DIETHYLENE TRIAMINE PENTA(METHYLENE PHOSPONIC ACID), SODIUM SALT

This dossier on diethylene triamine penta(methylene phosphonic acid), sodium salt (DTPMP sodium salt) presents the most critical studies pertinent to the risk assessment of DTPMP 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 3 category, which includes DTPMP and its sodium salts (OECD, 2004a,b). Where possible, study quality was evaluated using the Klimisch scoring system (Klimisch *et al.*, 1997).

Screening Assessment Conclusion – DTPMP sodium salt is classified as a **tier 1** chemical and requires a hazard assessment only.

1 BACKGROUND

DTPMP sodium salt is a UVCB substance. DTPMP sodium salt is not biodegradable and it adsorbs strongly to sediment and soil. However, there are degradation modes operative in the environment which could prevent long-term persistence. DTPMP sodium salt has a low potential for bioaccumulation. DTPMP and its sodium salts are of low toxicity concern to aquatic organisms.

2 CHEMICAL NAME AND IDENTIFICATION

Chemical Name (IUPAC): [bis[2-[bis(phosphonomethyl)amino]ethyl]amino]methylphosphonic acid; sodium salt

CAS RN: 22042-96-2

Molecular formula: $C_9H_{28}N_3O_{15}P_5.xNa$

Molecular weight: Not applicable. This substance is a UVCB substance.

Synonyms: Diethylene triamine penta(methylene phosphonic acid), sodium salt; [[(phosphonomethyl)imino]bis[(ethylenenitrilo)bis(methylene)]]tetrakisphosphonic acid, sodium salt; [bis[2-[bis(phosphonomethyl)amino]ethyl]amino]methylphosphonic acid; sodium salt

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 DTPMP (CAS No. 15827-60-8) and DTPMP sodium salt

Property	Value	Klimisch score	Reference
Physical state at 20°C and 101.3 kPa	Brown liquid	2	ECHA
Melting Point	>450°C (DTPMP) (pressure not provided)	1	ECHA

Property	Value	Klimisch score	Reference
Boiling Point	>480°C (DTPMP) (pressure not provided_	1	ECHA
Density	1300 to 1400 kg/m^3 (DTPMP) @ 20°C	2	ECHA
Vapour Pressure	Negligible	2	ECHA
Partition Coefficient (log K_{ow})	-3.4 (DTPMP) (temperature not provided)	2	ECHA
Water Solubility	>520 g/L @ 25°C (DTPMP)	2	ECHA
Dissociation Constant (pKa)	1.03 – 12.58 (temperature not provided)	2	ECHA

DTPMP can ionise by loss of a hydrogen ion up to six times. Thus, it is a strong complexing agent and is highly hydrophilic. The sodium salts of DTPMP will dissolve readily in water to give a speciation state that is dictated by the pH of the aqueous medium. DTPMP has 10 possible ionisation states. Eight pK_a values were reported by Martell and Sillen (1968): 2.8, 4.45, 5.5, 6.38, 7.17, 8.15, 10.1, and 12.04, which were measured in 0.1 M potassium chloride. In a source giving no experimental details, DTPMP is described as having 10 pK_a values: 1.03, 2.08, 3.11, 4.15, 5.19, 6.23, 7.23, 8.30, 11.18, and 12.58 (Tomson et al., 1994).

At pH 7, DTPMP in water will be almost fully ionised five times, with a majority of the molecules ionised six times, and some seven or eight times.

DTPMP, sodium salt (CAS No. 22042-96-2) is a UVCB substance that can potentially have 1-10 sodium salts.

This dossier contains information on DTPMP (CAS No. 15827-60-8) as well as the sodium salts of DTPMP. The read-across of the acid to the sodium salts is justified because sodium is not significant with respect to the properties under consideration in this dossier. In dilute aqueous conditions of defined pH, a salt will be completely dissociated and will behave no differently to the parent acid, at the identical concentration of the particular speciated form present. Thus, some properties (measured or expressed in aqueous media) for a salt can be directly read-across (with suitable mass correction) to the parent acid and vice versa; the effect of the sodium ion, in this case, will not be significant. In biological systems and the environment, polyvalent metal ions will be present, and the phosphonate ions show very strong affinity to them (OECD, 2004b).

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 DTPMP sodium salt.

NICNAS has assessed DTPMP sodium salt in an IMAP Tier 1 assessment and concluded that it poses no unreasonable risk to human health[1] .

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

DTPMP sodium salt is not biodegradable and it adsorbs strongly to sediment and soil. However, there are degradation modes operative in the environment which could prevent long-term persistence. DTPMP sodium salt has a low potential for bioaccumulation.

