(1-HYDROXYETHYLIDENE)-1,1-DIPHOSPHONIC ACID
[ETIDRONIC ACID]

This dossier on (1-hydroxyethylidene)-1,1-diphosphonic acid (HEDP) presents the most critical studies pertinent to the risk assessment of HEDP in its use in water treatment systems. It does not represent an exhaustive or critical review of all available data. The information presented in this dossier was obtained primarily from the ECHA database that provides information on chemicals that have been registered under the EU REACH (ECHA), and from the OECD-SIDS documents on the Phosphonic Acid Compounds Group 2 category, which includes HEDP (OECD, 2004a,b). Where possible, study quality was evaluated using the Klimisch scoring system (Klimisch et al., 1997).

Screening Assessment Conclusion: HEDP is classified as a **tier 1** chemical and requires a hazard assessment only.

1 BACKGROUND

HEDP has the consistency of a syrup at room temperature. HEDP is a strong complexing agent, and is high hydrophilic. HEDP is of low acute toxicity to fish and invertebrates; it does exhibit moderate toxicity concern to algae, which may be due to the complexation of HEDP with essential trace metals.

2 CHEMICAL NAME AND IDENTIFICATION

Chemical Name (IUPAC): (1-Hydroxy-1,1-diyl)bis(phosphonic acid)

CAS RN: 2809-21-4

Molecular formula: $C_2H_8O_7P_2$

Molecular weight: 206.03 g/mol

Synonyms: Etidronic acid; etidronate; HEDP; (1-hydroxyethylidene)-1,1-diphosphonic acid; (1-hydroxyethylidene)-1,1-bisphosphonic acid; (1-hydroxyethylidene)diphosphonic acid; 1-hydroxy-ethylidene-1,1-diphosphonic acid; 1-hydroxy-1,1-ethanediyl ester; 1-hydroxyethylidene-1,1-diphosphonic acid; ethane-1-hydroxy-1,1-diphosphonic acid; hydroxyethanediphosphonic acid; hydroxyethylidene diphosphonic acid

3 PHYSICO-CHEMICAL PROPERTIES

Key physical and chemical properties for the substance are shown in Table 1.

Table 1 Overview of the Physico-chemical Properties of HEDP

Property	Value	Klimisch score	Reference
Physical state at 20°C and 101.3 kPa	Syrup	2	ECHA
Melting Point	198-199°C; 228°C (decomposition)	2	ECHA

Property	Value	Klimisch score	Reference
Boiling Point	Decomposes before boiling	2	ECHA
Density	1450 kg/m^3 @ 20^{o}C	4	ECHA
Vapor Pressure	~0 Pa	2	ECHA
Partition Coefficient (log K_{ow})	-3.5	2	ECHA
Water Solubility	690 g/L (very soluble)	2	ECHA
Dissociation constants (pKa)	Four pKa values (at 0.1 M ionic strength potassium nitrate): 1.6, 2.7, 6.9, 11	4	OECD, 2004a,b

HEDP is a diphosphonic acid. The properties of HEDP and its salts are profoundly directed by its ionisation behavior. HEDP can ionise by the loss of a hydrogen ion up to five times to give the corresponding anion. The fifth ionisation (of the hydroxyl group) cannot be attained under normal aqueous conditions. As a consequence of ionisation, HEDP is a strong complexing agent and is highly hydrophilic (OECD, 2004a,b).

4 DOMESTIC AND INTERNATIONAL REGULATORY INFORMATION

A review of international and national environmental regulatory information was undertaken (Table 2). This chemical is listed on the Australian Inventory of Chemical Substances – AICS (Inventory). No conditions for its use were identified. No specific environmental regulatory controls or concerns were identified within Australia and internationally for HEDP.

Table 2 Existing International Controls

Convention, Protocol or other international control	Listed Yes or No?
Montreal Protocol	No
Synthetic Greenhouse Gases (SGG)	No
Rotterdam Convention	No
Stockholm Convention	No
REACH (Substances of Very High Concern)	No
United States Endocrine Disrupter Screening Program	No
European Commission Endocrine Disruptors Strategy	No

5 ENVIRONMENTAL FATE SUMMARY

A. Summary

HEDP is not readily biodegradable. There is evidence for partial degradation over short time periods, and with evidence of mineralisation, particularly in light, over long periods. It strongly absorbs to inorganic surfaces, sediment and soils. HEDP has a low potential for bioaccumulation.

