DATA ON MANUFACTURE, IMPORT, EXPORT, USES AND RELEASES OF:

- **DIARSENIC TRIOXIDE (CAS NO: 1327-53-5);**
- **DIARSENIC PENTAOXIDE (CAS NO: 1303-28-2);**
- **LEAD HYDROGEN ARSENATE (CAS NO: 7784-40-9); AND**
- **TRIETHYL ARSENATE (CAS NO: 15606-95-8),**

AS WELL AS INFORMATION ON POTENTIAL ALTERNATIVES TO THEIR USE

FINAL REPORT
(PHASES I & II)

prepared for

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CONTENTS

Executive Summary

Background

In the framework of the REACH authorisation process, Annex XV dossiers have been prepared for four arsenate compounds:

- *diarsenic trioxide (CAS No: 1327-53-5);*
- *diarsenic pentaoxide (CAS No: 1303-28-2);*
- *lead hydrogen arsenate (CAS No: 7784-40-9); and*
- *triethyl arsenate (CAS No: 15606-95-8).*

Following receipt of comments from Member States and other interested parties, the European Chemicals Agency (ECHA) is obliged to prioritise the candidate chemicals for inclusions into Annex XIV. To assist with this prioritisation, ECHA commissioned Risk & Policy Analysts (through the REACH Framework Contract led by DHI) to provide additional information on the uses and the releases of the four arsenates under consideration.

Manufacture & Imports

Diarsenic trioxide is imported and manufactured within the EU in quantities of several thousand tonnes per year. Much smaller quantities (a few hundred tonnes per year) of diarsenic pentaoxide are imported and, possibly, manufactured within the EU. Very small quantities (less than 100 kg per year) of triethyl arsenate are imported but there appear to be no imports or manufacture of lead hydrogen arsenate.

Uses

The main uses of diarsenic trioxide are for lead alloys (especially in lead-acid batteries), glass (and, to a lesser extent, enamel) production and as a source of high-purity arsenic for use in the electronics industry. Diarsenic trioxide is also used as an intermediate for other arsenic compounds.

Historically, diarsenic pentaoxide was used in chromated copper arsenate (CCA) wood preservative. This use is now banned although one site still formulates CCA (for export) and there may be articles (with 'old' CCA treated wood) still being imported and/or reused. Otherwise the use of diarsenic pentaoxide is limited.

Triethyl arsenate is used for specialist applications in electronics while no (current) uses of lead hydrogen arsenate have been identified.

Alternatives

For many of the current uses, there are probably alternatives to the use of arsenic and its compounds. However, there are no direct alternatives for arsenic use in some electronic and special glass applications.

0. BACKGROUND

0.1 Annex XV Dossiers

In the framework of the REACH authorisation process, Annex XV dossiers have been prepared for four arsenate compounds by France and Norway in which they are concluded to be carcinogenic, mutagenic and reprotoxic (CMR) substances. They have, therefore, been put forward for consideration as substances of very high concern (SVHC) and, potentially, for subsequent inclusion on Annex XIV of the REACH Regulation.

The four arsenates under consideration are:

- diarsenic trioxide (CAS No: 1327-53-5);
- diarsenic pentaoxide (CAS No: 1303-28-2);
- lead hydrogen arsenate (CAS No: 7784-40-9); and
- triethyl arsenate (CAS No: 15606-95-8).

0.2 Consultation & Prioritisation

In accordance with the procedures[1], the Annex XV dossiers for the four arsenates (and a number of other chemicals) were published[2] and circulated to Member States for comment. Following receipt of comments from Member States and other interested parties, the European Chemicals Agency (ECHA) is obliged to prioritise the candidate chemicals for inclusions into Annex XIV.

To assist with this prioritisation, ECHA commissioned Risk & Policy Analysts (through the REACH Framework Contract led by DHI) to provide additional information on the uses and the releases of the four arsenates under consideration.

A Phase I report was submitted in November 2008 which was used to inform the meeting of the Member State Committee held in Helsinki in December 2008. This Phase II report incorporates some (limited) additional information on uses and releases of arsenates with particular regard to batteries and glass.

0.3 Objectives of the Study

As stated in the Terms of Reference, the specific objectives of the study are:

- to obtain information on manufacture, import and export as well as releases from manufacturing sites in the EU for assessment of the contribution to the total mass balance and releases;

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1 ECHA (2007): **Guidance for the preparation of an Annex XV dossier on the identification of substances of very high concern**, dated June 2007.

2 The four dossiers are available from the ECHA website: www.echa.europa.eu

- to obtain information on uses, conditions of use and the lifecycle of the substance including the complexity of the supply chain for mapping the mass flow;
- to identify the in quantitative terms most relevant uses of the substances;
- to get an overview on releases from uses and to identify the uses causing the highest releases to working environments and the environment. Releases from consumer use of preparations and articles shall be considered as well;
- to identify the potential alternative substances and to obtain information on their intrinsic hazard properties, hazards and risks allowing comparison with the substances in question; and
- to identify the potential alternative techniques and to obtain information on their potential hazards and risks to human health and the environment allowing comparison with the substances in question.

Following submission of the Phase I report in response to these objectives, ECHA requested further information (relating specifically to diarsenic trioxide and pentaoxide) on:

- release potential from use in articles (such as batteries and glass);
- release potential associated with recovery/recycling of such articles; and
- (potential) use of alternative arsenic compounds.

0.4 Approach to the Study

The approach to data collection for this study involved three key elements:

- reviewing the Annex XV dossiers and comments received as a result of their publication and circulation;
- reviewing of available data from other documents, the Internet and online data bases[3]; and
- consulting directly with users and/or their trade associations through the use of e-mail questionnaires.

At the outset, three observations may be made:

- the Annex XV dossiers (and associated comments) contain little information on the uses (and associated releases) of the arsenates under consideration;
- although there is a wealth of information on past uses of arsenic and its compounds in general, locating specific data on current uses is difficult; and
- due to the short timescale of the study, it was not possible to develop and implement a reliable survey of all the key stakeholders.

With these points in mind, it is not surprising that the analysis presented in the following sections remains uncertain.

[3] Particular use was made of Science Direct, PubMed, Google Scholar, Wiley Interscience and Scirius.

In relation to the additional questions which arose following the submission of the Phase I report, it is unfortunate that the period allowed for responding coincided with the Christmas/New Year holiday period making further consultation with stakeholders very difficult. Further attempts were made to elicit information from online data bases.

0.5 Structure of Report

Section 1 presents the information available on the manufacture, import and export of the arsenates under consideration together with a commentary on associated releases. Section 2 provides further detail on the uses (and associated releases). Where appropriate, quantitative data is summarised and presented in Annex 1.

Consideration is given to alternatives in Section 3.

1. INFORMATION ON MANUFACTURE, IMPORT AND EXPORT AND RELEASES FROM MANUFACTURE

1.1 Manufacturing Sites and Manufacturing Processes

1.1.1 Availability of Arsenic in Nature

Arsenic is usually found combined with one or more other elements such as oxygen, chlorine and sulphur. Inorganic arsenic compounds are usually solids at environmental temperatures, of low volatility and variable solubility in water (Environment Agency, 2008).

Arsenic may be obtained from roasting arsenopyrite, the most abundant ore mineral of arsenic, as well as from copper, gold, and lead smelter dust (the highest mineral concentrations can be found as arsenides of copper, lead, silver, and gold, but high levels may also be found in some coal (World Bank Group, 1998)). Arsenic may be recovered from:

- enargite, a copper mineral, and associated alteration products;
- realgar (diarsenic disulphide) and orpiment (diarsenic trisulphide) in China, Peru, and the Philippines;
- copper-gold ores in Chile; and
- associated with gold occurrences in Canada.

In Sichuan Province, China, orpiment and realgar from gold mines are stockpiled for transport and later recovery of arsenic. Global resources of copper and lead contain approximately 11 million tons of arsenic (USGS, 2008).

1.1.2 Production Processes for Selected Arsenic Compounds

Diarsenic Trioxide

Globally, the major source of arsenic is as a by-product of the smelting of copper, lead, cobalt, and gold ores. Diarsenic trioxide[4] is volatilised during smelting and accumulates in the flue dust, which may contain up to 30% arsenic trioxide. Further processing can give a purity of 99%. Elemental arsenic can be prepared by the reduction of diarsenic trioxide with charcoal (ATSDR, 2007).

As suggested in Section 1.2, diarsenic trioxide is the main basis for manufacturing arsenic and its compounds.

Diarsenic Pentaoxide

Diarsenic pentaoxide[5] can be synthesised by reacting diarsenic trioxide with oxygen under pressure, or by dehydration of crystalline arsenic acid at temperatures above

[4] Also known as arsenic trioxide, arsenic(III) oxide, arsenous anhydride and white arsenic.

[5] Also known as diarsenic pentoxide, arsenic pentaoxide, arsenic pentoxide, arsenic(V) oxide and arsenic anhydride.

200°C, or by reacting diarsenic trioxide with oxidising agents such as ozone, hydrogen peroxide and nitric acid.

Lead Hydrogen Arsenate

Lead hydrogen arsenate, also called lead arsenate or acid lead arsenate ($PbHAsO_4$), is an inorganic insecticide produced using the following reaction:

$$Pb(NO_3)_2(aq) + H_3AsO_4(aq) \rightarrow PbHAsO_4(s) + 2HNO_3(aq)$$

It was used successfully against moths and other pests particularly in the US (Peryea, 1998). Within the EU, it was used extensively in the UK and France until after the Second World War.

Triethyl Arsenate

No information is currently available on the production processes relevant to this substance.

1.2 Tonnages and Production Locations

Diarsenic Trioxide

According to US sources, 13 countries produce arsenic and its compounds (primarily diarsenic trioxide). The largest producer is China, followed by Chile, Morocco and Peru. Production figures for the last three years are presented in Table 1.1.

Table 1.1: Production of Arsenic and Compounds (primarily Diarsenic Trioxide) by Country (in tonnes/annum of diarsenic trioxide)

Country	2005	2006	2007
China	30 000	30 000	25 000
Chile	11 700	11 700	11 400
Morocco	8 939	8 900	8 950
Peru	3 150	4 399	4 321
Mexico	1 664	1 595	1 600
Kazakhstan	1 500	1 500	1 500
Russia	1 500	1 500	1 500
Belgium	1 000	1 000	1 000
Canada	250	250	250
Bolivia	120	240	200
Iran	100	100	100
Japan	40	40	40
Portugal	15	15	15
Total	**60 000**	**61 200**	**55 900**

Source: USGS, 2008

Note that although 1000 tonnes of diarsenic trioxide contains about 757 tonnes of arsenic, it is important to stress that, within the overall accuracy of these and subsequent estimates, there is little merit in attempting to distinguish between them. As such, no attempt has been made to convert estimates to the same basis.

World reserves and reserve base are thought to be about 20 and 30 times, respectively, annual world production (USGS, 2008).

However, increasingly, the recovery of arsenic (as diarsenic trioxide) forms an integral part of metal recovery from mining waste (by-product) streams and recyclable products. By way of example, the Umicore facilities in Belgium have the capacity to produce 1,000 t/yr arsenic from lead processing (Vanbellen, 2004) which is consistent with the figure presented in Table 1.1.

There is a further major facility in Germany (PPM Metals - Bhattacharya *et al*, 2007) which is understood to focus on metal recovery - but is not included in Table 1.1. In relation to the reported production in Portugal, this may be associated with the arsenic rich minerals (particularly arsenopyrite) from the tungsten mines of Panasqueira.

Although uncertain, it is estimated that about 1 000 t/yr are recovered from mining by-products (perhaps at two or three sites) and a further 1 100 t/yr are recovered from metal/electrical waste (perhaps at five to ten sites).

Diarsenic Pentaoxide

Production locations for this compound within the EU have not been confirmed. However, it would be reasonable to assume that two of the companies involved in the production of diarsenic trioxide may also be involved in the production of the pentaoxide. For the purposes of this study, it has been assumed that the associated production quantities are less than 100 t/yr.

Lead Hydrogen Arsenate

As lead hydrogen arsenate is no longer used in pesticides, it is unlikely that there is any production of this compound within the EU (or, indeed, elsewhere).

Triethyl Arsenate

As far as can be ascertained, there is no production of triethyl arsenate within the EU.

1.3 Import and Export of Arsenates as Substances or in Preparations

The world production of arsenic compounds is around 50-60 000 tonnes per annum, half of which is produced in China.

Although there is some production within the EU, any significant uses of arsenic within the EU will require imports - probably from China.

One of the largest Chinese exporters[6] is Chenzhou Chenxi Metal Company which provides the data presented in Table 1.2.

[6] Various data on Chinese producers and exporters can be located. For example, Hengyang Guomao Chemicals claims to have a production capacity of 3 600 tonnes/annum for diarsenic trioxide.

Table 1.2: Profile of One of China's Largest Exporters		
Compound	**Exports (tonnes/annum)**	**Comment**
Diarsenic Trioxide	2 400	
Diarsenic Pentaoxide	480	
Arsenic Acid	not given	
Arsenic Metal	1 800	Claimed to represent 35-40% of Chinese exports of arsenic metal
Lead Arsenic Alloy	720	Used in lead acid batteries
Copper Arsenic Alloy	not given	
Source: www.chenzhoumetal.com		

The vast majority of trade in arsenic involves diarsenic trioxide. This compound is used to produce other arsenic compounds. Although detailed estimates are available for the US, such data are not readily available for the EU.

