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EXPLORATORY REPORT ANTIMONY AND
ANTIMONY COMPOUNDS .

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Mailing list exploratory report Antimony and Antimony compounds

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SUMMARY

This report contains general information on Antimony and antimony compounds concerning the existing standards, emissions, exposure levels and effect levels. The document is to be considered as a start for the national discussion during an exploratory meeting on integrated criteria documents.

Antimony is not produced in the Netherlands, but antimony is found in various ores processed in the Netherlands. Antimony is applied as a fire retardant, in alloys and pigments, as a catalyst and in light bulbs. Many antimony-emitting sources are known but the emission figures are often lacking. The most important known sources of emissions to air are light bulb production and pigment industry, and possibly the burning of fire retardants, whereas hunting, shooting and sport fishing contribute significantly to emissions to soil and water.

Concentration levels of antimony in the environment are, relative to other heavy metals, scarcely available.

It was concluded that, with regard to the carcinogenic effect of antimony, it seems as yet justified to use at threshold extrapolation method for risk assessment. The risk of antimony in food and drinking water for humans is small (if present at all), considering the difference between the tolerable daily intake of $0.86 \mu\text{g} \cdot \text{kg}^{-1}$ bw and the actual estimated daily intake of 0.17 to $0.33 \mu\text{g} \cdot \text{kg}^{-1}$ bw. The risk of current antimony concentrations in air for humans is also considered small. An average exposure concentration in urban areas of $23 \text{ ng Sb} \cdot \text{m}^{-3}$ has been reported, which is below the tentative maximum tolerable concentration of $3200 \text{ ng Sb} \cdot \text{m}^{-3}$. These exposure levels date from two decades ago and may be lower today.

For aquatic organisms a tentative maximum tolerable concentration of $3 \mu\text{g} \cdot \text{l}^{-1}$ was derived (as "dissolved" Sb; $< 0.45 \mu\text{m}$). The average antimony concentrations (total Sb) in Dutch surface waters are usually below $1 \mu\text{g} \cdot \text{l}^{-1}$ with peak levels of $3 \mu\text{g} \cdot \text{l}^{-1}$. The risk of antimony to aquatic organisms is within acceptable limits for Dutch surface waters, possibly localities in the vicinity of waste water outlets excepted. Although there are no data to derive a maximum tolerable concentration in soil the current antimony levels are considered not to present a risk to soil organisms in general. A point that may need attention is the contamination of the environment as a result from shooting, hunting and sport fishing.

It is recommended to determine antimony concentrations near some point sources in surfacewater and to evaluate the effects of shooting, hunting and sport fishing in combination with the effects of other contaminants such as lead.

1. INTRODUCTION

This scoping report is part of the preparation for drawing up the integrated criteria document antimony and antimony compounds. The objective of this report is to bring the knowledge of the participants in the scoping meeting to the same level, and to put forward points for discussion and decision-making as to the contents of the integrated criteria document.

It should be emphasized that the present report does not aim to be exhaustive: the actual standards and recommendations, the sources and exposure levels in the Netherlands are merely outlined, whereas on the other hand the principal effects and indicative (no) effect levels are described. Subsequently, problems will be pointed out and a proposal made as to the contents of the integrated criteria document antimony and antimony compounds to be drawn up.

2. ACTUAL STANDARDS AND GUIDELINES

Table 2.1 gives an overview of the actual standards and guidelines in force in the Netherlands (VROM, 1991). Antimony is considered a "black-list" substance for the environmental compartment soil. Furthermore antimony is considered a "attention substance".

Table 2.1 Actual standards and guidelines for antimony in the environment in the Netherlands

Environmental compartment/ type of standard	Concentration	Reference
AIR		
* indoor air (work space) MAC antimony	0.5 mg.m ⁻³	MAC (1989)
FOOD AND DRINKING WATER		
* drinking water	10 µg.l ⁻¹ (Cat I)	WLB (1984)
OTHER		
* chemical waste antimony and antimony compounds	50 mg.kg ⁻¹ d.w.	BACA (1991)

d.w. : dry weight

3. APPLICATIONS, SOURCES AND EMISSIONS

3.1 PRODUCTION

In the Netherlands antimony oxide (Sb_2O_3) is not produced from ore. Antimony is found in various processed ores in the Netherlands: phosphate ores contain on average 1 mg antimony per kg ore (depending on origin) and zinc ores 50-1100 mg Sb. Iron and tin ores contain small amounts of antimony; precise data are not known. Coal contains on average 1 mg antimony per kg coal (depending on the origin of the coal) (Meij, 1989).

