COVER PAGE

SIDS Initial Assessment Report for SIAM 18

Category: Phosphonic Acid Compounds Group 1

Amino tris(methylenephosphonic acid) and its sodium salts.

This category covers a phosphonic acid and various sodium salts of that acid. The different salts are prepared by neutralising the acid to a specific pH. Data are available for the acid and some salts. The substances are commercially available as aqueous solutions only and in an environmental context the speciation will be the same. The properties of the members of the category are consistent across all end points.

The category is expressed as Phosphonic Acid Compounds Group 1 because two other groups have been identified, with close structural analogy to the present one. Therefore three SIARs have been made available. The pattern of properties is very similar for all three groups. The three groups are known as the ATMP (amino tris(methylenephosphonic acid)) group, the HEDP (1-hydroxy-1,1-ethane-diphosphonic acid) group and the DTPMP (diethylene triamine penta(methylene phosphonic acid)) group. Whilst it has not been necessary to read across between groups, some review across the groups has been made to support some interpretations of data.

A SIAR for ATMP has previously been published, in 1993. The UK Technical Committee on Detergents and the Environment published a report that reviews these substances (DETR, 1998).

Category Members:

The proposed Category members are:

Chemical name		CAS no.
Amino tris(methylenephosphonic acid)	ATMP	6419-19-8
Amino tris(methylenephosphonic acid), xNa Salt	ATMP-xNa	20592-85-2
Amino tris(methylenephosphonic acid), Na Salt	ATMP-Na	none found
Amino tris(methylenephosphonic acid), 2Na Salt	ATMP-2Na	4105-01-5
Amino tris(methylenephosphonic acid), 3Na Salt	ATMP-3Na	7611-50-9
Amino tris(methylenephosphonic acid), 4Na Salt	ATMP-4Na	94021-23-5
Amino tris(methylenephosphonic acid), 5Na Salt	ATMP-5Na	2235-43-0
Amino tris(methylenephosphonic acid), 6Na Salt	ATMP-6Na	15505-05-2

It is proposed that all sodium salts can be included in the category.. Robust study summaries are detailed in three separate SIDS dossiers. One CAS number for the acid (6419-19-8) and one for the set of salts (20592-85-2) have been used. This is considered to be the most appropriate way to collect data: the acid is distinct from the salts, but the salts are closely related. The salts and the acid are compared in this SIAR.

Sponsor Country: United Kingdom

Shared partnership with: American Chemistry Council, Phosphonic Acids Compounds Panel
Panel members:
GE Betz
Giovanni Bozzetto, S.p.A.
Nalco Energy Services
Noveon, Inc.
Rhodia Consumer Specialties Ltd.
Rhodia Inc.
Solutia Services International
Solutia Inc.
Zschimmer & Schwarz Mohsdorf GmbH & Co KG

The assistance of Henkel KGaA is gratefully acknowledged

National SIDS Contact Point in Sponsor Country:

Dr Steve Robertson
Environment Agency
National Centre for Ecotoxicology & Hazardous Substances
Isis House, Howbery Park, Wallingford OX10 8BD, UK
Fax: +44 1491 828 556
e-mail: steve.robertson@environment-agency.gov.uk

HISTORY:

This substance is sponsored by the UK under the ICCA Initiative and is submitted for first discussion at SIAM 18.

PEER REVIEW PROCESS:

The industry consortium collected new data and prepared the updated IUCLID, and draft versions of the SIAR and SIAP. UK government peer-reviewed the documents and audited selected studies.

TESTING: No testing (X) Testing ()

COMMENTS: The industry contact point is

John DiLoreto
American Chemistry Council, Phosphonic Acids Compounds Panel
John_DiLoreto@AmericanChemistry.com

Due to changes of company ownership, it should be noted that reports referred to as Monsanto reports are now owned by Solutia, and those referred to as Albright and Wilson reports are now owned by Rhodia.

Deadline for circulation: 23rd January 2004

Date of circulation: 23rd January 2004

2. GENERAL INFORMATION ON EXPOSURE

Overview

ATMP and its salts have a variety of applications, set out below. A primary mechanism of how they function is by adsorption to crystals and micro-crystalline aggregates. Chelation of metal ions is an important aspect of that function but is not the mode of action of the effects on inorganic scale control. Chelation (complexation) properties are discussed in this document, but the substances are not sold primarily as chelating agents.