Although difficult to extrapolate from the US situation to that for the EU, the US data (as shown in Table 1.3) provide some indication of the nature of the trade in arsenic and its compounds which may have some relevance for the EU situation.

Table 1.3: Profile of US Imports (Mean of 2006 & 2007)					
Compound	**Imports (tonnes/ annum)**	**% from China**	**% from EU**	**% from Elsewhere**	**EU Export Countries**
Diarsenic Trioxide	10 810	53%	3%	44%	Belgium, Germany, UK
Arsenic Metal	915	87%	1%	12%	Germany, UK
Arsenic Sulphide	89	100%	0%	0%	
Arsenic Acid	18	44%	31%	25%	France, Germany
Source: USGS (2008)					

Further information on the trade in arsenic and its compounds can be derived from customs data. For this study, international trade data based on HS Code 280480 have been reviewed (BAC, 2008). Under the *Harmonized Commodity Description and Coding System* (HS) maintained by the World Customs Organization, HS Code 280480 is derived as follows:

28 Inorganic Chemicals; Organic or Inorganic Compounds of Precious Metals, of Rare-Earth Metals, of Radioactive Elements or of Isotopes

2804 Hydrogen, Rare Gases and Other Non-metals

2804.80 Arsenic

Whilst this is the appropriate code for arsenic metals, the oxides are covered by a different code:

2811 Other inorganic acids and other inorganic oxygen compounds of non-metals

2811.29 Other

Unfortunately, as HS Code 2811.29 also includes non-arsenic compounds - it makes derivation of trade figures for the tri- and pentaoxide difficult. Although there are considerable uncertainties over the robustness of such trade data (as provided), the data do provide an indication of which EU countries are most active in the import and export of arsenic (as covered by HS Code 2804.80) as shown in Tables 1.4 and 1.5.

Table 1.4: Profile of EU Imports (2007) of Arsenic (as recorded by HS Code 2804.80)

Country	**Imports (tonnes/ annum)**	**Main Supplier**	**Second Supplier**	**Third Supplier**
Belgium	469	China (82%)	Netherlands (12%)	Sweden (2%)
Ireland	137	USA (100%)	-	-
UK	70	Morocco (71%)	Netherlands (26%)	Germany (2%)
Italy	64	Netherlands (69%)	China (31%)	-
Bulgaria	30	China (83%)	Netherlands (17%)	-
Sub-Total	**770**			
Europe	889	Top 5 Importers as % of EU Imports		87%
Source: BAC (2008)				

Table 1.5: Profile of EU Exports (2007) of Arsenic (as recorded by HS Code 2804.80)

Country	**Exports (tonnes/ annum)**	**Main Market**	**Second Market**	**Third Market**
Belgium	117	Poland (32%)	France (30%)	Sweden (11%)
Netherlands	59	Belgium (46%)	Italy (17%)	Germany (9%)
Germany	32	Japan (38%)	Korea (11%)	Belgium (13%)
France	4.4	Morocco (41%)	Germany (25%)	UK (11%)
Poland	4	Estonia (50%)	Ukraine (50%)	-
Sub-Total	**216**			
Europe	220	Top 5 Importers as % of EU Imports		98%
Source: BAC (2008)				

A similar set of figures can be derived from the Eurostat Prodcom data using the product code 24131170: Arsenic[7] as shown in Tables 1.6 and 1.7.

Table 1.6: Main EU Imports (tonnes/annum) of Arsenic (Product Code 24131170)

Country	**2005**	**2006**	**2007**
Belgium	164	116	466
Netherlands	206	131	207
Spain	112	143	116
Ireland	48	149	87
Italy	54	52	64
United Kingdom	23	47	70
*Source: Eurostat (epp.eurostat.ec.europa.eu) data explorer for **Industry, trade and services***			

[7] Although there is another code (24111250) covering diarsenic trioxide, this particular code also covers the much larger trade in sulphur trioxide making it impossible to derive figures for diarsenic trioxide.

Table 1.7: Main EU Exports (tonnes/annum) of Arsenic (Product Code 24131170)			
Country	**2005**	**2006**	**2007**
Belgium	100	2 538	117
Netherlands	119	75	233
Germany	21	20	32
France	8	15	3
Italy	16	2	0
Poland	1	4	4
Source: Eurostat (epp.eurostat.ec.europa.eu) data explorer for ***Industry, trade and services***			

Discussion

The overall global production in arsenic and its compounds is 50-60 000 tonnes per annum[8] - half of which is produced in China. There is a substantial global trade in arsenic and its compounds with the US importing over 12 000 tonnes per annum (of which nearly 1 000 tonnes is as elemental arsenic).

Although data on the EU imports/exports of the oxides have not been located, analysis of one of the customs codes (HS 2804.80) and of Eurostat product data (Code 2431170) provide some indicative information on the trade in arsenic. These data suggest that imports of elemental arsenic into the EU are likely to be of the order of 500 to 1 000 tonnes per annum. However such data need to be treated with caution as adding the country data may lead to double-counting. For example, imports to Belgium via Rotterdam may also appear as imports to the Netherlands.

There is little doubt that most of the trade in arsenic and its compounds involves arsenic trioxide (as evidenced by Chinese exports, US imports and other sources). Whilst it is acknowledged that the US is regarded as the largest consumer of arsenic compounds, the imports of elemental arsenic to the EU are of a similar order to those to the US.

With these points in mind, it is suggested that imports to the EU of arsenic and its compounds are likely to be of the order of 2,500 to 3,000 tonnes per annum (30% of which is imported as elemental arsenic).

To provide further inputs to the quantitative analysis which follows, the imports (and exports) of arsenates as substances have been assumed to be as shown in Table 1.8.

Table 1.8: Assumed Imports/Exports of Substances (tonnes/annum)			
Compound	**Imports**	**Exports**	**Comment**
Diarsenic Trioxide	1 800	not known	Exports unlikely to be significant
Diarsenic Pentaoxide	<200	not known	
Lead Hydrogen Arsenate	0	0	No longer used
Triethyl Arsenate	<1	0	Very small quantities imported/used

[8] This global production figure covers more arsenic compounds than the four arsenates being considered here. It has been assumed that the global production of diarsenic trioxide is about 30 000 t/yr.

For completeness, the estimated manufactured quantities (within the EU) of the substances under are summarised in Table 1.9.

Table 1.9: Estimated EU Manufacture of Substances (tonnes/annum)			
Compound	**Source**	**Quantity**	**Comment**
Diarsenic Trioxide	Mining/smelting by-product	1 000	Perhaps at 2 or 3 sites
	Recovered from waste	1 100	Perhaps at 5 to 10 sites
Diarsenic Pentaoxide	from Arsenic Trioxide	<100	Perhaps at 2 or 3 sites
Lead Hydrogen Arsenate	n/a	0	No longer used
Triethyl Arsenate	n/a	0	Not manufactured in the EU

In relation to preparations, one potential export has been identified (from the consultation) - that of a wood preservative (CCA) containing diarsenic pentaoxide at less than 100 t/yr.

1.4 Import and Export of Articles Containing Arsenates

As discussed in the next section, the substances of interest are, in general, very unlikely to be present in articles. However, it is possible that old wood treated with the CCA preservative could be imported - but no data on such imports have been located.

1.5 Releases from Manufacture

Indicative information on releases of arsenic and its compounds can be derived from the European Pollutant Emission Register (EPER). The results for the possible manufacturing sites are shown in Table 1.10.

Table 1.10: Releases from (Possible) Manufacturing Sites (tonnes/annum)			
Location	**Compartment**	**2001**	**2004**
Umicore (Hoboken and Olen facilities, Belgium)	to Air	0.74t	0.57t
	to Water	0.28t	0.22t
PPM Metals (Germany)	to Air	not listed	
	to Water		
Minas de Panasqueira (Portugal)	to Air	no data	
	to Water	1.08t	0.30t
Source: EPER (eper.eea.europa.eu/eper/default.asp)			

2 INFORMATION ON USES AND RELEASES FROM USES

2.1 Identification of Uses

2.1.1 Use of CPA 2008

Within the EU, there are numerous systems in use for the classification of trade, products and activities. For this study, use has been made of the *Statistical Classification of Products by Activity in the European Economic Community, 2008 Version* (Eurostat, 2008), hereafter referred to as CPA 2008. Under CPA 2008, products are grouped at several levels as illustrated below using the example of a green arsenate dye:

C Manufactured Products
- **20** Chemicals and chemical products
  - **20.1** Basic chemicals, fertilisers and nitrogen compounds, plastics and synthetic rubber in primary forms
    - **20.12** Dyes and pigments
      - **20.12.1** Oxides, peroxides and hydroxides
        - **20.12.19** Other metal oxides, peroxides and hydroxide

CPA 2008 has been used to provide a framework for presenting the identified uses of arsenates and a summary is presented in Table 2.1. To ensure that CPA 2008 references are not confused with references to other sections of the report, the initial letter from the CPA Code (B or C) has been included. So, for example, C20.12 refers to the CPA 2008 classification for: *Dyes and pigments*.

2.1.2 Use of Arsenates

In the subsections which follow, brief outlines of the various identified uses of arsenates are presented. In each case, consideration is given as to whether the identified use is a current rather than historical use and, if so, whether it is likely to be significant. In addition, the relevant arsenate is identified where possible.

However it should be noted that only one use (semiconductors) has been identified for triethyl arsenate and in very small quantities (perhaps 100 kg/year) and no current uses have been (positively) identified for lead hydrogen arsenate.

Although small quantities of arsenic may be present in various articles in widespread use, it is important to stress that only a relatively small number of companies handle the arsenates under consideration. By way of example, the Irish Health and Safety Authority contacted 800 potentially relevant companies for this study and received just one response (from a laboratory chemical supplier) confirming arsenate use[9].

[9] As advised by email, 19 December 2008.

Table 2.1: Arsenates in Products by Section and 2, 3 and 4 Digit CPA 2008 Classification			
A	**PRODUCTS OF AGRICULTURE, FORESTRY AND FISHING -** *Not relevant*		
B	**MINING AND QUARRYING**		
	05	Coal and lignite	
	06	Crude petroleum and natural gas	
	07	Metal ores	
	08	**Other mining and quarrying products**	
		08.9	**Mining and quarrying products n.e.c.** *(n.e.c. = not elsewhere classified)*
			08.91 Chemical and fertiliser minerals
	09	Mining support services	
C	**MANUFACTURED PRODUCTS**		
	10	Food products	
	11	Beverages	
	12	Tobacco products	
	13	Textiles	
	14	Wearing apparel	
	15	Leather and related products	
	16	**Wood and of products of wood and cork, except furniture; articles of straw and plaiting materials**	
		16.1	**Wood, sawn and planed**
			16.10 Wood, sawn and planed
	17	Paper and paper products	
	18	Printing and recording services	
	19	Coke and refined petroleum products	
	20	**Chemicals and chemical products**	
		20.1	**Basic chemicals, fertilisers and nitrogen compounds, plastics and synthetic rubber in primary forms**
			20.12 Dyes and pigments
			20.13 Other inorganic basic chemicals
		20.2	**Pesticides and other agrochemical products**
			20.20 Pesticides and other agrochemical products
		20.3	**Paints, varnishes and similar coatings, printing ink and mastics**
			20.30 Paints, varnishes and similar coatings, printing ink and mastics
	21	**Basic pharmaceutical products and pharmaceutical preparations**	
		21.2	**Pharmaceutical preparations**
			21.20 Pharmaceutical preparations
	22	Rubber and plastics products	
	23	**Other non-metallic mineral products**	
		23.1	**Glass and glass products**
			23.13 Hollow glass
			23.19 Other processed glass, including technical glassware
	24	**Basic metals**	
		24.1	**Basic iron and steel and ferro-alloys**
			24.10 Basic iron and steel and ferro-alloys
		24.4	**Basic precious and other non-ferrous metals**
			24.43 Lead, zinc and tin
			24.44 Copper
	25	Fabricated metal products, except machinery and equipment *(may contain arsenic alloys)*	
	26	**Computer, electronic and optical products**	
		26.1	**Electronic components and boards**
			26.11 Electronic components
	27	Electrical equipment	
	28	Machinery and equipment n.e.c. *(may contain arsenic alloys)*	
	29	Motor vehicles, trailers and semi-trailers	
	30	Other transport equipment	
	31	Furniture	
	32	Other manufactured goods	

2.1.3 Mineral and Quarrying Products n.e.c.[10] (B08.9)

Mine tailings have been used as mineral fertilisers. In the US, one brand which was widely available to consumers was found to contain sufficiently high levels of arsenic to be classified as hazardous waste (Cullen, 2008). Although the brand is still marketed, since 2006 the mineral fertilisers no longer contain significant levels of arsenic (MDH, 2008).

Although no information has been located (or provided in consultation responses) to suggest that arsenic containing mineral fertilisers are marketed within the EU, such products might be considered as *inorganic secondary nutrient fertilisers* under the Fertilisers Regulation[11]. However, the regulation does not provide any limits for the presence of arsenic.

2.1.4 Wood, Sawn and Planed (C16.10)

During the second half of the 20th century, the major use of arsenic was as a wood preservative - particularly in the US. The most widely used arsenic-based wood preservative was chromated copper arsenate (CCA) and CCA treated wood was generally considered suitable for general indoor and outdoor use. The current situation regarding CCA is outlined in Section 2.1.7.

2.1.5 Dyes and Pigments (C20.12)

The arsenic sulphides orpiment and realgar have been used as yellow and red pigments respectively for thousands of years.