B. Partitioning

As discussed earlier, HEDP is a strong complexing agent and is highly hydrophilic. Removal from the aqueous phase occurs principally by irreversible adsorption to substrates present (minerals), and to a lesser extent removal by photodegradation, oxidation in the presence of iron(III) and limited biodegradation.

C. Biodegradation

In a closed bottle test, there was 0% degradation after 30 days (OECD, 2004a). In an OECD ready biodegradation test, 10% of HEDP was degraded after 28 days (ECHA) [Kl. score = 2]. In another OECD ready biodegradation test, 1-3% of HEDP was degraded after 28 days (HERA, 2004).

In a Zahn-Wellens inherent biodegradability test, the percentage of DOC removal after 28 days was 33% (HERA, 2004; ECHA) [Kl. score = 4]. Biodegradation of radiolabelled HEDP was 1.9 to 6.7% over a 210-day period in an SCAS test (HERA, 2004).

In non-sterile natural water, the ultimate biodegradation ($^{14}CO_2$ evolution) of HEDP was 2% in the dark and 2.7% in the sunlight after 60 days (HERA, 2004) [Kl. score = 4]. In the presence of sediment, the biodegradation was faster, with 7.1% degradation in 50 days (HERA, 2004) [Kl. score = 4].

In soils, there was 3 to 47% degradation of HEDP after 119 to 148 days (HERA, 2004) [Kl. score = 4].

If a chemical is found to be not readily or inherently biodegradable, it is categorised as Persistent since its half-life is greater than 60 days (DoEE, 2017).

D. Environmental Distribution

HEDP is a mineral-binding and complexing agent, with unusual chemical properties. HEDP and its salts adsorb strongly to inorganic surfaces, soils and sediments, in model systems and mesocosms, despite the very low log K_{ow}; this has implications for the approach to environmental fate modelling. High adsorption is consistent with similar behaviour seen for structural analogues, and other common complexing agents such as EDTA (ECHA).

Studies on analogous phosphonate complexing agents have revealed that adsorption is correlated with concentration in the aqueous phase and also relates significantly to the type and nature of inorganic content in the substrate. The normal approach to modelling binding behaviour in environmental exposure assessment assumes that the substance is binding only to the organic carbon present in soils, sediments, and WWTP sludges. This assumption does not apply to HEDP and its salts. The nature of the adsorption is believed to be primarily due to interaction with inorganic substrate or generalised surface interactions. While K_{oc} is the conventional indicator for adsorption, the interaction with organic carbon present in the substrate may be exceeded by these other interactions in the case of HEDP and its salts, meaning that K_{oc} as such is not a meaningful parameter. It is convenient for comparison purposes to determine the value of log K_{oc} that is consistent/equivalent to the degree of sediment or soil binding exhibited by the substance. Thus, a log K_{oc} of 4.22 was determined experimentally (ECHA; OECD, 2004a,b). [Kl. score = 2]

If released to soil, HEDP is expected to have little to no mobility due to its very strong adsorption properties. If released to water, because of its hydrophilic nature and strong complexing agent, HEDP will partition primarily to water and suspended sediments.

E. Bioaccumulation

The BCF values of HEDP in a carp (*Cyprinus carpio*) were determined to be <7 for the whole body and 71 for the non-edible portions (0.06 mg/L). At 0.6 mg/L, the BCF values were <2 for the whole body and 31 for the non-edible portions of the fish (ECHA). [Kl score = 2]

6 ENVIRONMENTAL EFFECTS SUMMARY

A. Summary

HEDP is of low acute toxicity to fish and invertebrates; it does exhibit moderate toxicity concern to algae, which may be due to the complexation of HEDP with essential trace metals.

B. Aquatic Toxicity

Acute Studies

Table 3 lists the results of acute aquatic toxicity studies conducted on HEDP.

Table 3 Acute Aquatic Toxicity Studies on HEDP

Test Species	Endpoint	Results* (mg/L)	Klimisch score	Reference
Onychorhynchus mykiss	96-hour LC_{50}	195	1	ECHA
Lepomis. macrochirus	96-hour LC_{50}	2,180	2	ECHA
Ictalurus punctatus	96-hour LC_{50}	695	2	ECHA
Lepomis. macrochirus	96-hour LC_{50}	868	2	ECHA
Onychorhynchus mykiss	96-hour LC_{50}	368	2	ECHA
Daphnia magna	48-hour EC_{50}	527	2	ECHA
Pseudokirchnerella subcapitata	96-hour EC_{50}	7.23 (biomass)	2	ECHA
Pseudokirchnerella subcapitata	96-hour EC_{50} NOEC	3 (biomass) 14 (growth rate)	2	ECHA

*Active acid or active ingredient.