One specific application for ATMP is as an intermediate for producing the salts. Depending on the production process, it may be used in situ (non-isolated intermediate, which is the usual case), or stored separately for further neutralisation (isolated intermediate).

Phosphonic acids are used in the areas described below. In general terms, industrial water treatment is the largest area, and use in consumer products is minor. In 1999, a voluntary initiative for Human and Environmental Risk Assessment on ingredients of household cleaning products (HERA) was established by the European Chemical Industry Council (CEFIC) and the International Association for Soaps, Detergents and Maintenance Products (AISE). Phosphonates are being considered under that initiative (www.heraproject.com/).

In each area a brief summary of life cycle after production is provided where practicable.

DETERGENT AND CLEANING APPLICATIONS

In consumer detergent applications, phosphonates are used in laundry detergents that will be used by the consumer, as additives providing a range of properties such as anti-redeposition and soil dispersion. Phosphonates are also used in laundry detergents as perborate and percarbonate stabilisers, preventing decomposition by transition metals. Further uses are in automatic dish washing products and in hard surface cleaners. However, the use of ATMP in detergents (laundry) and cleaners by the general public is minor (HERA volume for ATMP is only ca. 50 tonnes/year – a very small proportion of the total produced).

Phosphonates are used less in this area than was once the case.
Formulation: by specialist formulators
Use: by the public, resulting in release to the public waste water system.

Industrial and institutional cleaning formulations are specifically for uses in industrial settings and would not be expected to be supplied to the general public. In this sector phosphonates are used in hard surface cleaners, bottle washing, vehicle washing, etc.
Formulation: by specialist formulators
Use: in industry and institutions

INDUSTRIAL WATER TREATMENT

A major application of phosphonates is in water treatment of cooling and boiler water as scale inhibitors.

Industrial water treatment applications cover scale and corrosion control in open evaporative cooling towers. This accounts for approx 95% of industrial water treatment uses, though the use in 'once-through' systems is limited.
Formulation: by specialist formulators and at the point of use.
Use: phosphonates are added to process water, usually abstracted from groundwater, river water or drinking water, and discharges (e.g. from cleaning, overflow, water renewal) are made together with other waste streams. This may result in release to the receiving watercourse.

Scale and corrosion control in closed loop heating and cooling systems accounts for a small proportion (~3%) of use. Uses in steam boilers and ancillary equipment account for the balance. Other scale control applications include reverse osmosis water treatment and desalination by evaporation.

Phosphonates are also used to prevent scale formation in 'squeeze' treatment in off-shore oil production. In Oilfield applications, phosphonates are applied in the region of the wellhead for scale prevention through a process known as squeeze treatment. When a well loses its pressure, seawater is pumped into the well to push the remaining oil out (to squeeze it out). The seawater, the formation water and mixed water from both may form mineral precipitates leading to scale formation and potentially blocking of the pipes. The squeeze treatment involves pumping under pressure the desired amount of phosphonate into the well, where a significant proportion becomes adsorbed onto the rock formation. The absorbed material slowly bleeds back into the produced fluids providing scale protection for a significant period of time (typically between 3 months and 2 years), before another squeeze treatment is required.

Formulation: by specialist formulators and at the point of use.
Use: Closed systems are highly controlled. Offshore use may result in release to the marine environment.

PEROXIDE STABILISATION

Paper industry applications are peroxide stabilisation in pulp bleaching. They provide control of inorganic scale formation at the paper machine. Phosphonates are further used as stabilisers for hydrogen peroxide solutions and formulations.
Formulation: by manufacturers and at point of use
Use: In the paper industry, likely to result in some releases to the aquatic environment.

TEXTILES
Phosphonates are used in the scouring process to remove impurities, and in the bleaching process as peroxide stabilisers.
Formulation: by manufacturer and specialist formulators
Use: in textiles industry, likely to result in some releases to the aquatic environment.

SPECIALITY APPLICATIONS
Phosphonates are also used as complexing agents or as scale inhibitors in the photographic industry, as additives for cosmetic products (preventing metal catalysed degradation), as cement/concrete modifiers, corrosion inhibition, and various metal surface treatment processes.