B. Partitioning

As discussed earlier, DTPMP acid and its salts behave in aqueous medium in accordance with the pH and composition of the medium. DTPMP acid and its salts will partition primarily to water and suspended sediments. It is highly soluble.

Photodegradation in the presence of common metal ions has been observed. Half-lives less than 1 hour were measured for sodium salt of DTPMP in water at pH 3, pH 5-6 and at pH 10, irradiated by a middle pressure mercury lamp emitting between 190 and 600 nm. Half-lives were found to be shorter in the presence of iron ions at environmentally relevant concentrations (Lesueur et al., 2005).

C. Biodegradation

In a Zahn-Wellens/EMPA (OECD 302B) test, there was no biodegradation after 28 days (ECHA) [Kl. score = 2]. There was also no biodegradation after 28 days in an OECD 301E test (ECHA) [Kl. score = 1].

Using [^{14}C]-DTPMP, there was 64% and 62.6% biodegradation in riverbank soil and silt loam soil, respectively, after 148 days (ECHA) [Kl. score = 2].

There are degradation modes operative in the environment which could prevent long-term persistence. For instance, although biodegradation in soil has not been demonstrated for DTPMP

[1] https://www.industrialchemicals.gov.au/chemical-information/search-assessments?assessmentcasnumber=22042-96-2

and its salts, the role of abiotic removal processes is significant. The key data for soil adsorption are from the study by Michael (undated). There is no evidence for desorption occurring. Effectively irreversible binding is entirely consistent with the known behaviour of complexation and binding within crystal lattices. Largely irreversible binding is interpreted as a removal process; 5% remaining after 40 - 50 days which is equivalent to a half-life of 10 days (Monsanto internal report, cited by Gledhill and Feijtel, 1992). This abiotic removal rate is used in the chemical safety assessment of DTPMP and its salts. The available weight of evidence shows that removal from solution to a non-bioavailable bound form, and abiotic mechanisms, are important in the environmental exposure and risk assessment (ECHA).

D. Environmental Distribution

DTPMP adsorbs strongly to inorganic surfaces, soils and sediments. The nature of the adsorption is believed to be primarily due to interaction with inorganic substrates and not to organic carbon (OECD, 2004b).

A K_{oc} value of 9,748 was obtained for DTPMP by evaluating $K_{p(sediment\text{-}water)}$ data from a study by Michael (1979).

Based on this K_{oc} value and its solubility value (> 520 g/L), and assuming no biodegradability, if released to water DTPMP sodium salt will partition primarily to water and suspended sediments.

E. Bioaccumulation

DTPMP exhibits a low potential for bioaccumulation. After 28 days, the BCF values in carp were <10 and <94 for concentrations of 18.8 and 2.03 mg/L, respectively (ECHA). [Kl. score = 1]

6 ENVIRONMENTAL EFFECTS SUMMARY

A. Summary

DTPMP and its sodium salts are of low toxicity concern to aquatic organisms.

B. Aquatic Toxicity

Acute Studies

No acute toxicity studies are available for the sodium salts of DTPMP. Table 3 lists the results of acute aquatic toxicity studies on DTPMP.

Table 3 Acute Aquatic Toxicity Studies on DTPMP

Test Species	Endpoint	Results (mg active acid/L)	Klimisch score	Reference
Oncorhynchus mykiss	96-hour LC_{50}	180 - 252 (mean: 216)	2	ECHA
Chironomus tentans	48-hour EC_{50}	7,589	2	ECHA

Algal studies have also been conducted on DTPMP and its sodium salts, but the results have not been provided because of the following confounding factors:

a). Algal growth may be stimulated by the presence of supplementary phosphorus released by the photolytic degradation of phosphonic acids.

b.) Algal growth may be inhibited by the complexation of micronutrients (trace metals) by phosphonic acids. This inhibition is an algistatic rather than algicidal effect. Under the standard test conditions used for most studies, the trace metals will be fully and strongly bound to the DTPMP, with the strong possibility that their bioavailability will have been reduced considerably.

