent, similar to another extensively used chelating agent EDTA. EDTA is allowed in NOP as “inert ingredients.” EDDS is expected to cause similar chemical interactions with other substances used in organic crop or livestock production. However, direct evidence to support this expectation is still very limited.

Based on the germination and seedling growth of the water cress *Rorippa* sp., Temara et al. (2006) indicated that the germination was not significantly affected by EDDS. On the other hand, in the phytoextraction experiments, the application of EDDS in soil released adsorbed heavy metals to water-soluble. The excess heavy metals inhibited the “normal” growth of plants (e.g. Epelde et al., 2008; Duquene et al., 2009; Wu et al., 2007).
As given in the answer to question #5, EDDS was approved to be used in pesticides and in food-contacting paper or paperboard. US EPA concluded that (S,S)-EDDS is a low-toxicity materials (see above “Toxicity” in the “Properties”).

The following is directly quoted from the petition:

**Evaluation Question #7**: Are there adverse biological or chemical interactions in the agro-ecosystem by using the petitioned substance?  (From 7 U.S.C. § 6518 (m) (5).)

As given in “Appendix B: Biodegradation of EDDS,” the use of and research on EDDS are relatively recent events. The data relevant to this question are limited. Jaworska et al. (1999) assessed the environmental risk of EDDS used in detergent application. By using mathematical models and making numerous assumptions of relevant parameters, a “no immediate concern” conclusion was generated.

**Evaluation Question #8**: Are there detrimental physiological effects on soil, organisms, crops, or livestock by using the petitioned substance?  (From 7 U.S.C. § 6518 (m) (5).)

The petitioned substance EDDS works as a strong chelating agent, similar to another extensively used chelating agent EDTA. EDTA is allowed in NOP as “inert ingredients.” EDDS is expected to cause similar physiological effects on soil, organisms, crops, or livestock. However, direct evidence to support this expectation is still very limited, since the use of and research on EDDS are still relatively recent events.

**Evaluation Question #9**: Is there a toxic or other adverse action of the petitioned substance or its breakdown products?  (From 7 U.S.C. § 6518 (m) (2).)

As given above in “Toxicity” of “Properties,” the petitioned substance EDDS itself is considered to be of low toxicity by US EPA. The petitioned EDDS is made from 1,2-di bromoethane and L-aspartic acid. In Schowanek et al. (1997) experiment, EDDS was synthesized from 1,2-dibromoethane and L-aspartic acid. Exactly, $^{14}$C labeled L-aspartic acid was used and the material EDDS was labeled on the succinate part. This $^{14}$C labeled EDDS was added to a simulated sewage system, and the $^{14}$C activity in evolved CO$_2$ gas was measured. By comparing the $^{14}$C activity in CO$_2$ gas with the $^{14}$C activity originally added to the simulated sewage system, Schowanek et al. (1997) concluded that 96% of EDDS added to the sewage system degraded to inorganic carbon in about two months.

![Chemical Reaction Diagram](Image)

Although the measured $^{14}$C activity in CO$_2$ gas (i.e. inorganic carbon) was about 96% of the $^{14}$C activity which was added originally to the simulated sewage system as EDDS (i.e. organic carbon), that does not necessarily mean that all
of EDDS had decomposed to inorganic carbon already. As shown in the above figure, EDDS was actually labeled with $^{14}$C partially. The labeled part of EDDS did decompose to CO$_2$ gas, but that did not necessarily assure that the unlabeled part also decomposed to CO$_2$ gas, since that part was not directly measured. In other words, EDDS as a whole compound did decompose in about two months, but the breakdown products might not be totally inorganic. The breakdown products of the unlabeled part of EDDS may still need to be clarified.

The potentially unbroken part is originated from 1,2-dibromoethane, a substance banned by US EPA in 1984 for most kinds of uses (See above in Question 4).

Evaluation Question #10: Is there undesirable persistence or concentration of the petitioned substance or its breakdown products in the environment? (From 7 U.S.C. § 6518 (m) (2).)

The petitioned substance EDDS was claimed to be biodegraded quickly. As given in “Biodegradability” of “Properties,” and as discussed in Appendix B: Biodegradation of EDDS, EDDS might degrade in natural environments, but the evidence to support the claim is still weak,

As given in Question #9, the breakdown products of (S,S)EDDS might not be totally inorganic but no further information is available.