Estimated Production or Import Volume

ATMP, HEDP and DTPMP (and their salts) are prominent phosphonates which are primarily used in water treatment applications, industrial and institutional cleaners, and pulp and paper production. Published data indicates that US consumption of these products in 1998 was estimated to be 27,000 metric tonnes, accounting for nearly 90% of total US production. In Western Europe, approximately 20,000 metric tonnes of these substances were produced for similar applications. Japan consumed approximately 800 metric tonnes of these organophosphonates in 1998. Current worldwide production of these compounds is estimated to be in the range of 50,000 to 100,000 metric tonnes annually.

Although the largest use of phosphonates is in industrial water treatment, other applications across diverse industries make monitoring of production volume difficult. Production volume figures on individual phosphonates on a global, industry-wide basis is non-existent. In order to provide an estimate of production of these substances, confidential company data from existing individual producers has been combined with data from published chemical industry market research reports from several industry segments. In addition, these estimates have been aggregated for all substances addressed in the three phosphonate subgroups.

Data for this industry is also made difficult by inconsistent reporting which combines data from companies reporting production in terms of active acid or active salt, while others have reported actual volume of product in solution. Another source of uncertainty can arise when companies produce an acid which is used as an intermediate for salts, accounting separately for both lines of production.

Public Domain Information

The data presented in tables 2.1 and 2.2 are derived from the SPIN database of product register data (Substances in Preparations in Nordic Countries; sourced online at www.spin2000.net/spin.html).

Table 2.1 SPIN data for ATMP 6419-19-8

Country	Year	Number of preparations	Tonnes	Presence in consumer preparations
Finland	2001	11	87.8	
Denmark		137	79.4	
Norway		62	21.6	x
Denmark		122	4780.1	
Sweden	2000	119	144.0	x
Norway		63	18.1	
Finland		9		
Sweden	1999	110	115.0	x

Table 2.2 SPIN Named uses by country

Country	Named applications
Denmark	Cleaning/washing agents (General cleaning/washing agents (floor wash, basic cleaning); Cleaning/washing agents for washing machines; Boiler- and tank cleansing agents (see also Cleaning/washing agents); Other cleaning/washing agents; Degreasers (Cold degreasing, de-waxing, de-polishing); Foam cleaning/washing agents), Water softeners, Lime deposit remover, Inhibitors (see also Process-regulating agents; Stabilizers) Complexing agents, Corrosion inhibitors (Corrosion inhibitors (Additives) (see also Anti-corrosion materials), Softeners, Surface active agents, Surface treatment, Non-agricultural pesticides and preservatives
Norway	Cleaning/washing agents, Lubricants and additives, Photochemicals, Developers, Lubricants (See also Cutting oils)
Sweden	Cleaning/washing agents (Washing-up detergents (machine); Degreasing agents; High pressure cleaning agents) Lime removers, Process regulators, Corrosion inhibitors, Complexing agents, Stabilisers, Others, Photochemicals, Detergents, Anti-shell agents

Country	Named applications
Finland	Dyestuff/pigments, Laboratory chemicals, Building materials and additives, Feed additives Cleaning/washing agents, Corrosion inhibitors, Others

2.1 Environmental Exposure and Fate

The most important properties are indicated in table 2.3 below. The vapour pressure and boiling point estimates were made using the Syracuse Research Corporation EPIWIN suite of programs. Further discussion, including comparison with results from other QSAR software, are given in Annex I.

It must be stressed that properties involving aqueous media at buffered or set pH should give identical results for the acid and the salts, once concentration as 'acid equivalent' is accounted for.

Table 2.3 Key properties for environmental exposure and fate

Parameter	Values / results		Reliability	Reference/ Discussion
	6419-19-8	**Salts**		
Vapour pressure	1.91×10^{-10} Pa (estimate)	$<1.91 \times 10^{-10}$ Pa (estimate)	2	Annex I; requires estimated boiling point as input.
Solubility	Up to 50% w/w, with no pH adjustment	≥50% w/w	2	Industry use information based on production materials
Log K_{ow}	-3.53		2	P.R. Michael, Monsanto (1979)
Biodegradability (see 2.1.5)	Not rapidly degradable		2	V.W. Saeger et al., Monsanto (1978)

The properties of ATMP and its salts are profoundly directed by its ionisation behaviour. ATMP can ionise by loss of a hydrogen ion up to six times. As a consequence it is a stong complexing agent, and is highly hydrophilic. Because ionisation is a rapid and reversible process, salts such as sodium and potassium salts will dissolve readily in water to give a speciation state dictated by the pH of the medium. In a primary data source for information on pKa values and stability constants (Martell and Sillen 1968), six pKa values of ATMP are reported, of <2, <2, 4.30, 5.46, 6.66, 12.3. These were measured in 1 M potassium nitrate. The original source (a 1967 paper) is cited in the data book.