Scheele's green (copper arsenite) pigment was discovered in 1775 but was subsequently displaced by copper acetoarsenite (discovered in 1814) under various names (including Schweinfurt Green, Brunswick Green, Paris Green and emerald green).

Green wallpaper was particularly popular during the early part of the 19th century but arsenic health concerns and the commercial development of aniline dyes in the 1860s led to its demise (Cullen, 2008).

2.1.6 Other Inorganic Basic Chemicals (C20.13)

As outlined in Section 1.3, much of the arsenic imported into the EU will be in the form of diarsenic trioxide. As such, **diarsenic trioxide** is used as the feedstock for the production of other arsenic compounds within the EU. Consultation for this study also indicates that **diarsenic pentaoxide** is used for this purpose.

[10] Not elsewhere classified.

[11] **Regulation (EC) No. 2003/2003 of the European Parliament and of the Council of 13 October 2003 relating to fertilisers**, (OJ L304, 21/11/2003, p1).

2.1.7 Pesticides and Other Agrochemical Products (C20.20)

Relevant Substances

During the second half of the 20th century, the major use of arsenic was as a wood preservative[12] - particularly in the US. The most widely used arsenic-based wood preservative was CCA. CCA is a preparation comprising copper (from the oxide or sulphate), chromium (from the oxide or a sodium chromate) and **diarsenic pentaoxide**, typically in the range 20-45%. **Diarsenic trioxide** and ammoniacal copper zinc arsenate (ACZA) were also used in timber treatment but to a much lesser extent. CCA (diluted to 2-5% in water) is applied to the wood under pressure and, hence, is often referred to as pressure-treated wood (RPA, 2005)

Historically, lead arsenate was reportedly the most extensively used arsenical insecticide (Peryea, 1998). Two principal formulations of lead arsenate were marketed: basic lead arsenate ($Pb_5OH(AsO_4)_3$, CAS No. 1327-31-7) and **lead hydrogen arsenate**. However, it is understood that it is no longer in use either in the EU or the US and this has been confirmed by the European Crop Protection Association during consultation for this project[13].

Recent Developments

Although CCA treated wood was generally considered suitable for general indoor and outdoor use, increasing concerns over its use led to a series of regulatory actions including:

- **Directive 89/677/EEC** (amending for the eighth time Directive 76/769/EEC on Marketing and Use restrictions) stipulated that arsenic compounds may not be used as substances and constituents of preparations intended for use in the preservation of wood unless solutions of inorganic salts of the CCA type were used in industrial installations using vacuum or pressure to impregnate wood.

- Several years later, **Directive 2003/2/EC** (adapting Directive 76/769/EEC to technical progress for the tenth time) restricted the use of CCA-treated timber to a limited number of end uses where structural integrity is required for human or livestock safety and skin contact by the general public is unlikely. This had to be implemented by 30th June 2004. These limited end uses account for a small proportion of the requirement for treated timber.

- Another issue of importance to the evolution of the EU markets for wood treatment formulations is the **Biocidal Products Directive (98/8/EC)**. Arsenic pentaoxide was notified by industry as an active substance following the provisions of the Directive; however, a dossier was not eventually submitted. This effectively prevents the use of arsenic in wood preservatives in the EU (but see points on imports below).

12 Within the CPA classification, a wood preservative such as CCA could be classified as an insecticide (C20.20.11) and/or as a fungicide (20.20.15).

13 Nevertheless, as the substance has been pre-registered under REACH, one company, at least, has an interest in lead hydrogen arsenate.

- **Voluntary label amendments** by the CCA registrants in the USA and Canada have limited the treatment of CCA in wood to be used by consumers in these countries. In the US the voluntary ban took effect at the beginning of 2004.

- **Directive 2006/139/EC** (adapting Directive 76/769/EEC to technical progress), prescribes that arsenic shall not be used in the preservation of wood. Under Point 20 of Annex 1 to Directive 76/769/EEC as amended by Directive 2006/139/EC, CCA type C cannot be used to treat wood in the EU due to the fact that it has not been authorised under Directive 98/8/EC. A request for authorisation could, however, be made in the future in line with the requirements of Directive 98/8/EC (EC, 2008).

Current Situation

Although wood newly treated with CCA may not be imported or placed on the market, one company (in a Nordic country) has been identified which formulates CCA for export.

However, certain types of old CCA treated wood are still permitted to be reused (and imported) under the details of Directive 2006/139/EC[14]. The extent to which this practice is being done is not known.

2.1.8 Paints, Varnishes etc. (C20.30)

Although the introduction of aniline dyes led to the demise of arsenic in wallpaper, the use of arsenic compounds continued to be used as paint pigments (particularly the green) - probably until the 1950s (van Alphen, 1998). No current use of the arsenates as pigments (within the EU) have been identified and this has been confirmed in consultation[15].

Diarsenic trioxide is used in vitrifiable enamels (classified under *C20.30.21 Prepared pigments, opacifiers and colours, vitrifiable enamels and glazes, engobes, liquid lustres and the like; glass frit*). It can be used as an opacifier in glazes, although it is claimed to be not as effective as tin. It creates a fine matrix of bubbles that impede light passage (Ceramic Materials Database, 2003). It is also used as decolourising agent, through oxidising effect of As_2O_3 on ferrous ion, adding to colour stability and increasing brilliancy. However, in enamels, its toxicity limits applications to special products, e.g. jewellery (UBCeram, 2005).

2.1.9 Pharmaceutical Preparations (C21.20)

Arsenic compounds have been used in medicines for millennia. Fowler's solution (diarsenic trioxide dissolved in vegetable alkali) was developed in 1783 and was used

14 As clarified to the consultants by DG Enterprise (30 September).

15 By ETAD (Ecological and Toxicological Association of Dyes and Organic Pigments Manufacturers) (2 October).

as a cure (tonic) for a range of illnesses through to the 20th century. The development of organoarsenical compounds from the 1860s led to widely used medicines (such as Salvarsan) for the treatment of venereal disease through to the Second World War. However, the use of arsenic compounds in (Western) medicines progressively tailed off during the latter part of the 20th century and had disappeared by the mid-1990s (Cullen, 2008).

However, the use of arsenic (as injected diarsenic trioxide) has reappeared following extensive study in China. Diarsenic trioxide has been found to be effective in the treatment of a particular type of leukaemia (acute promyelocytic leukaemia). This use was authorised in the US in 2000 under the trade name Trisenox[16].

Although (potential) medical uses are important, the associated quantities are not significant for the arsenates under study in the EU and, as such, are not explored further.

2.1.10 Glass and Glass Products (C23.1)

Relevant Substances

Generally, arsenic compounds are used in the manufacture of glass (special glass and lead crystal) and enamel (as mentioned above, see Section 2.1.8) either to control the colour of the articles or for refining purposes (i.e. to remove bubbles).

Diarsenic trioxide is used in the manufacture of lead crystal and special glass as well as the decolourisation of glass (and enamel). It is used as decolourising agent, through oxidising effect of As_2O_3 on ferrous ion, adding to colour stability and increasing brilliancy.

Diarsenic pentaoxide is reportedly used in the manufacture of special glass. However, in response to consultation for this study, the European glass industry trade association has suggested that pentaoxide is not used within Europe (CPIV, 2008a).

Types of Glass

The most widely used classification of glass type is by chemical composition, which gives rise to four main groupings: soda lime glass, lead crystal and crystal glass, borosilicate glass and special glasses (CPIV, 2008).

Lead oxide can be used to replace much of the calcium oxide in the batch to give a glass known as **lead crystal**. A typical composition is 54-65% SiO_2, 25-30% PbO (lead oxide), 13-15% Na_2O or K_2O, plus other various minor components. This type of formulation, with lead oxide content over 24%, gives glass with a high density and refractive index, thus excellent brilliance and sonority, as well as excellent workability allowing a wide variety of shapes and decorations (CPIV, 2008).

The **special glass** sector produces around 6% of the glass industry output, and in terms of tonnage is the fourth largest sector. Special glass products have a relatively

16 www.fda.gov/cder/consumerinfo/druginfo/Trisenox.HTM

high value and represent an extremely broad sector covering a wide range of products. The main products are: lighting glass (tubes and bulbs), optical glass, laboratory and technical glassware, borosilicate and ceramic glasses (cookware and high temperature domestic applications), and glass for the electronics industry (LCD panels) (CPIV, 2008). Until recently, the product list would have included cathode ray tube (CRT) glass for televisions and monitors, However, there has been a dramatic shift to LCD screens in recent years (EC, 2008b) and CRT glass is no longer made in the EU (CPIV, 2009).

Fining and Homogenisation

The glass melt must be completely homogenised and free of bubbles before it can be formed into the products. This involves the complete dissolution and even distribution of all components and the elimination of all bubbles by refining. These bubbles must be eliminated from the glass melt as they potentially cause defects in the finished product affecting mechanical strength and appearance.

The general principle of chemical fining is to add materials which when in the melt will release gases with the appropriate solubility in the glass. **Diarsenic trioxide** is used as a fining agent.

2.1.11 Basic Iron and Steel and Ferro-Alloys (C24.10)

Some steels (and alloys) under particular conditions are susceptible to hydrogen embrittlement which depends on the presence of ‘dissolved’ hydrogen in the steel. The presence of arsenic promotes hydrogen diffusion into the steel (and alloys) thus enhancing the potential for hydrogen embrittlement. These factors are used in metallurgical testing (by enhancing hydrogen diffusion) to determine whether hydrogen embrittlement is likely to be significant for a particular situation.

A review of various documents suggests that the metallurgy tests involve the addition of **diarsenic trioxide** (as suggested in the Annex XV dossier) in solutions in the range 1 to 250 mg/L. Examples include:

- a study of the susceptibility to stress corrosion cracking (SCC) of the Al-Zn-Mg-Cu French 7010 alloy of different temper by Slow Strain Rate Testing (Puiggali *et al*, 1998);
- a study of the relation between steel microstructure and its properties in inert and aggressive environments (Zieliński & Serbiński, undated);
- an investigation of the influence of hydrogen on the microstructure and on the character of corrosion degradation of ferritic and austenitic stainless steels (Lublińska *et al*, 2008); and
- a study on the effect of cathodic charging on the mechanical properties of aluminium (Watson *et al*, 1988).

Although no quantitative data on this use of diarsenic trioxide within the EU have been located, the quantities used will be small - as, in effect, the arsenate is being used as a test chemical in specialised laboratories. As such, no further data on usage are presented in this report.

2.1.12 Basic Precious and other Non-Ferrous Metals (C24.4)

The Annex XV dossiers suggest that **diarsenic trioxide** and **diarsenic pentaoxide** may be used in the manufacture of alloys with arsenic conferring increased hardness to the other metals. Particular references can be found to lead and copper alloys[17].

No specific references to the use of diarsenic pentaoxide in the manufacture of alloys have been identified (or provided in consultation responses). As such, in the analysis which follows, it has been assumed that the arsenic used in alloys is produced from diarsenic trioxide or is imported as arsenic metal.

Lead, Zinc and Tin (C24.43)

Battery grids: trace quantities of arsenic are added to lead/antimony grid alloys used in lead-acid batteries using liquid electrolyte (Subramanian *et al*, 2002).

Ammunition: the addition of arsenic (0.5–2%) improves the sphericity of lead shot (Subramanian *et al*, 2002). Small quantities of arsenic (<1%) may also be used to assist in the hardening of lead/antimony alloys used for casting bullets (Kelter, undated).

Cable sheathing: arsenical lead is also used for cable sheathing. Lead sheathing extruded around electrical power and communication cables gives the most durable protection against moisture and corrosion damage, and provides mechanical protection of the insulation. Chemical lead, 1% antimonial lead, and arsenical lead are most commonly employed for this purpose (Gray Environmental, 2007).

Diarsenic trioxide (and/or arsenic metal) may be being used for these uses within the EU.

Copper (C24.44)

Hardening of copper with arsenic goes back in time. It is suggested that that the Moche people of northern Peru were among the first to use copper, often with the addition of arsenic to harden the metal and improve the quality of the cast (McGuinness, 2008).

The effects of arsenic to copper alloys have been described (Mehta Group, 2008) as follows:

- in comparison to pure copper, the copper/arsenic alloys provide some advantages in casting. With an increased amount of arsenic, the melting temperature of the metal is decreased. The addition of 0.5% arsenic to copper prevents porosity even when casting under oxidising conditions;
- it reduces the crystal size in castings that may result in the increase of tensile strength, as it increases with the decreasing grain size. With an addition of up to 1% arsenic, the formation of solid solution slightly increases the tensile strength, however the ductility of material is not influenced; and

[17] Reference has also been found to the use of arsenic in gold alloys to produce a 'blue gold'.

- with up to 18% arsenic, the copper alloys have found to be highly ductile in hot working at 500 and 600°C. The improved work harden-ability of copper-alloys has found to be advantage over pure copper if it is required to produce hard edges.

Copper alloys such as brass (copper-zinc) containing arsenic (primarily for corrosion resistance) are used, *inter alia*, in condenser tubes, heat exchanger and distillation tubes (Davis, 2001; CDA, 2005).

2.1.13 Electronic Components (C26.11)

Relevant Substances

It is suggested that **diarsenic trioxide** and **triethyl arsenate** are used in the electronic industry. Diarsenic trioxide is used to produce high purity arsenic[18] which is the basis for gallium arsenide (GaAs) semiconductors. It is also suggested that the substance is used in the production of copper foil in printed circuit boards (Öko-Institut, 2008).