The world production of Sb comprises about 60,000 tonnes. This production takes place in a large number of countries all over the world, for example: Bolivia, Canada, South Africa, Turkey, (former) Yugoslavia, Thailand, Australia, China and the former Soviet Union.

In table 3.1 data are presented as registered by the Central Bureau of Statistics (CBS) for 1988 and 1989.

Table 3.1 CBS import and export data on antimony and antimony compounds (partly undefined) for 1988 and 1989 (in tonnes)

Description	1988			1989		
	import	export	nett im- port	import	export	nett im- port
antimoniates	135	8	127	128	15	113
antimony (III) oxide	1805	467	1438	1794	527	1267
Unpurified antimony	80	45	35	80	6	74
Other compounds	31	none	31	2	3	-1

In table 3.2 the results from a survey sent to various companies (Ewijk et al., 1990) are compared with CBS-data on the import of Sb and Sb compounds during 1988.

Table 3.2 Imported Sb in 1988 according to the companies surveyed and the CBS

Import	Survey (tonnes Sb)	CBS-1988 (tonnes Sb)
Antimoniates (as Sb) ¹	45	82
Antimony oxide (as Sb) ²	1073	1507
Undefined antimony (Sb)	96	80
Other compounds (as Sb) ³	6	12
TOTAL (as Sb)	1220	1681

¹ Assuming 100% antimoniates of which 60% is Sb

² Assuming 100% Sb_2O_3 of which 83.5% is Sb

³ Assuming that these Sb compounds consist of 40% Sb

The difference in import figures as depicted in table 3.2 is mainly due to the difference in the data reported for the import of antimony (III) oxide, probably resulting from the fact that the Dutch suppliers named in the survey had not been sent a questionnaire. In total 112 tonnes antimony had been purchased by Dutch companies not included in the survey. Therefore the total antimony import from the companies surveyed probably amounts to 1332 tonnes. If the CBS import data are assumed to be correct, the survey accounts for 79% (direct and indirect) of the total Sb import into the Netherlands.

Export data are summarized as follows: in 1988 727 tonnes Sb were exported by the companies surveyed. This export comprises data both from companies importing only Sb and Sb compounds and exporting it again, and from companies exporting semi-manufactured products containing Sb (e.g. pigments) or products. The CBS registered an export of 390 tonnes Sb for 1988 and 456 tonnes for 1989. Antimony in products and probably also semimanufactured products are not accounted for by the CBS.

Every year 375 tonnes Sb (of which 293 tonnes are purchased in the Netherlands) present in metal alloys, usually lead, are recycled. These alloys are recycled into such substances as cable lead, soft and hard lead and battery paste. Yearly 297 tonnes Sb are exported in recycled alloys. The remaining 78 tonnes Sb are brought onto the Dutch market.

3.2 APPLICATIONS

Table 3.3 presents the amount of Sb used yearly by the companies surveyed in the Netherlands by Ewijk et al. (1990). The total annual use reflected in the survey will always be lower than the actual use because not all the suppliers in the Netherlands were approached for the survey.

Table 3.3 Summary of the yearly use of Sb in the various applications in the Netherlands according to the survey described by Ewijk et al. (1990)

Application	Sb use (tonne) Survey	Remarks
Catalyst:		
- Polyester	67	
- Ammonia manufacture	0.056	concerns one order
Alloys	110	
Pigments	172	
Fire retardant:		
- Synthetics	639	
- Textiles	17	3-9 tonnes/company
Light bulbs:		
- Flu-powder	< 1	used in fluorescent lighting
- Glass	1-100	not for fluorescent lighting
Catalyst in cobalt cementation	1.3	
Fireworks	0.007	concerns one company
Veterinary pharmacy	0.06	concerns one company

The most important application of antimony oxide, along with organobromine and organochlorine compounds, is that of fire retardant. Fire retardants are additive

or reactive. An additive fire retardant is mixed with the material to be fireproofed, for instance, textiles. Antimony oxide as additive is always used in combination with organohalogenic compounds.