Ionisation of a particular functionality occurs most sharply at the pKa value, but at one pH unit lower than the pKa there is still 10% ionisation. In the present case, this means that at pH 7, ATMP in water will be almost fully ionised four times, with a majority of the molecules ionised five times.

In order of decreasing complexation strength, values (Gledhill and Feijtel, 1992) of the $\log_{10}$ of the stability constants of representative metals with ATMP are:

Hg	21.7
Co	18.4
Cu	17
Pb	16.4
Ni	15.5
Zn	14.1
Cd	12.7
Ca	7.6
Mg	6.7

The stability constants of phosphonates were critically reviewed for IUPAC (Popov *et al,* 2001). They reviewed techniques for determining stability constants for the chelation of metal ions by a number of phosphonates. Their paper presents and critically evaluates stability constants, and is quite complex as they consider the different protonation levels for the compounds separately. The data are consistent with the overall values reported above.

2.1.1 Sources of Potential Release to the Environment

Manufacturing process

ATMP and its salts are produced as aqueous solutions. Given the hazards of the raw materials, closed systems are used in manufacture. Raw materials and products are transferred between vessels through fixed piping and pumps. Releases to waterways are possible as a result of clean-out operations, but are expected to be minor during normal production operations. Actual emissions will depend on the applied control and abatement systems, e.g. waste water treatment units.

The substances are virtually not volatile and direct releases to air and soil are negligible. Production operations of dry products (powder/granules) potentially give rise to emissions of dust into the atmosphere but the actual emissions will depend on the applied control measures (dust filters etc.).

Downstream uses

In most downstream uses phosphonates are applied in water based processes. The final concentration in the water used in the application will be at ppm level (typically varying from less than 1 to 10 ppm for scale inhibition, to less than 1000 ppm in textile processing). Depending on the exact nature of the process, the phosphonates may remain present in the aqueous effluent and the discharge streams. These streams will be treated on the user's site, discharged to sewer systems or discharged to waterways (wide dispersive use). For many applications, the discharge is to sewer systems, followed by effluent treatment. This includes amongst others the I&I (Industrial and Institutional cleaning) use of phosphonates.

Given the low volatility and the high water solubility of the substances, direct releases to air and soil can be considered negligible. However, as phosphonates may partition to the sludge, the use of sewage sludge for land treatment may lead to releases to soil. In waterways, partitioning to the sediments is possible. Hence, dredging of sediments may also lead to releases to soil.

Modelling of the environmental releases of phosphonates has been reported for Europe (Gledhill and Feijtel, 1992) and for detergent products in Sweden (Landner and Walterson, 1993) and the Netherlands (WM, 1997).

2.1.2 Photodegradation

An overall conclusion regarding degradability is given at the end of section 2.1.5.

Photodegradation of ATMP (6419-19-8) in water was examined (Saeger, Monsanto (undated, believed to be 1979)). 2% transformation (phosphonate to orthophosphate) was measured after 17 days at pH 7 (0% at pH 4 and 10). Levels of degradation in the presence of ferric (Fe III), chromic, zinc and cupric nitrate were higher, with 26% transformation by day 3 in the presence of ferric nitrate at pH7 (by day 17: 44% at pH7, 45% at pH4 and 38% at pH10). The effect of other metals was less significant.

Degradation in the presence of ferric (Fe III) ions reflects the ability of that ion to absorb light, and because it can be strongly complexed by ATMP, that energy can be transferred to the complexing anion, resulting in degradation. It is possible that ferrous (Fe II) ions would be formed in this process, and, due to the presence of oxygen, ferric would be regenerated.