Although earlier studies have suggested that gallium arsenide may not be being produced within the EU (IARC, 2006; Öko-Institut, 2008), consultation for this study indicates that diarsenic trioxide is indeed being used within the EU to produce high purity arsenic metal which is either used to manufacture GaAs semiconductors or as a dopant for special semiconducting silicon qualities.

Applications

Gallium Arsenide Applications

Gallium arsenide (GaAs) may be used as a semiconductor substrate, as a dopant in semiconductor material, and as a substrate in LED applications (Öko-Institut, 2008).

GaAs semiconductors are used in lasers, space research and solar cells, and GaAs is an important component in light emitting diodes, which has contributed to stronger sales of GaAs. Gallium-arsenide and indium-arsenide semiconductors used in computers and electronic devices require high-purity (99.9999%) arsenic metal. GaAs wafers are used for electronics applications. A mobile phone typically contains GaAs in its microelectronic circuitry, of which the arsenic content is less than one milligram. High-purity arsenic may also be used for germanium-arsenide-selenide or GaAs specialty optical materials (USGS, 2008).

Arsenic as a Dopant

On the other hand, doping is a routine process in fabricating semiconductor devices. Arsenic is an n-type dopant (donor) in silicon (along with the other elements of Group V of the Periodic Table, notably antimony and phosphorous). N-type describes a semiconductor material that has negatively charged conductivity (a surplus of electrons) (M+W Zander, 2006).

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18 Whether or not the high-purity arsenic used in a particular application is derived from diarsenic trioxide or from refined (and possibly imported) arsenic metal has not been determined.

Consultation has indicated that the use of triethyl arsenate has been developed for use in specialised doping applications

Selenium Alloys

Small amounts of high-purity arsenic are used in arsenic-selenium alloys for photoconductors used in photocopiers, infrared detectors photovoltaic cells, etc. (STDA, undated). Consultation suggests that there is at least one electronics company in Western Europe using arsenic for this purpose.

2.2 Quantification of Uses

2.2.1 Overview

For the current uses of arsenates, as identified above, estimates are provided, where possible, for the quantities involved as well as the basis for the estimates.

2.2.2 Intermediate for Other Arsenic Compounds

As identified in Section 2.1.6, consultation for this study has confirmed that diarsenic trioxide and diarsenic pentaoxide are used as intermediates for the production of other arsenic compounds within the EU.

Although no precise data have been provided, the following (uncertain) estimates have been made (based on the consultation responses) for the production of other arsenic compounds:

- 1300 t/yr of diarsenic trioxide are used at two or three locations within Western Europe; and
- <100 t/yr of diarsenic pentaoxide are used at one location within Western Europe.

2.2.3 Wood Preservative (CCA)

As identified in Section 2.1.7, there may be imports into, and (re)use within, the EU of wood previously treated with CCA in articles (and, as such, these will contain diarsenic pentaoxide). Although this is understood to occur in one of the Nordic countries, no quantitative estimates for this use have been derived.

2.2.4 Glass & Glass Products

As outlined in Section 2.1.10, diarsenic trioxide is used in two types of glass - special glass and lead crystal. It is also used as a vitrifiable enamel (Section 2.1.8).

Special glass will tend to be produced in a few large facilities. By way of example, arsenic glass (up to 1% arsenic) is used for transparent cooker hobs (and wood stove windows) and there are two major manufacturers located in Western Europe. Of course, such articles are also imported (particularly from the Far East). Similar arguments would apply to the manufacture of:

- optical glass - for eye glasses, micro camera lens, etc;
- glass cookware;
- technical glass (including laptops, mobile devices, monitors, etc); and
- pharmaceutical packaging glass.

The total quantity of diarsenic trioxide used in special glass manufacture within the EU is estimated to be less than 1 000 t/yr (CPIV, 2008a).

Although historically, arsenic was used in the manufacture of lead crystal, it is considered that this usage has declined (CPIV, 2008a). Nevertheless, it is of note that, unlike special glass, lead crystal glass is made in small production units throughout the EU[19]. There remains the possibility, therefore, that there is a small but widespread use of arsenic for use in production of lead crystal[20].

Overall, the estimate for EU usage of diarsenic trioxide in glass processing has been taken as 1 000 t/yr, most of which is used for the production of special glass. Although no reliable data on the usage of diarsenic trioxide in vitrifiable enamels have been located, it is likely to be a much lower consumption than for glass and an estimate of 200 t/yr has been assumed.

Current usage of diarsenic pentaoxide for glass processing has not been verified. As such, any usage within the EU is likely to be small (say, <10 t/yr).

2.2.5 Use in Alloys (Lead and Copper)

As indicated in Section 2.1.12, it has been assumed that the arsenic used in alloys is produced from diarsenic trioxide or is imported as arsenic metal. Further consideration to the resultant mass balances is presented in Section 2.2.7.

Battery Grids (Lead)

Given the extent of lead-acid battery usage, the quantities of arsenic are significant. Indeed, Bhattacharya *et al* (2007) suggest arsenic usage in lead-acid batteries increased from 2 200 to 2 600 t/yr over the period 1995-2000 within the EU-15. As explored further below, current usage is likely to be somewhat lower.

Although a large number of lead-acid batteries are imported, these tend to be those used as back-up/portable power supplies (for computers, lighting, etc.) which do not have liquid electrolyte (and, as such, do not require the use of arsenic). Perhaps

19 Information from the trade association (CPIV, 2008) suggests that there may be as many 140 installations (mostly SMEs) producing domestic glass across the EU. However, not all of these will be producing lead crystal and, in any event, may not be using arsenates.

20 Recent events suggest that the lead crystal industry will be a victim of the current economic crisis with the collapse of Waterford crystal in Ireland (BBC News, 5 January 2009) and closure of some of the major Czech factories (Radio Prague, 23 December 2008 and associated consultation).

surprisingly, a large number of 'standard' car batteries are still produced within the EU and it is these that utilise the strengthened arsenic grids.

The analysis is based on the number of standard car batteries using liquid electrolyte which, in turn, require strengthened battery grids. These have been assumed to use arsenic. This may be a cautious (or pessimistic) assumption resulting in an overestimate of the arsenic consumption.

Data drawn from Eurostat are presented in Table 2.2.

Table 2.2: Indicative Data on Lead Acid Batteries (millions per year)

Battery Type	Parameter	2005	2006	2007
Standard Car Battery (>5kg Liquid Electrolyte for Piston Engines - Code: 31402150)	Imports (I)	7.0	6.6	6.7
	Exports (E)	6.0	6.5	6.1
	Production (P)	57.7	66.3	58.0
	Consumption (I+P-E)	**58.6**	**66.4**	**58.6**
Those for Back-up Supplies, etc (excl. Starting Piston Engines, Traction and Liquid Electrolyte - Code 31402270)	Imports (I)	36.9	36.1	54.1
	Exports (E)	3.8	3.7	5.8
	Production (P)	15.3	13.1	7.5
	Consumption (I+P-E)	**48.4**	**45.5**	**55.8**

Source: Eurostat (epp.eurostat.ec.europa.eu) data explorer for ***Industry, trade and services***

Examination of the associated country data suggests that the main manufacturers are located in Germany, France, Italy and Greece. Furthermore, the estimated consumption of around 60 million car batteries is consistent with the estimated EU car battery volume of 80 million (60m aftermarket and 20m in new cars in 2007[21]).

Assuming that a standard car battery contains 15kg of lead with 0.15% arsenic[22], then production of, say, 60 million batteries per annum would consume:

$$60 \times 10^6 \times (15/1000) \times (0.15/100) = 1\ 350 \text{ t/yr arsenic}$$

This figure has been carried forward in the analysis which follows - although it is acknowledged that this may be an overestimate.

Ammunition (Lead)

The estimated EU consumption of lead shot was estimated to be over 30 000 tonnes in 2003 (COWI, 2004). Taking a 1% arsenic content would suggest a consumption of 300 tonnes of arsenic. With increasing (environmental) concerns over the use of lead shot, it is likely that this will have dropped as users have switched to less toxic shot; perhaps, to less than 200 t/yr.

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21 Figures from the Association of European Storage Battery Manufacturers (http://www.eurobat.org/).

22 As discussed in Section 3.1.4, lead-antimony grids may contain up to 0.25% arsenic although consultation responses suggest that a more typical value would be up to about 0,15%.

Other Uses

Other uses identified in Section 2.1.12 were lead-arsenic alloys in cable sheathing and use of copper-arsenic alloys in heated environments (such as heat exchangers). No further detail on such uses has been obtained.

For the purposes of this analysis, it has been assumed that 'other uses' could total as much as 300 t/yr.

2.2.6 Electronic Components

The current consumption of high-purity arsenic for the production of electronic components within the EU is estimated to be no more than 200 t/yr. This may be produced directly from diarsenic trioxide or from arsenic metal. In addition, triethyl arsenate is imported at no more than 0.1 t/yr.

The estimated breakdown by uses is shown in Table 2.3.

Table 2.3: Electronic Components - Uses

Substance	Use	Quantity (t/yr)
High-purity Arsenic	GaAs Semiconductors	180
	Doping Silicon	20
	Selenium-Alloys (copiers, etc.)	20
Triethyl arsenate	Semi-conductor processing	<0.1

Source: Stakeholder responses and associated literature review

2.2.7 Summary and Material Flows

The associated material flows for each of the arsenates for which uses have been identified (i.e. diarsenic trioxide, diarsenic pentaoxide and triethyl arsenate) are summarised in Figures 2.1 to 2.3. As should be clear from the above text, there remain considerable uncertainties as to the precise quantities involved.

Furthermore, the material flows and associated mass balances are, in some cases, rather complex. Nevertheless, the material flows, as presented in Figures 2.1 to 2.3, are consistent with the text and with summary information provided in tabular form in Annex 1 to this report.

This can perhaps be illustrated by two examples. Firstly, the mass balance for arsenic metal (which is closely linked to the use of diarsenic trioxide as shown in Figure 2.1) is presented in Table 2.4.

Table 2.4: Mass Balance for Arsenic (within EU)			
Arsenic Supply		**Arsenic Consumption**	
Description	**Quantity**	**Description**	**Quantity**
Arsenic metal imports to EU	750 t/yr	Use in semiconductors	200 t/yr
Arsenic metal from processing	1 300 t/yr	Use in lead-acid batteries	1 350 t/yr
		Use in ammunition	200 t/yr
		Other uses (including cable-sheathing and copper alloys)	300 t/yr
Total	**2 050 t/yr**	**Total**	**2 050 t/yr**

A similar table can be developed for the wider picture of arsenic and diarsenic trioxide supply and consumption (based on Figure 2.1) as shown in Table 2.5.

Table 2.5: Mass Balance for Arsenic/Diarsenic Trioxide (within EU)			
Supply		**Consumption**	
Description	**Quantity**	**Description**	**Quantity**
Arsenic metal imports to EU	750 t/yr	Arsenic in semiconductors	200 t/yr
Diarsenic trioxide imports to EU	1 800 t/yr	Arsenic in lead-acid batteries	1 350 t/yr
Diarsenic trioxide from mining/smelting by-products	1 000 t.yr	Arsenic in other alloys (ammunition, cable sheathing and copper alloys)	500 t/yr
Diarsenic trioxide recovered from metal/electrical waste	1 100 t/yr	Diarsenic trioxide in glass/ enamel processing	1 200t/yr
		Diarsenic pentaoxide	100 t/yr
		Other arsenic compounds	1 300 t/yr
Total	**4 650 t/yr**	**Total**	**4 650 t.yr**

Within the timeframe for this study, it was not possible to further develop the precise material flows. By way of example, it has not been possible to determine the proportions of the arsenic used in lead shot (ammunition) which have been:

- imported as arsenic metal from outside the EU;
- supplied as arsenic metal from within the EU;
- imported as diarsenic trioxide from outside the EU and processed at the lead shot production facility; and
- supplied as diarsenic trioxide from within the EU and processed at the lead shot production facility.