Applications for fireproofing textiles are found, for example, in industrial clothing (fire brigade, police, laboratory), interiors (carpeting, curtains, furniture), industry (insulation material, air and oil filters for motors and sailcloth), industrial fibres (canvas, nonwovens and towlines) and the army (camouflage fabrics and radar-reflective and absorptive fibres). Clothing has a 30-40% fire-retardant content (Klingenberg, 1988). Every year 17 tonnes Sb is used in the Netherlands (according to the survey; Ewijk et al., 1990) for fireproofing textiles.

Besides for clothing fireproofing is also applied to synthetics. According to the companies surveyed, 639 tonnes of Sb are used annually in the Netherlands for fireproofing synthetics. The percentage fire retardant in a synthetic varies per application and material. Table 3.4 presents an overview of the different amounts of fire retardant applied to synthetics, with the percentage of Sb_2O_3 in the fire retardant included when known.

Every year 13.5 tonnes Sb is imported in the form of antimony blocks. These blocks, consisting of 100% Sb, are mainly used in metallurgy. Antimony contributes the hardness, mechanical strength, corrosion-resistance and better conduction to alloys. Antimony alloys easily with lead, tin and iron. Table 3.5 shows a large number of alloy applications in which Sb is found.

Table 3.4 Percentages of fire retardant applied to synthetics, including the Sb_2O_3 percentage in the fire retardant (Nametz, 1984; Klingenberg, 1988; Ewijk et al., 1990)

Synthetic	Fire retardant (%)	Sb_2O_3 in fire retardant (%)
ABS (Acrylonitril Butadiene Styrene)	10-20 (max: 35)	12-25
PET (PolyEthylene Terephthalate)	unknown	5.7
PP (PolyPropene)	≈ 3%	unknown
PS (PolyStyrene)	10-15	25-40

Table 3.5 Percentages of Sb in various iron, tin and lead alloy applications (Ewijk et al., 1990; PBNA, 19??; Van Bon and Boersema, 1988)

Alloy application	Sb (%)
Cable (iron), pewter, lead solder, battery plates, battery paste, lead pipe, hard lead for grates, sheet metal, axles, lead shot (ammunition), cable casing	0 - 5
Lead blocks, lead shot (sinkers)	5 - 10
White metal (tin), sulphuric acid-resistant lead, hard lead for stench-traps, bearing metal/lettering metal, hard lead for grenades	10 - 20

Most of the antimony alloy applications are found in the lead used for batteries and for lead shot. Sheet metal is much used as well. Every year about 110 tonnes Sb are incorporated into metal alloys.

Various inorganic pigments consist of Sb compounds or mixtures of substances containing Sb compounds. Export of Sb-containing pigments is an important contributor to sales (126 tonnes of Sb in the Netherlands). The yearly contribution of Sb supplied, processed in or destined for manufacture of pigments and glazes is about 172 tonnes.

Pigments and pigment dispersions with Sb are applied in paints, synthetics, glass enamels and glazes. A ceramic pigment (with about 20% Sb) is added to glass enamels and glazes in average quantities of about 10%. One Dutch pigment manufacturer uses Sb in the post-treatment: the Sb deposits in this way on to the pigment and affords protection against penetration from outside [Bruggeman, pers. comm.]. Antimony pigment is applied as pigment in rubber. In a study on coloured rubber in shoes, 84 mg Sb per kg was found, which contrasts with 10 mg Sb per kg found in other rubber (RIVM, 1990).

In the petrochemical industry Sb is added in the Fluid Catalytic Cracking (FCC) process; several hundred ppm Sb (to a maximum of 1500 ppm) are added. The Sb deposits onto the FCC catalyst.

During polyester manufacture Sb, in the form of Sb_2O_3 , is added to the basic chemicals as catalyst. It is certainly applied as catalyst in the polycondensation reaction in the preparation of polyethylene terephthalate (PET) at 1 kg Sb_2O_3 for 2,600 kg PET (0.04% Sb_2O_3). During the polymerisation reaction Sb is absorbed into the polyester at a concentration of 200-400 mg Sb per kg polyester. The survey shows a yearly use in the Netherlands of 67 tonnes Sb as catalyst in the polymerisation reaction.

In the production of zinc from zinc-ore concentrates potassium antimonyl tartrate ($C_4H_4KO_7Sb$) is applied as catalyst, purified from cobalt. The Sb from $C_4H_4KO_7Sb$ is deposited by this cobalt cementation. The cobalt cement is then sold. Every year 1.3 tonnes Sb is used in cobalt cementation as $C_4H_4KO_7Sb$.