Evaluation Question #11: Is there any harmful effect on human health by using the petitioned substance? (From 7 U.S.C. § 6517 (c) (1) (A) (i), 7 U.S.C. § 6517 (c) (2) (A) (i) and), 7 U.S.C. § 6518 (m) (4).)

As given in “Toxicity” of “Properties,” (S,S)-EDDS is considered to be of low toxicity by US EPA. US FDA approved the use of (S,S)-EDDS in food-contacting paper or paperboards.

Evaluation Question #12: Is there a wholly natural product that could be substituted for the petitioned substance? (From 7 U.S.C. § 6517 (c) (1) (A) (ii).)

EDDS is petitioned to be used as a chelator in organic pesticides. Chelators are a class of chemical compounds which combine with metal ions to form water-soluble complexes. Some chelators such as EDTA are synthetically manufactured, and some chelators such as rhizobactin are found as trace or minor components in natural products (Bucheli-Witschel and Egli, 2001). No chelators are found as wholly natural products or as major components in natural products.

EDDS, a simple compound, is found to be produced by microorganisms in soil (Nishikiori et al., 1984; Schowanek et al., 1997; Zwicker et al., 1997; Takahashi et al., 1999). EDDS can be synthetically manufactured but EDDS has not been found as a wholly natural product.

Evaluation Question #13: Are there other already allowed substances that could be substituted for the petitioned substance? (From 7 U.S.C. § 6517 (m) (6).)

EDTA is already listed in NOP as “inert ingredients” in pesticides. Generally, EDTA, used as a chelating reagent, is sufficiently available, provides better complex capability than the petitioned substance EDDS, and has been used in domestic, industrial and agricultural applications for 40-50 years.

EDTA, a synthetic substance, was found in natural waters at 10-60 μg/L (Barber et al., 1995; Sillanpaa & Oikari, 1996). The existence of a synthetic substance in natural environment has a variety of effects, as quoted below, and prompted searches for alternative chelators to replace EDTA (Zwicker et al., 1997; Takahashi et al., 1999).

Chelating agents have the potential to perturb the natural speciation of metals and to influence metal bioavailability, and their presence may lead to the remobilization of metals from sediments and aquifers, consequently posing a risk to groundwater and drinking water (Nowack, 2002).

EDTA is used in domestic, industrial and agricultural applications for a long time and has received substantial researches (Nortemann, 1999; Nowack, 2002). For example, the research on its biodegradation at least started in 1967 (Bunch and Ettinger, 1967).

The petitioner claimed that “EDDS occurs naturally in the environment and has a better environmental fate and degradation profile than the chelating agents currently allowed in organic pesticides;” and “EDDS degrades rapidly
and is completely mineralized.” However, the use of and research on EDDS are relatively recent events, as discussed in “Appendix B: Biodegradation of EDDS.” The biodegradation of EDDS in soil has been investigated but an unambiguous conclusion might still be too soon to make (Appendix B). EDDS might be biodegraded faster than EDTA, but the environmental consequence of EDDS might be less understood than that of EDTA currently.

**Evaluation Question #14:** Are there alternative practices that would make the use of the petitioned substance unnecessary? (From 7 U.S.C. § 6517 (m) (6).)

Chelation is a process in which chelators (chelating reagents) combine with metal ions to form complex and to keep metal ions water-soluble without changing other significant properties such as solution pH and metal ion concentrations. In this sense of keeping other significant properties such as pH and metal ion concentrations unchanged, the use of chelator can not be replaced by other alternative practices.

The substance EDDS is petitioned to be used as “inert ingredients” in organic pesticides. As a chelator, the petitioned substance EDDS can be replaced with other kinds of chelators, if available. In fact, EDTA, a chelator, is currently listed in NOP as “inert ingredients” in pesticides.

The use of EDTA has some environmental concerns, as given in “Evaluation Question #13.”
Appendix A: Chelation and Related Issues

The following is quoted from “Glossary of Terms Used in Physical Organic Chemistry (IUPAC Recommendations 1994).”