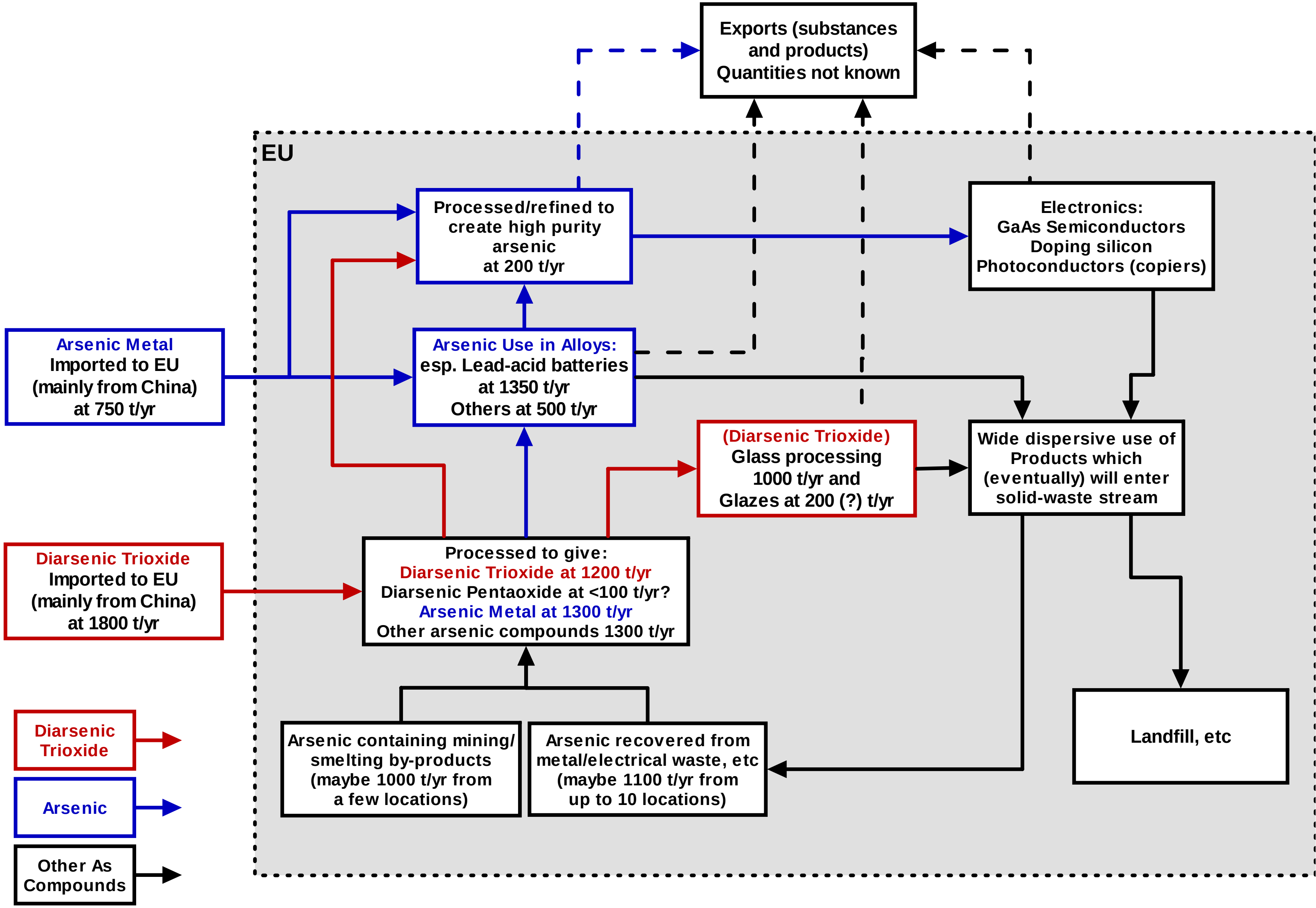

Figure 2.1: Material Flows for Diarsenic Trioxide

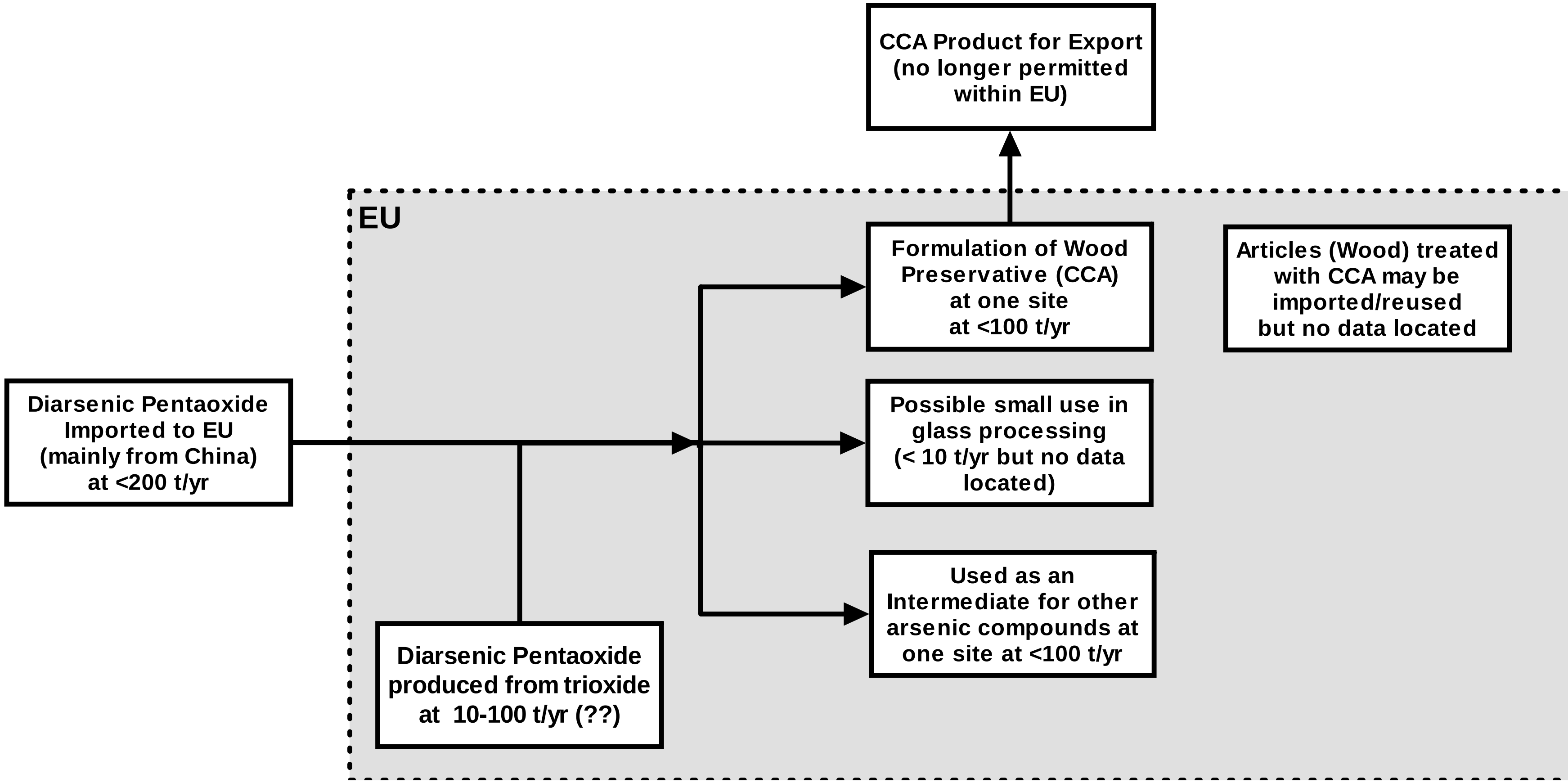

Figure 2.2: Material Flows for Diarsenic Pentaoxide

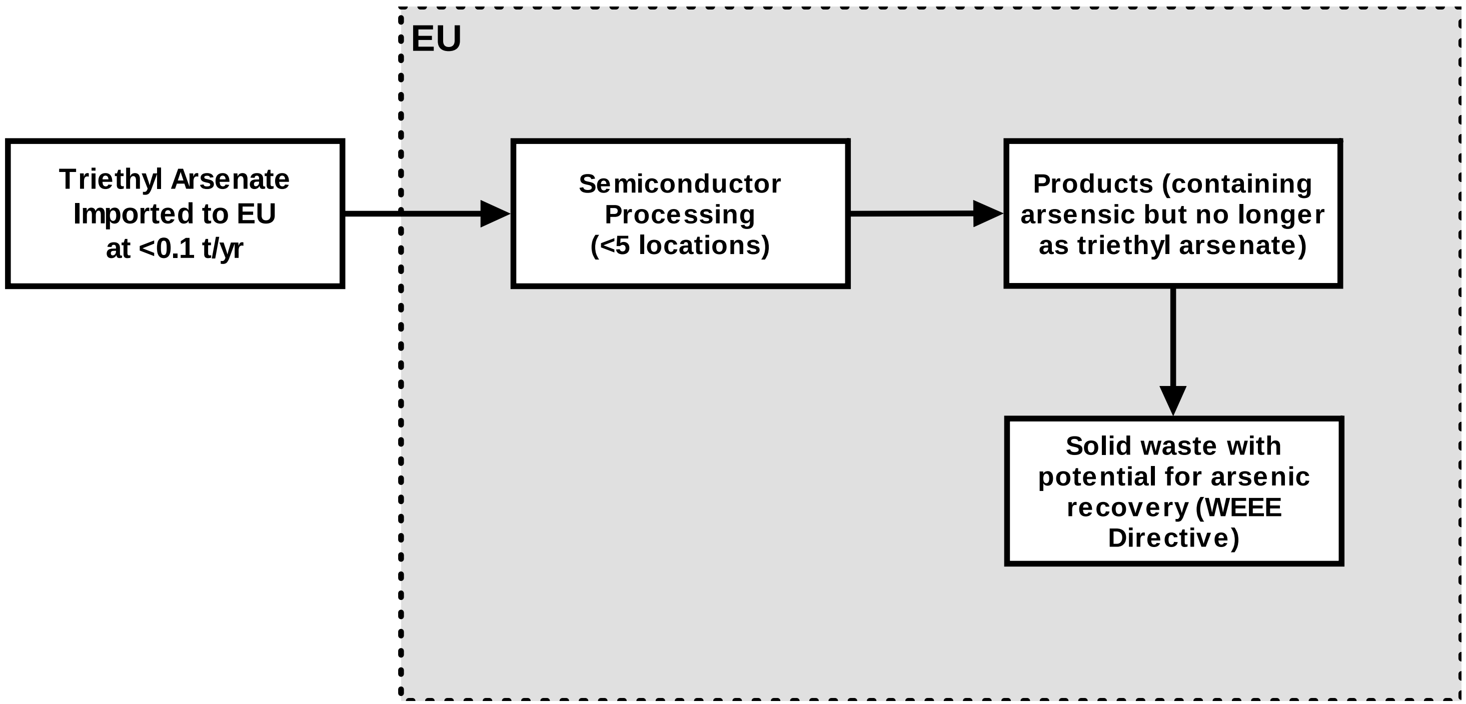

Figure 2.3: Material Flows for Triethyl Arsenate

2.3 Quantification of Releases from Uses

2.3.1 Overview

A summary of current uses and an overview of possible releases are presented in Table 2.6. Where there are uses with potential releases, the associated NACE code[23] is also provided.

Table 2.6: Potential Releases from Uses

Use	Compound	Stage of Use	Comment on Releases	NACE/CPA Code
Wood preservative (CCA)	Diarsenic Pentaoxide	Formulation	One site identified. Potential releases and occupational exposure	C20.20
		Product Use	Extent of import/use of articles (old treated wood) unknown - potential consumer exposure	?
		Recovery	Unlikely that attempts would be made to recover CCA from articles	n/a
Use in enamels	Diarsenic Trioxide	Processing	Little (if any) usage - potential occupational exposures	C20.30
		Product Use	Diarsenic trioxide not present in products	n/a
		Recovery	Unlikely that attempts would be made to recover diarsenic trioxide from articles	n/a
Glass processing	Diarsenic Trioxide and Pentaoxide (?)	Processing	Potential occupational exposures and releases	C23.1
		Product Use	Diarsenic trioxide (and pentaoxide) not present in products	n/a
		Recovery	Some special glass and lead crystal may be collected and re-processed in specialist facilities. Potential for occupational exposure	C23.1
Use in alloys (lead and copper)	Diarsenic Trioxide	Processing	Potential occupational exposures and releases	C23.1
		Product Use	Diarsenic trioxide not present in products	n/a
		Recovery	Alloys (especially lead) likely to be re-processed giving rise to potential occupational exposures	C23.1
Use in electronics	Diarsenic Trioxide and Triethyl Arsenate	Processing	Potential occupational exposures and releases	C26.11
		Product Use	Diarsenic trioxide and triethyl arsenate not present in products	n/a
		Recovery	Small amounts of gallium arsenide may be recovered from processing of electronic wastes	C26.11

[23] While the CPA classification is based on 'products by activity', there is another similar classification of 'economic activities' (NACE). Where classifications overlap, the CPA 2008 and the NACE (Revision 2) codes are now the same. CPA 2008, NACE (Revision 2) and PRODCOM (products) form an integrated EU classification system (see circa.europa.eu/irc/dsis/nacecpacon/info/data/en/index.htm).

As can be seen from Table 2.6, releases of the arsenates under study will tend to be associated with processing. As such, the arsenates are not associated with wide dispersive use but rather any releases will be under controlled working environments.

Further comment on the three major uses - glass, alloys and electronics - are presented below.

2.3.2 Glass Processing

The use of arsenic in the glass industry has long been recognised as requiring care for both the health of the workers and the surrounding environment. Although major glass production facilities within the EU do use significant quantities of arsenic, their emissions to the environment are less than for many other facilities (such as power stations and major steel works[24]). Nevertheless, there are several glass manufacturing facilities (across the EU) each with arsenic emissions in the range 0.1 to 0.7 t/yr.

More generally, glass manufacture is covered by IPPC[25] resulting in a requirement reduce emissions to the environment. This, in turn, led to the development of an *IPPC Reference Document on Best Available Techniques*[26] in 2001 which is now being updated (EC, 2008a). Interestingly, although there are several references to (di)arsenic trioxide, there are no references to the use of the pentaoxide.

As noted in Table 2.6, during product use consumers will not be exposed to the arsenates under study as they are not present (as the original compounds) in the glass. Furthermore, because the arsenic is bound into the glass matrix, the potential for migration and exposure (to arsenic) would be expected to be very low. By way of example, one detailed study (GTS, 2002) into elemental migration from glass (including lead crystal) in contact with food found that, in general, accelerated migration testing did not result in detectable levels of various elements (including arsenic).