Antimony is incorporated into the Flu powder applied to the inside surface of fluorescent light bulbs. Flu powder contains 0.45% Sb. Of the approximately 2 tonnes of Flu powder applied to fluorescent light bulbs yearly in the Netherlands less than one tonne Sb is brought onto the market. Antimony is also used in the glass for other light bulbs. In the Netherlands this amounts yearly to several thousand tonnes of glass containing several dozens of tonnes Sb. It is not known how much is exported after manufacture.

3.3 EMISSIONS AND WASTE

Textile industry

Emissions arise from leaching Sb out of polyester fibres and in fireproofing textiles.

In the manufacture of polyester Sb_2O_3 is used as a catalyst. It is in the processing of the fibres (textile finishing processes) that Sb can leach out (Tebodin, 1988). These processes are washing, texturizing (loosening the yarns with a high pressure water spray) and high temperature dyeing. Taking an yearly turnover of 8,700 tonnes of polyester fibre in the textile finishing industry, and assuming a discharge of 200-400 mg Sb per kg polyester and a leaching loss of 10-35% from wet finishing processes, 460 kg Sb (with an uncertainty range of 200-950 kg per year) is discharged into the sewerage system by the textile finishing companies (Tebodin, 1988).

In fireproofing textiles antimony is discharged into the waste water by drawing off Sb-containing production kettles and baths to the sewer, rinsing equipment, rinsing after spillage or leaks and washing out the treated textile. Estimated is that about 400 kg Sb per year enters the waste water, representing a loss of a maximum of 1% of the Sb_2O_3 used (Tebodin, 1988).

Synthetics industry

In the synthetics industry 500 tonnes of Sb is used yearly in the production of polyesters: 38 tonnes as catalyst during the polymerization reaction and 462 tonnes as fire retardant. In the survey one company indicated it had discharged 150 kg Sb in 1988 and 110 kg Sb in 1989. The emission to the air is negligible.

Metallurgical industry

Antimony emissions in the metallurgical industry arise, for example, through secondary lead extraction from lead alloys. Batteries are used for secondary lead extraction: the lead is recycled; during this process Sb is released from the batteries. One company processes about 95% of all the old batteries turned in the Netherlands every year. The company estimated that 60 kg Sb per year was discharged into the sewerage system, with the prognosis for 1990 set at 12 kg Sb (Bertels, pers. comm.).

Cable roasting furnaces

Cable roasting furnaces burn underground cables. These cables are coated with impregnated paper and jute which cannot (yet) be removed by stripping or shredding. Emissions from cable roasting furnaces are highly varied: seven measurements at three roasting furnaces showed levels of 1 and 31 mg Sb per kg cable, on the average 5.6 mg kg^{-1} (Tauw, 1988). Considering that about 13,000 tonnes of underground cable are burnt every year the amount of Sb emitted to the air per year is about 100 kg (Bremmer, 1990).

Ore-processing industry

In the zinc processing industry Sb is released from the ore. Zinc-ore concentrates consist on average of 0.02% Sb. From the survey it appears that in 1988 80 tonnes of Sb were imported via zinc-ore concentrates. The Sb from the ore lands up in the iron fraction, which is separated out as jarosite. Antimony from the catalyst also lands up in the jarosite; the amount in 1988 was 1.3 tonnes. The

jarosite (containing 81 tonnes of Sb in 1988) is stored as chemical waste.

Pigment industry

From the survey (Ewijk et al., 1990) it would seem that emissions to water and air differ from company to company. The companies surveyed discharge 3,000 kg Sb every year into the sewerage system and emit 1,350 kg Sb into the air. Sb concentrations in water (measured by companies) amount to 12.7 - 52 mg.l⁻¹, with peaks up to 5,200 mg.l⁻¹. Air concentrations measured come to 0.48 - 27.4 mg.m⁻³, with peaks up to 3,417 mg.m⁻³. The quantity of waste, of which half is dumped and half recycled, amounts to about 2,700 kg.