**Chelation**

The formation or presence of bonds (or other attractive interactions) between two or more separate binding sites within the same ligand and a single central atom. A molecular entity in which there is chelation (and the corresponding chemical species) is called a "chelate". The terms bidentate (or didentate), tridentate, tetradentate... multidentate are used to indicate the number of potential binding sites of the ligand, at least two of which must be used by the ligand in forming a "chelate". For example, the bidentate ethylenediamine forms a chelate with Cu(I) in which both nitrogen atoms of ethylenediamine are bonded to copper. (The use of the term is often restricted to metallic central atoms.)

The phrase "separate binding sites" is intended to exclude cases such as [PtCl₂(CH₂=CH₂)]. ferrocene, and (benzene)tricarbonylchromium in which ethene, the cyclopentadienyl group, and benzene, respectively, are considered to present single binding sites to the respective metal atom, and which are not normally thought of as chelates (see haptoc). See also cryptand.

Analogous to wrapping medicine pills with protective coats so that medicine pills are less reactive and exert longer effects, chelation could be intuitively understood as a process in which metal ions are wrapped with chelating agents so that metal ions are less reactive. The reactivity includes precipitation, adsorption, reaction with other components, and assimilation by organisms, etc.

**Complex stability and reversible process:** Metal ion "M" combines with ligand “L” to form complex “ML.”

Chelation is a reversible process: M + L ⇌ ML. Metal “M” and ligand “L” form complex “ML” at one condition, but complex “ML” decomposes to metal “M” and ligand “L” at another condition. The stability constant $k$ of “ML” is expressed as: $k = [ML] / ([M] × [L])$, where square brackets denote concentrations. The higher the $k$ value, the stable the complex “ML” is.

**Ligand stability:** A ligand decomposes itself to its components and loses the chelating capability. The ligand decomposing process is not reversible.

**Competition:** Assume there are two metal ions (calcium, Ca²⁺ and lead, Pb²⁺) and one ligand EDTA. The stability constant $k$ of Pb-EDTA complex is much greater than that of Ca-EDTA complex. In this case, EDTA forms Pb-EDTA preferentially. If lead is added to a system which contains Ca-EDTA originally, Ca-EDTA will decomposes and Pb-EDTA is formed.

Initially, Ca-EDTA complex is formed: Ca + EDTA → Ca-EDTA.

After Pb is added, Ca-EDTA decomposes and Pb-EDTA is formed: Pb + Ca-EDTA → Ca + Pb-EDTA.

**Kinetics:** Competition based on the consideration of complex stability is just one side of a story. A real complex process is controlled by the complex kinetics.

With these concepts of “complex stability,” “ligand stability,” “reversible process,” “competition,” and “kinetics,” several processes are described here.

**Basic application:** Example 1: Hard water contains high concentrations of calcium and magnesium. These ions form “soap scum” with detergents. Chelating agents added to detergent forms complex with these metal ions. Calcium and magnesium stay dissolved and soap scum is not formed. Example 2: Chelating reagents added to pesticides modify the effects of heavy metals in pesticides.

**Soil washing:** Soil is soaked with water containing chelating reagents. Heavy metals such as copper, lead, and zinc, initially precipitated or adsorbed to soil, are converted to complex which is water-soluble and rinsed away from soil.

**Phytoextraction:** Phytoextraction is an enhanced accumulation of metal ions in harvestable plant. It is an alternative remediation technology for soils polluted with heavy metals. Chelating agents enhance phytoextraction by making precipitated/adsorbed metals in soil water-soluble and available for plants.
Appendix B: Biodegradation of EDDS

Chelation makes metal ions less reactive and water-soluble. On one hand, chelation is used, for example, in "soil washing" in which toxic metals such as copper and lead precipitated in and/or adsorbed to soil are released back to water-soluble and rinsed away from soil. On the other hand, released toxic metals are transported to undesired places such as to groundwater reservoirs which might be sources of drinking water. An ideal chelator might be strong in forming complex and quick in decomposing. “Biodegradation” is a process in which a substance is decomposed to components by microorganisms.

From several chelators, Procter & Gamble selected EDDS in order to “commercially develop a chelator that performed equally to currently available materials but with a greatly improved biodegradation potential.” (Schowanek et al., 1997).

The list below is not exhaustive but includes most major literature about EDDS in the areas of biodegradability, soil washing and phytoextraction.