Recycling & Reuse

Many items of special glass may be collected and, possibly, recycled. However, it is of note that the collection and physical sorting of different glasses is unlikely to lead to significant exposures to arsenic within the EU. By way of example, the traditional CRT (cathode ray tube) monitor/television comprises the high quality panel (screen) which may contain arsenic and the 'funnel' which is usually made of leaded glass (without arsenic). These two components are physically separated to create two recovery streams (Wood, 2008):

- the high quality panel glass which may be sent to specialist facilities (probably outside the EU) for re-use in electronic displays; and

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24 By inspection of the European Pollutant Emission Register (eper.eea.europa.eu/eper/default.asp).

25 Most recently codified as: **Directive 2008/1/EC of the European Parliament and of the Council of 15 January 2008 concerning integrated pollution prevention and control**, OJ L24, 29.01.02008, pp 8-29.

26 Sometimes referred to as a BREF.

- the leaded glass stream which may be used to recover both lead and glass.

On the other hand, although glass from cookers and stoves is likely to be collected and recovered, it cannot be simply added to a general glass recycling stream (since the special glass would have a much higher melting point). As such, the glass would either be (safely) disposed of to landfill[27] or would be recycled in specialist facilities (CPIV, 2009) in which occupational exposure to arsenic would be minimal.

The situation is similar for lead crystal. Although discarded items of lead crystal may enter the general glass recycling stream (through domestic glass collection schemes), they would separated before the recovered glass entered the furnace. As for the cooker/stove glass, the lead crystal would either be (safely) disposed of to landfill or would be recycled in specialist facilities (CPIV, 2009).

2.3.3 Alloys (Non-Ferrous)

As for glass manufacture, the production of non-ferrous alloys is also covered by IPPC and there is an associated BREF (EC, 2001). Although this contains many references to arsenic, these tend to be associated with the removal of arsenic impurities from other non-ferrous metals rather than with the intended addition of arsenic to alloys. As a result, many of the emissions of arsenic from metal industries (both ferrous and non-ferrous - as listed on the European Pollutant Emission Register) are associated with 'impurities' rather than with the intentional use of arsenic and its compounds.

However, the emissions of arsenic (and its compounds) associated with the production of alloys are likely to be no greater than those associated with the manufacturing sites listed in Table 1.10.

As noted in Table 2.6, during product use consumers will not be exposed to the arsenates under study as they are not present (as the original compounds) in alloys. Furthermore, because the arsenic is bound into an alloy, the potential for migration and exposure (to arsenic) would be expected to be very low[28].

Recycling and Reuse (of Batteries)

Within the EU, the vast majority (90% or more[29]) of car batteries are collected locally, taken to centralised (regional) facilities and separated into their main constituents (acid, plastic/rubber and lead). Consultation with battery recyclers indicates that lead-acid batteries are treated as a single input to secondary lead production. In other words, no attempt is made to segregate the lead from batteries according to the level of arsenic present.

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27 Although no specific scientific papers on leaching of arsenic from special glass in landfills have been located, it would be expected that the leaching rate would be low as the arsenic is bound into the glass matrix.

28 No relevant scientific papers on this issue have been located. By way of example, the key words "copper alloy" AND "arsenic" provide numerous references to Bronze Age jewellery with a few relating to analytical measurements.

29 See, for example, information from the International Lead Association (www.ila-lead.org/)

In some cases, the lead is then sent (along with lead recovered from other sources) to a smelter (either within the EU or overseas) in which the arsenic is treated as an impurity (along with copper, tin and antimony) and is separated from the recovered lead. On this basis, it would be expected that much of the arsenic present in the lead from the batteries would be recovered for re-use.

However, in other cases, the majority of arsenic is retained within the smelted lead for re-use mainly in batteries. Prior to dispatch, the composition of the recovered lead (containing, perhaps, 0.1% arsenic) is adjusted (where this could include adding additional arsenic metal) to the requirements of the battery manufacturers (mainly within the EU).

In any event, any occupational exposure would be limited to a limited number of smelters where the degree of exposure to arsenic would be strictly controlled.

2.3.4 Electronics

The electronics industry relies on extremely clean working environments in order to avoid contamination of micro/nano scale components during their production. This effectively results in the contained use of the high purity materials under strict supervision to ensure the required quality control in the production process. Furthermore, the potential for occupational exposure to arsenic during production of gallium arsenide and maintenance of associated facilities has been recognised for some time (see, for example, Edelman, 1990 and Flora, 2000).

With this in mind, it is difficult to envisage that there will be any significant (uncontrolled) releases of the arsenates under study from the use of up to 200 t/yr of high-purity arsenic (derived from diarsenic trioxide and/or arsenic metal) and the 0.1 t/yr of triethyl arsenate.

As for glass and alloys, during product use consumers will not be exposed to the arsenates under study as they are not present (as the original compounds) in electronic deveices. Furthermore, because the arsenic is bound into the semi-conductors, the potential for migration and exposure (to arsenic) would be expected to be very low.

Recycling and Reuse

Waste electrical and electronic equipment (WEEE) and restrictions on hazardous substances (RoHS) in such equipment are governed by the WEEE Directive (2002/96/EC) and the RoHS Directive (2002/95/EC). Currently, arsenic and its compounds (such as gallium arsenide) are not governed by the RoHS Directive. Furthermore, although many WEEE items are collected and treated in accordance with the Directive, perhaps 40% are not accounted for (EC, 2008b).

Although the quantities of arsenic compounds (such as gallium arsenide) used in electronics are relatively low, they may be present in minute quantities in numerous devices (such as mobile phones). The current level of recovery of arsenic from electronic equipment has not been determined. However, use of heated strong acids has enabled recovery rates of >99% for arsenic (and gallium) from semi-conductor manufacturing wastes (Chen, 2005).

2.3.5 Summary

Summaries of the releases and their (geographical) distribution by substance and use are presented in Annex 1.

3 INFORMATION ON ALTERNATIVES

3.1 Identification of Alternative Substances and Techniques

3.1.1 Overview

A range of uses for the arsenates under study have been identified. In all cases, the use of arsenic and its compounds is recognised as being of potential concern and, as a consequence, actions have been taken to limit exposure. In some cases, this has resulted in a move towards alternative substances though regulatory action and/or market pressures and/or voluntary action. However, not all the current uses will be covered by the REACH authorisation process and Table 3.1 provides an overview of the uses identified and whether they may be exempt from the procedures.

Table 3.1: Review of Uses and REACH Authorisation

Use	Substance	Exempt?	Comment
Wood preservative (CCA)	Diarsenic Pentaoxide	No	Although EU import/use banned (albeit with exemptions for ‘old’ treated wood), export permitted but formulation could require authorisation.
Use in enamels	Diarsenic Trioxide	No	Although arsenates not present in consumer products, the enamel process could require authorisation
Medicinal use	Diarsenic Trioxide	Yes	Covered by Medicinal Products Directive
Glass processing	Diarsenic Trioxide and Pentaoxide (?)	No	Although arsenates not present in consumer products, the glass processing could require authorisation
Testing steels	Diarsenic Trioxide	Yes?	The use of diarsenic trioxide to assess the corrosion resistance of steels may be considered as ‘scientific research and development’ and therefore exempt (under Article 56(3))
Use in alloys (lead and copper)	Diarsenic Trioxide	No	Although arsenates not present in consumer products, the alloy production/formulation could require authorisation
Use in electronics	Diarsenic Trioxide	No	Although arsenates not present in consumer products, the production of the required high-purity arsenic could require authorisation
Use in electronics	Triethyl Arsenate	No	Although arsenates not present in consumer products, the production process could require authorisation

In summary, it would appear that authorisation under REACH could be required for all the current identified uses - apart from medicinal use. However, the focus of interest for those uses requiring authorisation would be the production stage as the associated products (apart from CCA) do not contain the arsenates as substances.

A brief overview of alternatives with particular regard to the use of arsenic and its compounds in the various products is presented. Clearly, use of alternative products would reduce the demand for upstream use of the arsenates under study. It should be noted that, for the purposes of this study, the possible use of alternative arsenic compounds has not been given consideration.

3.1.2 Wood Preservative (CCA)

As discussed in Section 2.1.7, CCA has been banned and, as a consequence, a number of alternatives have been developed (USGS, 2008; US EPA, 2008; Barrie, undated). These include use of alternative construction materials (such as concrete) and alternative treatment chemicals including:

- alkaline copper quaternary;
- ammoniacal copper quaternary;
- copper azole;
- copper citrate;
- borates;
- cyproconazole;
- propiconazole;
- copper HDO (bis-(n-cyclohexyldiazeniumdioxy)-copper);
- copper dimethyidithiocarbamate;
- polymeric betaine; and
- acid copper chromate.

3.1.3 Use in Enamels and Glass Processing

Fining Agents

Diarsenic trioxide is used as a fining agent (to remove bubbles from the glass melt). The industry has advised (CPIV, 2008a) that arsenic acid may also be used for this purpose - albeit under different processing conditions (CPIV, 2009). Due to concerns over the use of arsenic compounds, there are various other established alternative substances including:

- sodium sulphate (used in lead crystal);
- antimony trioxide (used in lead crystal);
- sodium/potassium nitrates with antimony trioxides (used in special glasses); and
- cerium oxide.

Decolourising Agents

Diarsenic trioxide and, possibly, pentaoxide are used as decolourising agents in glass and enamels[30]. The industry has advised (CPIV, 2008a) that arsenic acid may also be used for this purpose - albeit under different processing conditions (CPIV, 2009). As with the fining agents, there are various established alternative non-arsenic substances including:

- antimony trioxide (decolourising agent for glass and an opacifier in ceramics and enamels);

[30] In enamels, diarsenic trioxide may also be used as an opacifier (i.e. to make material opaque) .

- selenium (particularly in lead crystal); and
- cerium oxide (in special glass and as an opacifier in enamels/ceramics).

Arsenic-Free Glass

It is of note that several major glass producers and computer companies are now promoting the use of arsenic-free glass in computer monitors.

3.1.4 Use in Alloys (Lead and Copper)

Battery Grids

As for ammunition (see below), various metals are added to improve the strength of the lead grids and other parameters (corrosion resistance, gassing minimisation, etc.) to ensure maintenance-free service. However the main types remain those based on lead-antimony and lead-calcium alloys. Both use arsenic but the levels are much higher in lead-antimony grids (<0.25%) than in those using lead-calcium alloys (<0.002%) (EV Battery Monitoring, 2007).

More generally, although there has been extensive research into battery grids (Bagshaw, 1995), use of other metals and heat treatment methods to improve the hardening of lead are still being explored (Engineers Edge, 2008; Key to Metals, 2008).

Ammunition

As detailed in Kelter (undated), a wide range of bullet hardness may be obtained by varying the relative amounts of lead, antimony and tin in bullet alloys - without using arsenic. As such, arsenic is not critical for cast bullets.

In relation to lead shot, the issue is not the use of arsenic but the use of the lead itself - particularly in wetlands (see, for example, CIC, 2008). This, of course, is not a new issue and a detailed review of alternatives was commissioned in 2004 (COWI, 2004). This review concluded that there were alternative materials for shot including steel, bismuth and tungsten (and associated alloys).

Other

As for battery grids and ammunition, varying mixtures of alloys in other uses (including cable sheathing and copper alloys) have been used to produce products of a similar performance to those using arsenic.

3.1.5 Use in Electronics

In response to Norway's proposals[31] to restrict/prohibit consumer articles containing, among a number of other hazardous substances, arsenic compounds, an industry stakeholder observed that every cell (mobile) phone contains gallium arsenide (EETimes, 2007).

This response highlights the key difference between electronics and the other current uses identified - in that major sectors of the electronics industry are built upon the intrinsic properties of arsenic rather than arsenic providing performance enhancing characteristics which could, in many cases, be derived from other means.

As such, there are no direct alternatives to gallium arsenide or to the doping of silicon with arsenic (for the specific applications for which arsenic is used) - and this has been confirmed by industry stakeholders during consultation. It is accepted, however, that there are similar materials which perform similar functions - so for example, and as previously noted (Section 2.1.13), phosphorous is also an n-type dopant like arsenic. As such, it is possible that technological advances using phosphorous (or other materials) as a dopant may result in a new generation of components for which arsenic is not required.

One example of the development of new technologies is to be found in copiers. As mentioned in Section 2.1.13, small amounts of high-purity arsenic are used in arsenic-selenium alloys for photoconductors. As an alternative, organic photoconductors (based on polymers) were developed (Narita *et al*, 1996) in competition with inorganic photoconductors.

3.2 Information on Alternatives

3.2.1 Human Health and Environmental Effects

Wood Preservative (CCA)

The function of wood preservatives is to discourage biological activity and, as a consequence, such substances may well cause human health and environmental effects. For this reason the use of such substances is regulated by the Biocidal Products Directive[32] (under Product Type 8: Wood Preservatives) to ensure that the continued presence of such substances on the market does not lead to undue risks to human health and the environment.

Use in Enamels and Glass Processing

Many of the alternatives to the use of arsenic in glass/enamel processing may be considered potentially harmful to human health and the environment. By way of

[31] The original proposal from May 2007 has now been slightly modified - as outlined on the SFT (Norwegian Pollution Control Authority) website: www.sft.no/artikkel____42883.aspx?cid=29292.

[32] **Directive 98/8/EC of the European Parliament and of the Council of 16 February 1998 concerning the placing of biocidal products on the market** (OJ L123, 24/4/1998, p1).

example, antimony trioxide is the subject of an (as yet unpublished) EU Risk Assessment Report under the Existing Substances Regulation[33]. However, such potential effects are taken into account in developing appropriate operational practices.