The toxicity of HEDP to algae may be the consequence of nutrient limitation caused by the complexation of HEDP with essential trace metals and not true toxicity (OECD, 2004a,b).

Chronic Studies

The 28-day NOEC from a 28-day *Daphnia magna* reproduction toxicity study is 6.75 mg HEDP/L (ECHA). [Kl. score = 2]

The 14-day NOEC to *Pseudokirchnerella subcapitata* was 14 mg HEDP/L (growth rate) (ECHA). [Kl. score = 2]

C. Terrestrial Toxicity

The 14-day LC_{50} value to the earthworm *Eisenia foetida* was >1,000 mg HEDP/kg dw soil (ECHA). [Kl. score = 2]

The 14-day EC_{50} and NOEC of HEDP to the growth of *Avena sativa* were >960 mg HEDP/kg dw soil (HERA, 2004). [Kl. score = 4]

The 96-hr LC_{50} values for the mallard duck (*Anas platyhynchos*) and the bobwhite quail (*Colinus virginianus*) are >284 mg HEDP/kg (ECHA). [Kl. scores = 2]

7 CATEGORISATION AND OTHER CHARACTERISTICS OF CONCERN

A. PBT Categorisation

The methodology for the Persistent, Bioaccumulative and Toxic (PBT) substances assessment is based on the Australian and EU REACH Criteria methodology (DEWHA, 2009; ECHA, 2008).

HEDP is not readily biodegradable; thus it meets the screening criteria for persistence.

The BCF values in fish for HEDP are <2 to 71. Thus, HEDP does not meet the criteria for bioaccumulation.

The lowest chronic aquatic NOEC is >0.1 mg/L. Thus, HEDP does not meet the criteria for toxicity.

The overall conclusion is that HEDP is not a PBT substance.

B. Other Characteristics of Concern

No other characteristics of concern were identified for HEDP.

8 SCREENING ASSESSMENT

Chemical Name	CAS No.	Overall PBT Assessment [1]	Chemical Databases of Concern Assessment Step		Persistence Assessment Step		Bioaccumulative Assessment Step	Toxicity Assessment Step			Risk Assessment Actions Required[3]
			Listed as a COC on relevant databases?	Identified as Polymer of Low Concern	P criteria fulfilled?	Other P Concerns	B criteria fulfilled?	T criteria fulfilled?	Acute Toxicity [2]	Chronic Toxicity[2]	
(1-hydroxyethylidene)-1,1-diphosphonic acid	2809-21-4	Not a PBT	No	No	Yes	No	No	No	1	1	1

Footnotes

1 - PBT Assessment based on PBT Framework.

2 - Acute and chronic aquatic toxicity evaluated consistent with assessment criteria (see Framework).

3 – Tier 1 – Hazard Assessment only.

Notes:

NA = not applicable

PBT = Persistent, Bioaccumulative and Toxic

B = bioaccumulative

P = persistent

T = toxic

9 REFERENCES, ABBREVIATIONS AND ACRONYMS

A. References

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B. Abbreviations and Acronyms

°C	degrees Celsius
AICS	Australian Inventory of Chemical Substances
BCF	bioconcentration factor
COC	constituent of concern
HEDP	(1-hydroxyethylidene)-1,1-diphosphonic acid
DEWHA	Department of the Environment, Water, Heritage and the Arts
DOC	dissolved organic carbon
dw	dry weight
EC	effective concentration
ECHA	European Chemicals Agency
EU	European Union

g/L	grams per litre
HEDP	(1-hydroxyethylidene)-1,1-diphosphonic acid
IUPAC	International Union of Pure and Applied Chemistry
Kg/m^3	Kilogram per cubic metre
Kl	Klimisch scoring system
kPa	kilopascal
LC	lethal concentration
M	molar
mg/L	milligrams per litre
NOEC	no observed effective concentration
OECD	Organisation for Economic Co-operation and Development
Pa	pascal
PBT	Persistent, Bioaccumulative and Toxic
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals
SCAS	Semi-continuous activated sludge
SGG	Synthetic Greenhouse Gases
SIDS	screening information data set