<table>
<thead>
<tr>
<th>Year</th>
<th>Author(s)</th>
<th>Subject</th>
<th>Country</th>
<th>Relation to manufacture</th>
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<tr>
<td>1968</td>
<td>Neal &amp; Rose</td>
<td>EDDS isomers</td>
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<td>Schowanek et al.</td>
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<td>P&amp;G</td>
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<td>Belgium</td>
<td>P&amp;G</td>
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<tr>
<td>1997</td>
<td>Takahashi et al.</td>
<td>Degradability</td>
<td>Japan</td>
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<td>1997</td>
<td>Zwicker et al.</td>
<td>Production by bacteria</td>
<td>Germany</td>
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<td>Jaworska et al.</td>
<td>Environment assessment</td>
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<tr>
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<td>Germany</td>
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<td>Vandewere et al.</td>
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<td>Phytoextraction</td>
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<td>2003</td>
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<td>Phytoextraction</td>
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<td>Soil washing</td>
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<td>Wu et al.</td>
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<td>2008</td>
<td>Epelde et al.</td>
<td>Degradability and phytoextraction</td>
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<td>2010</td>
<td>Ko et al.</td>
<td>Extraction of Cu, Cr and As from wood</td>
<td>Taiwan</td>
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</table>

Most papers in the list did not investigate the biodegradability of EDDS, but almost all of those papers used “biodegradable” or “environmentally friendly” as an adjective to describe EDDS, and “non-biodegradable” to describe EDTA. Those papers eventually cited a limited number of papers as the basis for those claims. The papers relevant to biodegradability of EDDS were mostly contributed by the manufactures or by the people around the world who received EDDS from the manufactures.
The biodegradation of EDDS (i.e. EDDS acid) in a simulated sewage system was contributed by Takahashi et al. (1997) and Schowanek et al. (1997). A general conclusion was that EDDS acid was biodegradable. The biodegradation of EDDS complex in a simulated sewage system was contributed by Vandevivere et al. (2001). A general conclusion was that the biodegradation of EDDS complex depended on metal ions. For example, the Cu-
EDDS complex did not show significant biodegradation within an experiment period during which the EDDS complex of several other metal ions were degraded already (Vandevivere et al., 2001). Overall, the knowledge about the fate of EDDS in the environment was still limited in 2001 (Bucheli-Witschel and Egli, 2001; Vandevivere et al., 2001; and Nowack, 2002). The review article about APCAs by Bucheli-Witschel and Egli (2001) is 38 pages long, but the discussion about biodegradation of EDDS is merely ¼ page long and the discussion is totally based on the papers by Takahashi et al. (1997) and by Schowanek et al. (1997).

Most research about the biodegradability of EDDS in soil is five years or less (e.g. Tandy et al., 2006; and Meers et al., 2008). Contrast to the research on biodegradation of EDDS in a simulated sewage system (Takahashi et al., 1997; Schowanek et al., 1997; and Vandevivere et al., 2001), the research on biodegradation of EDDS in a simulated soil system (e.g. Tandy et al., 2006; and Meers et al., 2008) has the following differences.

- The soil system was an open and dynamic system with repeated evaporation-watering cycles, while the sewage system was a closed and steady-state system in which all of the materials were added at the beginning of the experiment and well mixed.
- The soil system was a heterogeneous system composing of soil (clay minerals, organic matters, sand, etc), water, and air. With repeated evaporation-watering cycles, the concentrations of metal ions in one physical location could be different from the concentrations of metal ions in other locations. The sewage system was a pseudo-homogeneous system.
- In the soil system, a probe-type sampler was used to collect samples for the analysis of EDDS or metal ions. The probe-type sample collected samples in the very vicinity of the probe.
- In the soil system, EDDS was applied to the top of soil, while the probe-type sampler might be placed in the middle or bottom of the soil.
- In the soil system, one gram of EDDS was added to about 1000 g of soil. Soil contains clay minerals and organic matter. EDDS could be trapped and adsorbed to soil. In the sewage system, one gram of EDDS was added to 1-3 g of sludge solid. The relative percentage of EDDS trapped/adsorbed to sludge solid should be very small.
- In the soil system where the ratio of EDDS to soil was about 1 g EDDS to 1000 g soil, the amount of metal ions could be higher than the amount of added EDDs. In other words, EDDS might exist as EDDS complex rather than EDDS acid. In the sewage system, the ratio of EDDS to solid was about 1:1. EDDS could exist mainly as EDDS acid. The stabilities of EDDS acid and EDDS complex could be significantly different.
- The adsorption of chelators and metal complex to soil is greatly affected by the ratios of chelator/soil and complex/soil. In the soil system and in the sewage system, these ratios were substantially different. In other words, the adsorption of chelators and complex to soil might not be insignificant at all.