Use in Alloys (Lead and Copper)

Battery Grids

The assessment of the effects of alternatives requires consideration not only of the direct hazards but also of the indirect consequences. By way of example, replacement of a lead battery grid strengthened with arsenic by a different lead alloy in which arsenic is substituted by a less hazardous substance is likely to be seen as beneficial (i.e. less harmful). However, such changes may lead to other problems such as loss of performance which outweigh the benefits. With these points in mind, it might be expected that the use of lead-calcium alloys would be less harmful to human health and the environment - assuming that other characteristics could be maintained.

Ammunition

There are alternatives to lead shot including steel, bismuth and tungsten (and associated alloys). With this in mind, it would be expected that ammunition without lead and/or arsenic is likely to be less harmful to human health and the environment than lead bullets/shot containing arsenic.

Other Uses

As for battery grids and ammunition, it is likely that other alloys can be employed which use metals which are less harmful than arsenic (or use arsenic in lower concentrations). In the absence of other adverse effects (such as loss of performance), it would be expected that the overall health and environmental effects of alternative alloys using no (or less) arsenic would be less severe than those with arsenic.

Electronics

Whilst the use of alternatives would reduce potential consumer exposure (albeit very small) to arsenic and its compounds, other effects (for example, PBT properties of alternative organic materials) have not been determined.

3.2.2 Technical and Economical Feasibility and Availability

Wood Preservative (CCA)

Given the range and diversity of CCA alternatives, there is little doubt that alternatives are readily available with suitable technical and economic characteristics.

33 European Chemical Substances Information System: Diantimony Trioxide (CAS 1309-64-4).

Use in Enamels and Glass Processing

Given the range and diversity of alternatives to the use of arsenates, it might be expected that alternatives would be available with suitable technical and economic characteristics for most applications. Although it is accepted that there are alternative for most domestic (lead crystal) applications, the glass industry (CPIV, 2008a) has highlighted a number of applications where there are technical difficulties in replacing arsenic in special glass:

- pharmaceutical packaging glass which would require further investigation into the suitability of any alternative materials;
- although some glass-ceramic hobs (cooker tops) are now arsenic-free, producing clear glass hobs remains a difficult challenge;
- some optical filter glass relies on the intrinsic properties (i.e. optical wavelengths) of arsenic for which there are no alternatives; and
- use of alkali-free glass in opto-electronic applications.

Use in Alloys (Lead and Copper)

<u>Battery Grids</u>

Removal of arsenic from lead-acid batteries would probably result in a move from lead-antimony to lead-calcium (and other lead alloy) batteries. Although there may be some loss of technical performance in some applications, it is likely that the supply of lead-acid batteries could continue without arsenic.

<u>Ammunition</u>

Alternatives to lead/arsenic ammunition are available. Although there are no technical/economic implications for cast bullets, the issues are not so clear cut for lead shot.

<u>Other Uses</u>

Whilst there are probably alternatives to other uses of arsenic containing alloys, some uses would be harder to replace than others. By way of example, arsenic is particularly useful in providing resistance to seawater corrosion in brass (CDA, 2005).

Use in Electronics

As discussed above (Section 3.1.5), direct alternatives to the use of gallium arsenide and the doping of silicon with arsenic are not available. Rather, there would need to be further technological advances to develop new components for which arsenic is not required. However, there are alternatives available for arsenic-selenium photoconductors.

4. REFERENCES

van Alphen M (1998): **Paint Film Components**, (Australian) National Environmental Health Forum Monograph No 2 and available from enhealth.nphp.gov.au/council/pubs/pdf/paint.pdf

ATSDR (2007): **Toxicological Profile for Arsenic**, US Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry, August 2007.

BAC (2008): **Trends and Prospects in International Trade in Arsenic**, Market Survey prepared by Business Analytical Center dated April 2008.

Bagshaw NE (1994): *Lead Alloys: Past, Present and Future*, Journal of Power Sources, Vol 53, pp 25-30.

Barrie DE (undated): *Alternatives to Pressure Treated Wood*, available from www.noccawood.ca/docs/cca_wood_alternatives.html.

Bhattacharya P *et al* (2007): **Arsenic in Soil and Groundwater Environment**, Elsevier (ISBN: 978-0-444-51820-0).

Ceramic Materials Database (2003): *Arsenic Trioxide*, available from ceramic-materials.com/cermat/material/69.html.

CDA (2005): **The Brasses - Properties & Applications**, Copper Development Association Publication 117 and available from www.copperinfo.co.uk/alloys/homepage.shtml.

Chen YF *et al* (2005): *Recovery of High-Purity Gallium from Wafer Grinding Pastes*, Environmental Informatics Archives, Vol 3 (2005), pp 278-285 (and available from: www.iseis.org/eai/pdfstart.asp?no=05036).

CIC (2008): *Lead Shot: Significant New Developments with Relevance to all Hunters*, International Council for Game and Wildlife Conservation news item dated February 2008: www.cic-wildlife.org/index.php?id=324.

COWI (2004): **Advantages and Drawbacks of Restricting the Marketing and Use of Lead in Ammunition, Fishing Sinkers and Candle Wicks**, Final Report prepared for DG Enterprise, dated November 2004.

CPIV (2008): *What is Glass?*, Standing Committee of the European Glass Industry, available from www.cpivglass.be/about/about1.html.

CPIV (2008a): *CPIV Answer to the Questionnaire of Arsenic Uses in the Glass Industry*, detailed response to RPA consultation, dated October 2008.

CPIV (2009): *Responses to additional RPA questions*, dated January 2009.

Cullen WR (2008): **Is Arsenic an Aphrodisiac?** Cambridge, Royal Society of Chemistry (ISBN: 978-0-85404-363-7).

Davis JR (2001): **Copper and Copper Alloys**, Materials Park, Ohio, ASM International (ISBN: 978-0-87170-726-8).

Edelman P (1990): *Environmental and Workplace Contamination in the Semiconductor Industry: Implications for Future Health of the Workforce and Community*, Environmental Health Perspectives, Vol 86, pp 291-295.

EETimes (2007): *Norway's Arsenic Proposal Shakes Industry*, news article by Drew Wilson dated 19 November 2007.

Engineers Edge (2008): *Battery Cell Construction Antimony/Calcium/Selenium/Tin Alloying*, available from www.engineersedge.com/battery/antimony_calcium_selenium_tin_alloying.htm.

Environment Agency (2008): *Arsenic and its Compounds*, Environment Agency for England and Wales, available from www.environment-agency.gov.uk/?substance_id=13.

European Commission (2001): **Reference Document on Best Available Techniques in the Non Ferrous Metals Industries**, December 2001, available from eippcb.jrc.ec.europa.eu/pages/FActivities.htm.

European Commission (2008): **Question and Agreed Answers Concerning the Implementation of Directive 76/769/EEC on the Restrictions to Marketing and Use of Dangerous Substances**, Version 4, Enterprise and Industry Directorate-General, dated 4 June 2008.

European Commission (2008a): **Draft Reference Document on Best Available Techniques in the Glass Manufacturing Industry**, Draft of February 2008 (updating the previous BREF dated December 2001), available from ec.europa.eu/environment/ippc/brefs/gls_d1_0208.pdf.

European Commission (2008b): **Impact Assessment - accompanying Proposal for revisions to the WEEE Directive (COM(2008) 810)**, SEC(2008) 2933, dated 3 December 2008.

Eurostat (2008): **Statistical Classification of Products by Activity in the European Economic Community, 2008 Version**, as implemented by **Regulation (EC) No 451/2008** of 23 April 2008 and available from ec.europa.eu/eurostat/ramon....

EV Battery Monitoring (2007): *Electrode Materials* in the online **Battery Book 2,** available from: evbatterymonitoring.com/BatteryBook2/Electrode_Materials.htm

Flora SJS (200): *Possible Health Hazards Associated with the Use of Toxic Metals in Semiconductor Industries*, Journal of Occupational Health, Vol 42, pp 105-110.

Gray Environmental (2007): *Elemental Lead*, available from www.grayenvironmental.com/lead_background.htm.

GTS (2002): **Investigation of the Significant Factors in Elemental Migration from Glass in Contact with Food**, report by Glass Technology Services Ltd for the UK Food Standards Agency, dated September 2002.

IARC (2006): **Cobalt in Hard Metals and Cobalt Sulfate, Gallium Arsenide, Indium Phosphide and Vanadium Pentoxide**, WHO IARC Monograph Volume 86, available from monographs.iarc.fr/ENG/Monographs/vol86/index.php .

Kelter R (undated): *Cast Bullet Alloys & Alloy Maintenance*, Los Angeles Silhouette Club article from: www.lasc.us/CastBulletAlloy.htm.

Key to Metals (2008): *Heat Treating of Lead and Lead Alloys*, available from www.key-to-metals.com/Article88.htm.

Lublińska K *et al* (2008): *Characterization of Corrosion Degradation of Hydrogen Charged Stainless Steels***,** available from www.korozja.pl/html/JCM/JCM_08_033. pdf .

McGuinness (2008): *South America – Peru, Chimú*, available from www.mcguinnessonline.com/gold/chimu.htm.

Mehta Group (2008): *Arsenic Copper Rod*, available from www.mehta-group.com/arsenic-copper-rod.html.

Minnesota Department of Health (MDH) (2008): **Screening Evaluation of Heavy Metals in Inorganic Fertilizers**, MDH report dated February 2008.

M+W Zander (2006): *Glossary*, available from www.mw-zander.com/hld-home-glossary/hld-glossary-microelectronic-p.htm.

Narita M et al (1996): *Organic Photoconductors for Plain Paper Copiers*, Fuji Electric Journal, Vol 69-5. (This and many related articles via: www.fujielectrci.com/products).

Öko-Institut (2008): **Study on Hazardous Substances in Electrical and Electronic Equipment, Not Regulated by the RoHS Directive**, report for DG Environment dated 28 April 2008, available from hse-rohs.oeko.info/fileadmin/user_upload/ Documents/Project_description.pdf.

Peryea FJ (1998): *Historical Use of Lead Arsenate Insecticides, resulting in Soil Contamination and Implications for Soil Remediation*, Proceedings, 16th World Congress of Soil Science, Montpellier, France, 20-26 August 1998, available from soils.tfrec.wsu.edu/leadhistory.htm.

Puiggali M *et al* (1998): *Effect of Microstructure on Stress Corrosion Cracking of an Al-Zn-Mg-Cu Alloy*, Corrosion Science, April-May 1998, Vol 40 (4-5), pp805-819.

RPA (2005): **Environmental Risk Reduction Strategy and Analysis of Advantages and Drawbacks**, report for UK Government (Defra), dated October 2005 and available from www.rpaltd.co.uk/reports-by-sector.shtml

STDA (undated): *Applications for Selenium*, Selenium Tellurium Development Association website http://www.stda.net/se-te.htm

Subramanian V et al (2002): *Arsenic in Our Environment - A Critical Review* in **Environmental Hazards in South Asia**, edited by V. Subramanian. Capital Publishing Company, New Delhi (ISBN 8 1-85589-05-4) pp.189-214, available from eprints.ictp.it/351/01/Arsenic_in_Our_Environment.pdf.

UBCeram (2005): *Arsenic Oxide*, available from www.ceramics.mmat.ubc.ca/int/KCM.html#AArsenicO.

US EPA (2008): **Chromated Copper Arsenate (CCA)**, available from www.epa.gov/oppad001/reregistration/cca/.

USGS (2008): **Arsenic - 2007 Minerals Yearbok**, dated September 2008, U.S. Geological Survey, available from minerals.usgs.gov/minerals/pubs/commodity/arsenic.

Vanbellen F (2004): *Improved Metal Recovery from WEEE at Umicore Hoboken*, presentation to a WEEE Workshop by Umicore in Antwerp on 6th October 2004 and available from: www.preciousmetals.umicore.com/publications

Watson JW et al (1988): *Effect of Cathodic Charging on the Mechanical Properties of Aluminum*, Metallurgical Transactions A, September 1988, Vol 19(a) pp2299, abstract available from www.springerlink.com/content/2n24755911273566/.

Wood L (2008): *Toxic Televisions - A New Approach to CRT Recycling*, Environmentalist, Issue 61, July 2008.

World Bank Group (1998): **Arsenic** (Pollution Prevention and Abatement Handbook), dated July 1998 and available from www.ifc.org/ifcext/sustainability.nsf/AttachmentsByTitle/p_ppah_pguiArsenic/$FILE/HandbookArsenic.pdf

Zieliński A & Serbiński W (undated): *Relation Between Steel Microstructure and its Properties in Inert and Aggressive Environments*, available from www.pg.gda.pl/mech/kim/AMS/012005/ams01200504.pdf.