Chronic Studies

The 60-day NOEC of DTPMP in *Oncorhynchus mykiss* was determined to be 25.6 mg active acid/L (ECHA). [Kl. score = 1]

The value of 25.6 mg equivalent active acid/L can be converted to units of mg DTPMP-xNa salt/L at relevant conditions of pH by considering the ionisation state of DTPMP (CAS No. 15827-60-8) at the 25.6 mg/L concentration. At pH 6 (the expected value of the test medium), DTPMP is ionised six times (pK_a6 = pH 6.23). Also for the calculation, the number of hydrogen atoms substituted by the sodium salt is removed, which is seven. The calculation is as follows:

MW of DTPMP-7Na / MW of DTPMP = 573.2 + ((21.982 – 1.008) x 6) / 573.2 = 1.22

25.6 mg DTPMP/L x 1.22 = 31 mg DTPMP-xNa/L

C. Terrestrial Toxicity

The 14-day dietary LC_{50} values to the Mallard duck (*Anas platyrhynchos*) and Bobwhite quail (*Colunus virginianus*) are >454 mg/kg; there was no mortality at the highest dose tested (OECD, 2004a,b).

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).

DTPMP and its sodium salts are not readily biodegradable; thus, they meet the screening criteria for persistence.

The BCF values from a fish study are <10 and <94 for concentrations of 18.8 and 2.03 mg/L, respectively. Thus, DTPMP does not meet the screening criteria for bioaccumulation.

The NOEC from a chronic fish study on DTPMP is >0.1 mg/L. Thus, DTPMP and its sodium salts do not meet the screening criteria for toxicity.

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

B. Other Characteristics of Concern

No other characteristics of concern were identified for DTPMP sodium salt

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]	
DTPMP sodium salt	22042-96-2	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

Department of the Environment, Water, Heritage and the Arts [DEWHA]. (2009). Environmental risk assessment guidance manual for industrial chemicals, Department of the Environment, Water, Heritage and the Arts, Commonwealth of Australia.

ECHA. ECHA REACH database: https://echa.europa.eu/information-on-chemicals/registered-substances

European Chemicals Agency [ECHA]. (2008). Guidance on Information Requirements and Chemical Safety Assessment, Chapter R11: PBT Assessment, European Chemicals Agency, Helsinki, Finland.

Gledhill, W E and Feijtel, T C J (1992). Environmental Properties and safety assessment of organic phosphonates used for detergent and water treatment applications. Handbook of Environmental Chemistry, Volume 3, Part F., Hutzinger, O. Ed. Springer-Verlag, Berlin; cited in ECHA.

Klimisch, H.J., Andreae, M., and Tillmann, U. (1997). A systematic approach for evaluating the quality of experimental and toxicological and ecotoxicological data. Regul. Toxicol. Pharmacol. 25:1-5.

Martell, A.E., and Sillen, L.G. (1968). Stability constants – Supplement No. 1 Special Publication 25. The London Chemical Society, Alden Press, London; cited in OECD (2004b).Lesueur C., et al. (2005). Photodegradation of phosphonates in water. Chemosphere 59 (2005) 685-691; cited in ECHA.

Michael, P.R. (undated, but believed to be 1979). Monsanto Report ES-79-SS-15; cited in OECD (2004b).

OECD (2004a). SIDS Dossier on [[(phosponomethyl)imino) bis[(ethylenenitrilo) bis(methylene)]]tetrakisphosphonic acid, sodium salt (CAS No. 22042-96-0). Available at: https://hpvchemicals.oecd.org/UI/SIDS_Details.aspx?id=0AA9E84E-9D74-4DE7-8E26-1B3F943CD10A.

OECD (2004b). SIDS Initial Assessment Report on Phosphonic Acid Compounds Group 3. Available at: https://hpvchemicals.oecd.org/UI/SIDS_Details.aspx?id=0AA9E84E-9D74-4DE7-8E26-1B3F943CD10A.

Tomson, M.B., Kan, A.T., Oddo, J.E. (1994). Acid/base and metal complex solution chemistry of the polyphosphonate DTPMP versus temperature and ionic strength. Langmuir 10: 1442-1449; cited in OECD (2004b).

B. Abbreviations and Acronyms

°C	degrees Celsius
AICS	Australian Inventory of Chemical Substances
BCF	bioconcentration factor
BCF	bioconcentration factor
COC	constituent of concern
DEWHA	Department of the Environment, Water, Heritage and the Arts
DTPMP	diethylene triamine penta(methylene phosphonic acid)
EC	effective concentration
ECHA	European Chemicals Agency
EMPA	Swiss Federal Laboratories for Materials Testing and Research
EU	European Union
g/L	grams per litre
IUPAC	International Union of Pure and Applied Chemistry
kg/m^3	kilograms per cubic metre
Kl	Klimisch scoring system
kPa	kilopascal
LC	lethal concentration
M	molar
mg/kg	milligrams per kilogram
mg/L	milligrams per litre
MW	molecular weight
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
SGG	Synthetic Greenhouse Gases
SIDS	Screening Information Data Set
UVCB	Unknown or Variable Composition, Complex Reaction Products and Biological Materials