Considering these, the research on the biodegradability of EDDS in a soil system could be more complicated than that in a sewage system. The conclusions proposed in the papers about EDDS degradation in soils might be well questioned with reasonable doubts. Two examples are provided below: paper 1 by Tandy et al. (2006) and paper 2 by Meers et al. (2008).

Paper 1

In “Biodegradation and speciation of residual SS-ethylenediaminedisuccinic acid (EDDS) in soil solution left after soil washing” (Tandy et al., 2006, hereafter termed as “the paper” within this section), it was stated that “This paper aims to investigate the degradation and speciation of EDDS-complexes (SS-ethylenediaminedisuccinic acid) in soil following soil washing. The changes in soil solution metal and EDDS concentrations were investigated for three polluted soils. EDDS was degraded after a lag phase of 7-11 days with a half-life of 4.18-5.60 days. … Our results show that even in polluted soils EDDS is degraded from a level of several hundred micromoles to below 1 μM within 50 days.” After a critical reading of the paper, it was found that the conclusions about the biodegradation of EDDS proposed in the paper might not be substantiated by the experimental results presented in the paper.

The paper’s experimental set up is quoted below with some numerical marks such as “§1 ▶)” inserted for later discussion convenience.

2.3. Experimental setup
Soil (12 kg DW of each) was placed in a plastic barrel with 120 l tap water and stirred with an electrical stirrer (200 rotations per minute). 20 mmol/kg Na₂EDDS was added (0.24 moles) and the solution adjusted to pH 7 if necessary with 1 M HNO₃. This equated to a EDDS:metal ratio of 1:1 for soil 1, 4:1 for soil 2 and 2:1 for soil 3. The barrels were covered and the soils were washed in this manner for 24 h. (§2►) The suspension was then allowed to settle for 24 h before the supernatant was removed by suction and (§3►) the soil was rinsed for 1 h with 120 l tap water. (§4►) After 24 h settling the supernatant was again removed. (§5►) The soil slurry was then poured into 3 1 black plant pots (4 replicates) with a disc of fine mesh (60 mm) in the bottom to prevent the soil leaking out and 2 Rhizon Flex soil moisture samplers (SMS) (Rhizosphere Research Products, Wageningen, Netherlands) were installed at a 45° angle. (§6►) The pots were allowed to drain over night and the clear solution present on top of the soil was removed. (§7►) The pots were then transferred to a climate chamber with a 16 h (21°C)/8 h (16°C) day/night cycle to simulate field conditions. The first soil solution was then extracted (time 0) see Section 2.4. This corresponds to day 4 after addition of EDDS. After two days no more drainage occurred and this was then taken to be 100% water holding capacity (WHC). (§8►) Soil solution was extracted every 7 days. One day prior to this the pots were made up to 100% WHC with ultra pure water and 24 h later the solution extracted. The pots were then allowed to dry until the next week.

The measured concentrations of EDDS in the extracted soil solution samples were presented in Fig. 1 of the paper.

By assigning the EDDS concentration at time zero as 100%, the EDDS concentrations in subsequent samples were 90-100% at day 7 (day 7 counted from time zero), 40-70% at day 14, 20-60% at day 21, about 15% at day 28, less 10% at day 35, and close to 0% at day 56. Based on the results, the paper concluded that EDDS was decomposed in soil solution.

Based on the experimental setup, EDDS was added to soil (§1). After mixing, EDDS existed as EDDS acid and/or as EDDS complex (noted as M-EDDS), could be kept in soil by different mechanisms (such as adsorbed, attached, or trapped), and was distributed in water and in soil. EDDS in water was discarded (§2). The EDDS-treated soil was washed with tap water (§3), and EDDS in this washing water was discarded (§4). EDDS in water phase was further discarded (§6). Some water remained in soil as “soil solution.”