2.1.3 Stability in water

See section 2.1.5; there is no standard study of hydrolysis, but no normal hydrolytic mechanism can be envisaged in pure water. This is supported by results from dark and/or sterile controls from several types of degradation study, in which no degradation (as production of orthophosphate) was observed over time periods of up to 60 days under ambient conditions in water. There is evidence (reliability 4) that partial breakdown (removal of one chain from the N atom, replaced by H) occurs, at a rate of 40% over 4 days (Steber and Wierich, 1987), and Schowanek and Verstraete (1991) report abiotic degradation half-lives of the order of 30 days in the presence of calcium, magnesium and iron divalent ions.

2.1.4 Transport between environmental compartments

It is necessary first to consider the behaviour of ATMP in respect of adsorption to solids, as this property profoundly affects the modelling of environmental distribution. This has been widely reported in the literature, and reviewed in Annex III.

2.1.4.1 Adsorption

Several conclusions can be drawn from the reported findings.

1. The phosphonic acids adsorb strongly to inorganic surfaces, soils and sediments, in model systems and mesocosms; this has implications for the approach to environmental fate modelling. The commonly used property in modelling is the adsorption coefficient to organic carbon, K_{oc}, although processes of interaction with organic carbon are not necessarily taking place at a molecular level for ATMP. Although values of K_{oc} are derived for modelling purposes, in the present case they do not indicate true adsorption to organic carbon. More detailed modelling should use Kd rather than Koc if possible.

2. The nature of the adsorption is believed to be primarily due to interaction with inorganic substrate. While K_{oc} is the conventional indicator for adsorption, there is not necessarily any interaction with organic carbon present in the substrate in the case of these substances.

3. At neutral pHs adsorption is likely to be high for ATMP.

4. The presence of calcium in solution tends to significantly increase the adsorption of ATMP. In natural waters this will play a part in the fate of ATMP, particularly in slightly alkaline waters.

Table 2.4 ATMP group: adsorption to various media

<table>
<tr><th>Adsorbent</th><th colspan="2">Result</th><th>Reliability</th><th>Reference</th></tr>
<tr><td>Goethite</td><td colspan="2">30% (pH 10, 40µM ATMP, 0.42 g/L FeOOH (goethite))
30 µM/g (pH 7.2).
Fe III, Cu II and Zn II have no discernible affect on adsorption</td><td>4</td><td>Stone and Knight (2002)</td></tr>
<tr><td>Goethite</td><td colspan="2">In the absence of metals:
pH8 ~100% adsorbed
pH10 ~50% adsorbed
pH12 ~0% adsorbed

The presence of Zn II, Cu II and Fe III has no discernible effect on this adsorption.</td><td>4</td><td>Nowack and Stone (1999a)</td></tr>
<tr><td>Goethite</td><td colspan="2">In the presence of calcium, the adsorption of ATMP increases significantly.</td><td>4</td><td>Nowack and Stone (1999b)</td></tr>
<tr><td>STP sludge</td><td colspan="2">>90% adsorbed in 24 hours</td><td>4</td><td>Gledhill and Feijtel (1992)</td></tr>
<tr><td>Activated sludge</td><td colspan="2">Studies conducted as a function of pH with Ca, Cu or Fe ions present. Adsorption from a 3.7 µM solution was 50 - 90%, consistent with a high adsorption coefficient.</td><td>4</td><td>Nowack (2002)</td></tr>
<tr><td>River sediment</td><td colspan="2">Mean value of Ksediment-water applicable to soft water is 1270 l/kg, and to hard water, 1500 l/kg.
Equivalent values of Koc = 11740,
log Koc = 4.07</td><td>2</td><td>Michael (undated, believed to be 1979).</td></tr>
<tr><th>Adsorbent</th><th>Adsorption coefficient</th><th>Freundlich isotherm constant</th><th>Reliability</th><th>Reference</th></tr>
<tr><td>Activated sludge (2.9g/l)</td><td>0.92-0.95</td><td>1360-3900</td><td rowspan="4">4</td><td rowspan="4">Steber and Wierich (1987)*</td></tr>
<tr><td>Alfisol (200g/l)</td><td>0.95-0.97</td><td>45-105</td></tr>
<tr><td>Spodosol (200g/l)</td><td>0.97</td><td>129-237</td></tr>
<tr><td>Entisol (200g/l)</td><td>0.94-0.96</td><td>32-86</td></tr>
</table>

*Koc cannot be obtained from the Freundlich constant from the information found in the paper, but the values are consistent with Koc > 1000.