Coal-fired power stations

The burning of coal leaves Sb behind in the various types of ash. Its concentration per ash type varies because enrichment has taken place. There will be a lower concentration in soil ash than in fly ash, the concentration in fly ash is in turn lower than in fly dust. Table 3.6 gives the Sb concentrations measured in one installation, These values can be seen as representative. Of the amounts emitted per year the only air emission source is fly dust.

Table 3.6 Concentrations (mg.kg⁻¹) and quantities of various types of ash from burning coal (Meij, 1989; SEP, 1990)

Type of ash	Quantity (t.a ⁻¹)	Conc. Sb	Remarks
Soil ash	81,100 (1988)	2.4	100% sales in road construction and concrete
Fly ash	712,400 (1988)	39	98% sales in cement, artificial gravel and asphalt
Fly dust	2,000 (1987) 1,300 (1990)	87	emission to air: 170 kg Sb in 1987 and 110 kg Sb in 1990

Other industries (Light bulb manufacture, ammonia manufacture, electronics industry, oil refineries)

In the production of Flu powder the yearly discharge of Sb into water is 150 kg, with a measured Sb concentration of 0.4 mg l⁻¹. Four tonnes of Sb are emitted to air, and besides this sludge containing 170 kg Sb yearly is dumped. In the production of glass for light bulbs 425 kg Sb is emitted into the air, with a concentration of 5 mg m⁻³ being measured at the point of emission. During the production of fluorescent light bulbs a waste stream of 450 kg Sb per year is formed, of which 180 kg is recycled or dumped, depending on the composition of the stream. The rest (270 kg Sb) is dumped.

In the electronic industry a waste stream amounting to 31,200 tonnes per year is expected from all the electronic equipment. Printing plates from colour TVs will contribute 1,609 tonnes and from PCs 4-6 tonnes. This results in a total Sb waste stream for TVs and PCs of 4-6 tonnes per year. It is not known how much Sb is contained in other electronic equipment (black and white TVs, videotape recorders, tuners, amplifiers, cassette recorders and record players). For the present it is assumed that of the total stream 40% is incinerated and 60% is dumped. There is nothing known about antimony emissions from ammonia production, in which potassium antimonyl tartrate is used as inhibitor.

During the production of semi-conductors a liquid waste stream comprising 0.007

mg Sb.l⁻¹ is formed; this waste stream is created during the sawing/cutting of silicon staffs into thin slices, and also when staffs are polished and rinsed, although how many litres are used is not known.

The use of several hundred ppm Sb as additive during the Fluid Catalytic Cracking (FCC) process in oil refineries results in a solid waste stream of de-activated FCC catalysts which are polluted with Sb. Sometimes these old catalysts are processed in the cement industry. The amount of de-activated FCC catalysts found per year in the Netherlands is not known.

Hunting, shooting and sport fishing

Lead shot used in hunting, for shooting and sport fishing contains 0-11%. Hunters and sport fisherman release about 600 tonnes of metallic lead into the environment. At a percentage of 0-3% Sb the total emission is a maximum of 20 tonnes Sb per year, of which 80% ends up on agricultural and similar lands (16 tonnes), the remainder ends up in freshwater sediments (4 tonnes) (Van Bon and Boersema, 1988).

Sport fishing is responsible for an yearly discharge of 226-540 tonnes metallic lead into the environment: 51-109 tonnes via fishing in inland waterways and 175-431 tonnes via offshore fishing. Of this 38-82 tonnes end up in freshwater sediments and 156-383 tonnes in salt-water sediments. Since most fishing inland is done close to home the distribution of lead conforms to the distribution of the Dutch population. Consequently, considering only sinkers consisting of lead shot containing 2-11% Sb, the following emissions are possible: in freshwater sediments: 3 tonnes Sb (with a range of 1-7 tonnes) distributed throughout the Netherlands and in salt-water sediments: 11 tonnes (with a range of 4-30 tonnes) (Van Bon and Boerseman, 1988).

Other diffuse sources (Fire from fire retardants; illegal cable roasting furnaces; fireworks; corrosion; battery acid)

The fire retardant action of Sb₂O₃ with organohalogenic compounds is based on the formation of an antimony halogenide which displaces oxygen. The antimony halogenide formed is gaseous, so that antimony emissions can be expected when materials containing fire retardant burn. However, it is difficult to estimate how much Sb is released in this way.

Illegal cable roasting furnaces may emit large quantities of antimony. The illegal cable roasting furnaces probably roast synthetic cable as well as underground cable. It is estimated that about 7,000 tonnes of cable per year are roasted in illegal furnaces (Bremmer, 1990).