Initially, 70 g of EDDS (as EDDS acid) was added to 12,000 g of soil (§1) (5.8 g of EDDS to 1000 g of soil). After the above preparation steps, it is not know how much EDDS remained in “soil solution,” how much EDDS was adsorbed/attached/trapped, and how much EDDS was discarded. Schowanek et al. (1997) indicated that the adsorption of EDDS to sludge/soil was insignificant. However, in Schowanek et al. (1997), the ratio of EDDS to sludge solid was about 1:1 to 1:3 and sludge solid contained less clay minerals than regular soil. In a review paper, Nowack (2002) indicated that the adsorption of chelators and complex to soil was significant: “Chelating agents have been developed to solubilize metals and keep them in solution. Therefore, it might be reasonable to assume that chelating agents decrease heavy metal adsorption by forming dissolved complexes. This, however, is only true for the very high concentrations of chelating agents used in technical applications. At low concentrations, chelating agents are able not only to decrease but also can significantly increase metal adsorption onto mineral surfaces.”

Except the first soil solution sample which was collected at time zero after the EDDS-treated soil was made “ready” in the plant pots (§7), the subsequent soil solution samples were collected after the EDDS-treated soil was repeatedly subject to day/night cycles (§7) and subject to additional input of ultra clean water (i.e. dry/wet cycles) (§8).

“Soil” and “soil solution” were not two clearly separated physical entities, but interchanged and interacted closely. EDDS was kept in soil either strongly or weakly. It could be well expected that initial soil solution samples contain more EDDS than the subsequent samples, since most weakly kept EDDS would be released from soil to soil solution quickly. In other words, the result of Fig. 1 would still be obtained even if EDDS did not degrade at all.

Even if the releasing of EDDS from “soil” to “soil solution” is not considered, it could be well expected that initial soil solution samples contain more EDDS than the subsequent samples. EDDS in soil solution was a limited source and would reach to zero content after ultra clean water was repeatedly added to the EDDS-treated soil. Each addition of clean water would deplete EDDS from the soil (or soil solution). Therefore, the result of Fig. 1 would still be obtained even if EDDS did not degrade at all.

Specific to the experiment setup, there could be at least three scenarios, individually or combined, to explain the experimental results of Fig. 1: differential release of EDDS from soil to soil solution, limited amount of EDDS in soil...
and/or soil solution relative to repeat depletion, and degradation of EDDS in soil solution. The paper ascribed the experimental results solely to the degradation of EDDS in soil solution without mentioning other potential mechanisms. In analog, one person can take pickles out of a bottle, wash the pickles initially, rinse the pickles repeatedly with fresh water, and measure the salt in the rinses. Not surprisingly the concentrations of salt will be higher in initial rinses and lower in subsequent rinses. It is true that the salt concentrations in these rinses decrease with increasing time, however, no one would conclude that salt is decomposed within this time period.

Paper 2

In “Degradability of ethylenediaminedisuccinic acid (EDDS) in metal contaminated soils: Implications for its use in soil remediation” (Meers et al., 2008, hereafter termed as “the paper” within this section), it was stated that “This study examines heavy metal mobilization in three polluted soils varying in soil composition, with specific attention for competitive behaviour for complexation between the various metals and major elements, such as Al, Fe, Mn, Ca and Mg. EDDS was fully degraded within a period of 54 d in all soils regardless of initial delay.” After a critical reading of the paper, it was found that the conclusions about the biodegradation of EDDS proposed in the paper might not be substantiated by the experimental results presented in the paper.

The paper’s experimental set up is quoted below with some numerical marks such as “(§1►)” inserted for later discussion convenience.

2.2. Soil experiment

The pot experiment was conducted under outdoor conditions to mimic behaviour of EDDS under natural conditions. The experiment was performed in open air, with collection and recirculation of percolate in case of excess rainfall to prevent leaching of the chelate and mobilized metals from the system. (§2►) Temperatures ranged between 6-18°C (night) and 16-30°C (day) over the course of the growing season. To induce biological activity in the soil experiments, pots containing 3 kg of soil (dry weight) were planted with Zea mays at the start of the growing season (May 2004). After 4 months of incubation, (§3►) the pots were treated with 7.5 mmol EDDS per pot added as Na₂EDDS (Octel Performance Chemicals, Cheshire, United Kingdom). Application was divided over three separate doses (dissolved in 3 × 200 mL deionized water), spread over a period of 1 week. (§4►) The pots were fitted with Rhizon soil solution samplers (MOM-type; Eijkelkamp Agrisearch, Giesbeek, the Netherlands). (§5►) Soil solution samples were collected at regular intervals over a period of 54 d following treatment. (§6►) …… (§7►) Dissolved organic carbon (DOC) in the soil solution was determined using a TOC-500 analyzer ( Shimadzu, Duisburg, Germany). (§8►) …… (§9►) DOC concentrations present more direct additional information in regards with chelate degradability.