Based on the data reported in Table 2.4, a Koc value of 11740 has been selected for use in environmental modelling. This value is applicable to ATMP and its salts.

2.1.4.2 Modelling

Because ATMP and its salts behave in aqueous medium in accordance with its pH and composition, the conclusions in this section apply to both acid and salts.

For the present purpose no degradability has been assumed (see 2.1.5).

The compartmental approaches expressed in the Mackay models at Level 1 and Level 3 have been used to give an indication of relative partition tendencies, but not predicted concentrations. This qualitative approach is sufficient for the present purpose.

INPUT DATA USED:

Molecular weight = 299
Data temperature = 20˚C
Log Kow = -3.53 initially, although a surrogate value is preferred when the program used does not allow input of Koc (see below).
Water solubility = 500,000 mg/l
Vapour pressure = 1.91×10^{-10} Pa
Melting point = 195˚ C

RESULTS

Using a fugacity based model (Mackay level 1) ATMP (6419-19-8) is predicted to migrate entirely to the aqueous compartment (100%) with 2.6×10^{-5}% in the soil, 0% in air and 0% in sediment.
However, this Level 1 model assumes a very low soil and sediment adsorption, and this is known to be incorrect. Therefore further level 1 modelling using a substitute log Kow of 4.45 has been performed. This input value of log Kow is set to obtain the correct Koc (11,740) within the Level 1 program, and gives the values set out in table 2.5 below:

Table 2.5 Level 1 outputs using an adjusted log Kow

Air	0%
Soil	94.1%
Water	3.8%
Fish	0.005%*
Sediment	2.1%

*This value is too high, as shown by low measured BCF of phosphonates, consistent with a low Kow; the need for the 'dummy' log Kow value gives an incorrect indication of bioconcentration into fish.

The Level 3 program has also been applied, with the default model, using the same input parameters and the adjusted log Kow. The resulting distribution between compartments is set out in table 2.6 below:

Table 2.6 Level 3 outputs using an adjusted log Kow

	Release:		
	100% To air	**100% To water**	**100% To soil**
% in air	0%	0%	0%
% in soil	99.6%	0%	99.6%
% in water	0.2%	54.1%	0.2%
% in sediment	0.17%	45.9%	0.17%

For the known use pattern, the most likely emission route will be directly to water. Direct emission to soil via spreading of sludge from waste water treatment plants is also possible.

The results reflect that most ATMP found in air would be precipitated to soil, and that there is very little movement between soil and water, because transfer via the air compartment is very slow, for a substance of low volatility. In water, the adsorption coefficient of ATMP results in significant adsorption to sediment.

The distribution in a sewage treatment plant has been estimated using the SimpleTreat model (implemented in EUSES 1.00) to be 0% degraded, 43.3% to water, 56.7% to sewage sludge. These outputs are based on non-biodegradability, and the properties given above for the fugacity-modelling of distribution.

Conclusions: Based on the relevant physical-chemical properties, the known use pattern (release to water) and the fact that it is non-readily biodegradable, ATMP and its salts will partition primarily to water and suspended sediments. In the sewage treatment plant the substance is not expected to degrade, but will be removed on sewage sludge (56.7%) and be present in the effluent (43.3%).

The sludge adsorption results reported in Table 2.4 (Gledhill and Feijtel, 1992; Nowack, 2002) demonstrate that high levels of adsorption have been observed.

2.1.5 Biodegradation

There are many biodegradation results available. Only the most reliable are listed here. Annex II gives a fuller set of results and an overview. The other studies, of low reliability, are not reported in detail here since they add nothing further to the overall understanding.