ANNEX 1

INFORMATION ON MANUFACTURE, IMPORTS, EXPORTS, USES AND RELEASES IN TABULAR FORM

Table 1: Overview on tasks related to work package 1 — Diarsenic Trioxide

Manufacture, trade and formation	Process (narrative description)	Locations (number of M sites; spatial distribution) [2]	Tonnage manufactured, imported, exported or formed	Releases to working environment [3]	Releases to environment (t/y released to air, wastewater or to waste)
Manufacture EU Process A	Produced from mining/ smelting byproducts	Probably produced at 2 or 3 sites in EU	1000 t/yr	low?	perhaps a few tonnes
Manufacture EU Process B	Reclaimed from metal/ electrical waste	Probably produced at 5 to 10 sites in EU	1100 t/yr	low?	perhaps a few tonnes
Total Manufacture		**Produced at several sites in EU**	**2100 t/yr (stable?)**	**low?**	**several tonnes?**
Import subst. on its own			1800 t/yr		
Import subst. in preparations			0 t/yr		
Import subst. in articles[2]			0 t/yr		
Import into EU (total)			**1800 t/yr (stable?)**		
Export subst. on its own			not known		
Export subst. in preparations			0 t/yr		
Export subst. in articles[1]			not known (but trioxide not present in articles)		
Export from EU (total)			**not known**		
Global manufacture			**30000 t/yr (mainly China with stable production)**		
Unintentional formation during incineration (EU)				0	0
Unintentional formation in processes (EU)				0	0
Unintentional formation by transformation/degradation (EU)				0	0
Total unintentional formation (EU)				**0 t/yr**	**0 t/yr**

1. A list of article types in which the substance is included shall be provided in addition.
2. In quantitative or geographical terms exact specifications are only required if the number of sites is low. If there are many sites a semi-quantitative or qualitative description of the manufacturing structure and spatial distribution of manufacturing sites (e.g. in which Member States, regions, etc.) may suffice.
3. In case a quantification of releases is not possible a qualitative description of the emission situation at the workplace(s) shall be given and a semi-quantitative estimate of the exposure situation provided (e.g. no exposure – very high exp.).

Table 2: Overview on tasks related to work package 2 — Diarsenic Trioxide

Uses	Use Process (description: narrative and by use descriptor system)	Amount used (t/y)	Number of sites of use [1] (#)	Spatial distribution of emission sites [1]	Releases to working environment [3]	Releases to environment (t/y released to air, wastewater or to waste)
Formulation						
Formulation 1						
∑ Formulation		**0 t/yr**	**0**	**n/a**	**0 t/yr**	**0 t/yr**
End uses						
End Use 1	Used to produce arsenic metal	1300 t/yr	5 to 10	Western Europe	low?	possibly a few tonnes
End Use 2	Used to in glass and enamel processing	1200 (?) t/yr	mass production: few sites	Western Europe	low?	possibly a few tonnes
			some small producers (eg for lead crystal)	Throughout EU	possibly significant	possibly significant
End Use 3	Used to produce diarsenic pentoxide	< 100 t/yr	2 or 3 (?)	Western Europe	probably negligible	probably negligible
End Use 4	Used to produce other arsenic compunds	1300 t/yr (uncertain estimate)	2 or 3 (?)	Western Europe	low?	possibly a few tonnes
∑ End Uses		**3900 t/yr (stable?)**	**Few large and many small**	**Few large sites in Western Europe**	**possibly significant**	**several tonnes?**
Consumer use						
Substance in articles [2] *Alloys & semi-conductors also use arsenic metal imports (at 750 t/yr)*	As alloy in lead-acid batteries	1350 t/yr	widespread	widespread		n/a – articles do not contain diarsenic trioxide
	Glass/Enamel articles	1200 t/yr	widespread	widespread		
	As other alloys (eg copper)	500 t/yr	not known	probably widespread		
	Semi-conductors, etc	200 t/yr	widespread	widespread		
Substance in preparations	n/a	0 t/yr				
∑ consumer use of subst. in articles and preparations		**3250 t/yr (stable?)**				**n/a – products do not contain diarsenic trioxide**

1 In quantitative or geographical terms exact specifications are only required if the number of sites is low. If there are many sites a semi-quantitative or qualitative description of the use structure and spatial distribution of sites of release (e.g. in which Member States, regions, etc.) may suffice.

2 A list of article types with the substance included and used by consumers shall be provided as well.

3 In case a quantification of releases is not possible a qualitative description of the emission situation at the workplace(s) shall be given and a semi-quantitative estimate of the exposure situation provided (e.g. no exposure – very high exp.).

Table 3: Overview of quantitative information requested at Member State level — Diarsenic Trioxide

YEAR 2007 (est)	Manufacturing (t/y)	Manufacturing # sites	Formulation (t/y)	Formulation # sites	Use 1/3/4 (t/y)	Use 1/3/4 # sites	Use 2 (t/y)	Use 2 # sites
Member state								
Austria								
Belgium								
…								
Total	2100 t/yr	5 to 10	0	n/a	2700 t/yr	5 to 10	1200 t/yr	Numerous (?)

YEAR 2008 (est)	Manufacturing (t/y)	Manufacturing # sites	Formulation (t/y)	Formulation # sites	Use 1/3/4 (t/y)	Use 1/3/4 # sites	Use 2 (t/y)	Use 2 # sites
Member state								
Austria								
Belgium								
…								
Total	2100 t/yr	5 to 10	0	n/a	2700 t/yr	5 to 10	1200 t/yr	Numerous (?)

Table 1: Overview on tasks related to work package 1 — Diarsenic Pentaoxide

Manufacture, trade and formation	Process (narrative description)	Locations (number of M sites; spatial distribution) [2]	Tonnage manufactured, imported, exported or formed	Releases to working environment [3]	Releases to environment (t/y released to air, wastewater or to waste)
Manufacture EU Process A	Diarsenic Pentaoxide produced from the trioxide	Probably produced at 2 or 3 sites in EU	<100 t/yr	small	small
Manufacture EU Process B					
Total Manufacture		**Probably produced at 2 or 3 sites in EU**	**<100 t/yr– probable downward trend (see Table 2)**	**small**	**small**
Import subst. on its own			< 200 t/yr		
Import subst. in preparations					
Import subst. in articles[2]	**in'old' treated wood**		**not known**		
Import into EU (total)			**< 200 t/yr (?) – probable downward trend (see Table 2)**		
Export subst. on its own			not known (but probably negligible)		
Export subst. in preparations			< 100 t/yr		
Export subst. in articles[1]			0 t/yr		
Export from EU (total)			**<100 t/yr**		
Global manufacture			**4000 t/yr (mainly China – trend not known)**		
Unintentional formation during incineration (EU)				0	0
Unintentional formation in processes (EU)				0	0
Unintentional formation by transformation/degradation (EU)				0	0
Total unintentional formation (EU)				**0 t/yr**	**0 t/yr**

1. A list of article types in which the substance is included shall be provided in addition.

2. In quantitative or geographical terms exact specifications are only required if the number of sites is low. If there are many sites a semi-quantitative or qualitative description of the manufacturing structure and spatial distribution of manufacturing sites (e.g. in which Member States, regions, etc.) may suffice.

3. In case a quantification of releases is not possible a qualitative description of the emission situation at the workplace(s) shall be given and a semi-quantitative estimate of the exposure situation provided (e.g. no exposure – very high exp.).

Table 2: Overview on tasks related to work package 2 — Diarsenic Pentaoxide

Uses	Use Process (description: narrative and by use descriptor system)	Amount used (t/y)	Number of sites of use [1] (#)	Spatial distribution of emission sites [1]	Releases to working environment [3]	Releases to environment (t/y released to air, wastewater or to waste)
Formulation						
Formulation 1	Formulation of CCA (wood preservative)	<100 t/yr	1	Nordic country	probably small	probably small
Formulation ***n***						
∑ Formulation		**<100 t/yr (CCA use is banned within EU so probable downward trend)**	**1**	**Nordic country**	**probably small**	**probably small**
End uses						
End Use 1	Intermediate for other arsenic compounds	<100 t/yr	1	Western Europe	probably negligible	probably negligible
End Use 2	Possible use in glass and/or glazes	<10 t/yr	probably few	not known	probably negligible	probably negligible
End Use ***n***						
∑ End Uses		**<110 t/yr – probable downward trend**	**probably few**	**not known**	**probably negligible**	**probably negligible**
Consumer use						
Substance in articles [2]	Product use not known but may include glass/enamel	100 t/yr	widespread	widespread		n/a – products do not contain diarsenic pentaoxide
diito	'Old' wood treated with CCA	not known	not known	not known		not known
Substance in preparations	CCA for export	n/a				
∑ consumer use of subst. in articles and preparations		**100 t/yr (?) – probable downward trend**				**not known**

1 In quantitative or geographical terms exact specifications are only required if the number of sites is low. If there are many sites a semi-quantitative or qualitative description of the use structure and spatial distribution of sites of release (e.g. in which Member States, regions, etc.) may suffice.

2 A list of article types with the substance included and used by consumers shall be provided as well.

3 In case a quantification of releases is not possible a qualitative description of the emission situation at the workplace(s) shall be given and a semi-quantitative estimate of the exposure situation provided (e.g. no exposure – very high exp.).

Table 3: Overview of quantitative information requested at Member State level — Diarsenic Pentaoxide

YEAR 2007 (est)	Manufacturing (t/y)	Manufacturing # sites	Formulation (t/y)	Formulation # sites	Use 1 (t/y)	Use 1 # sites	Use 2 (t/y)	Use 2 # sites
Member state								
Austria								
Belgium								
…								
Total	<100 t/yr	2 or 3 ?	<100 t/yr	1	<100 t/yr	1	<10 t/yr	probably few

YEAR 2008 (est)	Manufacturing (t/y)	Manufacturing # sites	Formulation (t/y)	Formulation # sites	Use 1 (t/y)	Use 1 # sites	Use 2 (t/y)	Use 2 # sites
Member state								
Austria								
Belgium								
…								
Total	<100 t/yr	2 or 3 ?	<100 t/yr	1	<100 t/yr	1	<10 t/yr	probably few

Table 1: Overview on tasks related to work package 1 — Triethyl Arsenate

Manufacture, trade and formation	Process (narrative description)	Locations (number of M sites; spatial distribution) [2]	Tonnage manufactured, imported, exported or formed	Releases to working environment [3]	Releases to environment (t/y released to air, wastewater or to waste)
Manufacture EU Process A					
Manufacture EU Process B					
Total Manufacture		**n/a**	**0 t/yr**	**0 t/yr**	**0 t/yr**
Import subst. on its own			<0.1 t/yr		
Import subst. in preparations			0		
Import subst. in articles[2]			n/a		
Import into EU (total)			**<0.1 t/yr (trend not known)**		
Export subst. on its own			0		
Export subst. in preparations			0		
Export subst. in articles[1]			n/a		
Export from EU (total)			**0 t/yr**		
Global manufacture			**<1 t/yr (trend not known)**		
Unintentional formation during incineration (EU)	n/a			0	0
Unintentional formation in processes (EU)	n/a			0	0
Unintentional formation by transformation/degradation (EU)	n/a			0	0
Total unintentional formation (EU)				**0 t/yr**	**0 t/yr**

1. A list of article types in which the substance is included shall be provided in addition.

2. In quantitative or geographical terms exact specifications are only required if the number of sites is low. If there are many sites a semi-quantitative or qualitative description of the manufacturing structure and spatial distribution of manufacturing sites (e.g. in which Member States, regions, etc.) may suffice.

3. In case a quantification of releases is not possible a qualitative description of the emission situation at the workplace(s) shall be given and a semi-quantitative estimate of the exposure situation provided (e.g. no exposure – very high exp.).

Table 2: Overview on tasks related to work package 2

Triethyl Arsenate

Uses	Use Process (description: narrative and by use descriptor system)	Amount used (t/y)	Number of sites of use [1] (#)	Spatial distribution of emission sites [1]	Releases to working environment [3]	Releases to environment (t/y released to air, wastewater or to waste)
Formulation						
Formulation 1						
Formulation 2						
……..						
Formulation ***n***						
∑ Formulation		**0 t/yr**	**0**	**n/a**	**0 t/yr**	**0 t/yr**
End uses						
End Use 1	Semi-conductor processing	<0.1 t/yr	<5	not known	negligible	negligible
End Use 2						
∑ End Uses		**<0.1 t/yr (trend not known)**	**<5**	**not known**	**negligible**	**negligible**
Consumer use						
Substance in articles [2]	Electronic products (precise products not known)	<0.1 t/yr	numerous ?	wide dispersive use?		n/a – products do not contain triethylarsenate
Substance in preparations	n/a	0				
∑ consumer use of subst. in articles and preparations		**<0.1 t/yr (trend not known)**				**n/a – products do not contain triethylarsenate**

1 In quantitative or geographical terms exact specifications are only required if the number of sites is low. If there are many sites a semi-quantitative or qualitative description of the use structure and spatial distribution of sites of release (e.g. in which Member States, regions, etc.) may suffice.

2 A list of article types with the substance included and used by consumers shall be provided as well.

3 In case a quantification of releases is not possible a qualitative description of the emission situation at the workplace(s) shall be given and a semi-quantitative estimate of the exposure situation provided (e.g. no exposure – very high exp.).

Table 3: Overview of quantitative information requested at Member State level — Triethyl Arsenate

YEAR 2007 (est)	Manufacturing (t/y)	Manufacturing # sites	Formulation (t/y)	Formulation # sites	Use 1 (t/y)	Use 1 # sites	Use n (t/y)	Use n # sites
Member state								
Austria								
Belgium								
…								
Total	0	n/a	0	n/a	<0.1 t/yr	<5		

YEAR 2008 (est)	Manufacturing (t/y)	Manufacturing # sites	Formulation (t/y)	Formulation # sites	Use 1 (t/y)	Use 1 # sites	Use n (t/y)	Use n # sites
Member state								
Austria								
Belgium								
…								
Total	0	n/a	0	n/a	<0.1 t/yr	<5		