The measured concentrations of DOC in soil solution samples were presented in Fig. 2 of the paper. Samples shown at time zero of Fig. 2 were the first samples collected following treatment (§5). DOC concentrations in the samples were 50 mg/L at day 0, 300-400 mg/L at days 2, 600-900 mg/L at day 9, 300-400 mg/L at day 30, and 50 mg/L at day 45. Based on the results, the paper concluded that DOC concentration decreased with increasing time after a lag phase, and EDDS was degraded in soil solution.

Based on the experimental setup, the application of 7.5 mmol EDDS was divided over three separate doses (dissolved in 3 × 200 mL deionized water), spread over a period of 1 week (§3). The concentration of 2.5 mmol of EDDS (Na₂EDDS or C₆H₄(N₂N₃O₄) in 200 mL of deionized water is 0.0125 mmol/mL or 0.0125 mol/L of EDDS. This solution contains 1.5 g/L or 1,500 mg/L of DOC.

Initially, 2.2 g of EDDS (as EDDS acid) was applied to 3000 g of soil (0.7 g of EDDS to 1000 g of soil). Soil solution samples were collected following treatment (§5). However, the concentrations of DOC in the first samples (at time zero) were 50 mg/L. After 600 mL of EDDS (1,500 mg/L DOC) was applied to 3 kg of soil in a period of one week (§2 & §3), the expected DOC concentration should be about 1,500 mg/L, even considering some dilution by water which was initially in soil. Where did the rest (actually more than 95%) of EDDS go?

DOC in soil solution then increased from 50 mg/L at time zero to a maximum of 600-900 mg/L at day 9. The paper indicated that “The initial increases in DOC and metal concentrations observed during the first 200-240 h are due to the treatment with EDDS, added in three applications spread over the duration of a week.” This statement is difficult to understand and to accept. After the application of EDDS, why did the DOC concentration kept increasing with
increasing time in 9 days? There seemed to be a source of DOC to the soil in these nine days. Then why was the
maximum concentration of DOC only 600-900 mg/L? This accounted for 50% of added DOC. Where was the other
50%? Was the other 50% decomposed (degraded) already in 9 days?

After 9 days, the DOC concentrations kept decreasing with increasing time. The paper concluded that EDDS
degraded. EDDS might really degrade. However, would there be other explanation(s)? Can the observed variations
of DOC concentrations from day zero to day nine be ignored since those variations did not support the conclusion of
“degradation of EDDS?” Experimental results should not be selectively used to support a conclusion. “A lag phase”
did not explain the increase in DOC concentration observed from day zero to day nine.

From the above discussion, it is very hard to accept that the conclusion about degradation of EDDS in soil was
substantiated by the experimental results.

The “Rhizon soil solution samplers” (§4) is a probe type sampler like a pH electrode, and collect soil solution at the
vicinity of probe. The paper did not specify how many samplers were used and where the samplers were placed (§4).
The following is just a speculation which might explain the observed results of Fig. 2.

The sampler (one or several) was placed somewhere between the top and the bottom of soil. EDDS was applied to the
top of soil. At time zero, the solution collected in the sampler contained 50 mg/L DOC since the applied EDDS was
still in the top of soil and had not reached to the sampler which was placed away from where EDDS was applied.
With time, the EDDS zone migrated down from the top of soil to the bottom of soil (and migrated sideways). This
migration was possible due to the experiment set up “The experiment was performed in open air, with collection and
recirculation of percolate in case of excess rainfall to prevent leaching of the chelate and mobilized metals from the
system” (§1). When the EDDS zone migrated towards to the sampler, the DOC concentration increased with
increasing time and reached to a maximum. When the EDDS zone migrated away from the sample, the DOC
concentration decreased with increasing time. With migration and rainwater input, EDDS was distributed and/or
retained in different places and the measured maximum concentration was substantially less than the expected
maximum concentration.

If the above speculation is reasonable, the concentration variations potentially caused by migration and other
mechanisms should not be used as the evidence to support the biodegradation of EDDS.
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