Table 2.7 Biodegradation results

Parameter	Values / results		Reliability	Discussion and reference
	6419-19-8	**salts**		
Ready biodegradability	 29 % after 30 days <10% (OECD 301B)	x = 4: 0% after 28 days (OECD 301E)	1 4 4	Douglas, M.T., Pell I.B. (1984) Henkel KGaA, unpublished results (IUCLID 2000a). Schoberl P. & Huber L. (1988).
Inherent biodegradability	(0.5±0.69% over 24 hour cycles in 7-month SCAS test). 23% after 28 days, in a Zahn-wellens test using adapted activated sludge.	No data	2 4	Saeger et al., Monsanto (1978) Steber J and Wierich P (1987). A second SCAS test showing loss of DOC is not as reliable and removal can be ascribed to adsorption.
Anaerobic biodegradability	0-21% over 56 days	No data	2	Brixham Report BLS1956/B
Coupled units	DOC removal. Mean retention time: 3 hours. Mean degradation rate: 35.6 +/- 6.3%	No data	4	Henkel (unpublished, IUCLID 2000a). Certain partial degradation products could be detected.
Degradability in natural water	10% (river water), 17% (lake water) over 60 days.	No data	2	The rise in temperature associated with light exposure may have had an effect. (Saeger V.W. et al., Monsanto (1978))
Degradability in natural soil	14% over 148 days Approx 10% degradation over 119 days, in three soils.	No data	2 4	Saeger V.W. et al., Monsanto (1978) Monsanto Report MO-77-0622

Parameter	Values / results		Reliability	Discussion and reference
	6419-19-8	salts		
Microcosm study	5 - 12 % after 28 days.		4	Monsanto unpublished.

Conclusions regarding degradability

While some biodegradation has been observed, the results for this group do not show significant biodegradation in the short term and they are not readily biodegradable. However, abiotic breakdown, and photodegradation in the presence of common metal ions have been observed. Based on evidence from a number of studies members of this group are considered to be partially degradable over short time periods, and with evidence of mineralisation, particularly in the light, over longer periods.

2.1.6 Bioaccumulation

Three reliable results are available. There is a report of bioaccumulation of ATMP in carp, bioconcentration factor in the exposure phase of –<4 - 22 (EG&G, 1976a). Two other results were reported in the 1993 SIDS data set: these are assumed to be reliable although the original reports were not available for review. The results are BCF = 5.2 – 17.7 and BCF = 18 – 24, both measured for ATMP acid in *Brachydanio rerio* (zebra fish).

Conclusions: Based on the measured BCF, ATMP and its salts are not expected to bioaccumulate.

2.2 Human Exposure

Human exposure in manufacturing and formulating is possible, but due to the use of personal protective equipment, limited to accidental situation. Where exposure can occur, dermal exposure is the most likely route of exposure. The concentration of the substance in the product, together with PPE/engineering controls are important factors in the assessment of risk associated with the hazardous properties (mainly corrosivity/irritancy). Where concentrated solutions are handled, engineering controls and PPE are used to control exposure and reduce the risk from the corrosive/irritant properties. In downstream uses, where consumer exposure is possible, much more dilute concentrations are used, which in turn lowers exposure, and significantly reduces or removes the likelihood of corrosivity/irritancy effects.

2.2.1 Occupational exposure

In manufacturing and at formulators, the concentrated products (typically 20 – 60% aqueous solutions) are handled. At these higher concentrations the substances can be corrosives or irritants. However, the potential for dermal exposure is low. The concentrated solutions are predominantly used in closed systems by professionals experienced in handling such chemicals. Where accidental dermal exposure can occur, in activities such as sampling or drumming off, the volumes will be very small and workers will use appropriate PPE. Recommended PPE consists of proper gloves, eye or full face protection and suitable protective clothing.

ATMP or its salts are not commercially available as solid products.

Industrial and professional users of formulated products (I&I cleaning products, water treatment products) are also expected to use proper PPE. Formulated products have a lower concentration of phosphonates, typically in the range of 0.1 – 5 %. At the formulated concentrations the adverse effects of the corrosive/irritant properties seen in the pure substances will be significantly reduced or covered by other properties of the final formulation.

2.2.2 Consumer exposure

Consumers in Europe may come in contact with detergent products (e.g. hard surface cleaners) containing 0.1 – 1 % of phosphonates. However, the use in consumer products of ATMP and its salts is very limited. While accidental dermal exposure, could occasionally occur, the low concentration in the formulated product used, will mean that consumer exposure to the substance is very low. In addition, the significant reduction in corrosive/irritant properties at these concentrations will remove or significantly reduce any possible effects from this hazard. Consumer exposure is being assessed in more detail as part of the HERA project (HERA, in progress www.heraproject.com/).