In the fireworks industry stibnite (Sb₂S₃) is used in Bengali (white) flares, which consist of 31.4% potassium chlorate, 39.2% barium nitrate, 13.7% accroides, 9.8% potassium nitrate and 5.9% stibnite. Antimony is released into the atmosphere when Bengali (white) flares are lighted and burnt. One of the companies surveyed emitted in this way 10 kg Sb₂S₃ yearly, of which about 7 kg was Sb.

One possible diffuse source is via corrosion of alloys containing antimony. Emission to the soil may take place via battery acid in which antimony is present and through leakages at auto wreckage sites.

Households

Two studies have been carried out to determine various Sb levels in household wastes (Van de Beek et al., 1989) in an old city quarter of Amsterdam and in Arnhem and Rotterdam. The concentrations found can be assumed to be representative for total household waste in the Netherlands. Per year this represents approximately 6.5 million tonnes wet waste of which 40% (2.6 million tonnes) is incinerated and 60% (3.9 million tonnes) is dumped. Based on an Sb content in wet waste of 3 mg kg⁻¹ the total would be 19.5 tonnes of which 7.8 tonnes is incinerated and 11.7 tonnes is dumped.

In the incineration of waste in a Dutch Waste Incineration Installation (AVI) Sb is encountered again in the slag, the electro-filter ash and the fly dust. Table 3.7 shows the average values obtained through measurements at an AVI, including measurements taken under circumstances where temperatures deviated (Hesseling, 1987).

Table 3.7 Average concentrations of waste materials obtained from measurements taken at an AVI

Waste material	Sb-concentration (mg.kg ⁻¹ waste)	Sb estimate (t.a ⁻¹)
Electro-filter ash	6 ± 5	16
Slag	13 ± 6	34
Fly dust	1 ± 1	3

The concentrations seem to be highly variable, depending on, for instance, incineration conditions and the type of waste. Besides household waste industrial waste is also incinerated at AVIs.

Antimony in sewage sludge

A few years ago sewage sludge in the Netherlands from installations processing waste water from the synthetics plants or plants processing fire retardants contained 200-300 mg Sb per kg sludge (d.w.). Although this content is decreasing (see section 4.2.2), it is not expected that levels under 50 mg.kg⁻¹ will be reached (Duvoort, 1988), the Chemical Waste Act limit. However, sewage sludge is exempted from this legislation: in future standards for sewage sludge, antimony will probably not be included, implying that sewage sludge with an Sb concentration greater than 50 mg kg⁻¹ will not have to be processed as chemical waste.

Every year about 5 million tonnes of sewage sludge is formed. It does not all contain ≥ 50 mg.kg⁻¹ Sb because not all of the sewage treatment plants have water polluted with Sb to treat. It is not clear how much Sb ends up in sewage sludge every year but it is probably several tonnes.

Table 3.8 presents an overview of the yearly emissions of Sb to soil, water and air. From this table it is clear that many antimony-emitting sources exist for which the emissions are unknown. For example, particularly in the burning of fire retardants large quantities are most probably emitted into the atmosphere. Fireworks may also form a large source of emission to air: the emission to air of 7 kg Sb of the only fireworks company indicating that it processed or used Sb

was obvious after lighting 150 kg Bengali (white) flares. How much of this type of fireworks is let off every year in the Netherlands is not known. In light bulb production Sb emission to air is usually due to Flu powder production. Hunting, shooting and sport fishing most likely account for a substantial amount of the total Sb pollution in the Netherlands, while the pigments industry contributes considerably to Sb water and air pollution.

Table 3.8 Summary of yearly emissions of Sb to soil, water and air

Emission source	Emission of Sb (kg)		
	Soil	Water	Air
Textile companies:			
-Catalyst	improb.	460	improb.
-Fire retardant	improb.	400	improb.
F.C.C.-process	?	?	improb.
Welding	improb.	improb.	?
Secondary lead extraction	improb.	(50)	(20)
Pigments	(1,400) ¹	(3,000)	(1,350)
Synthetics industry	improb.	(130)	improb.
Light bulb production	(620) ¹	(150)	(4,425)
Ore-processing industry	(81,000) ¹	improb.	improb.
Burning:			
- Cables	improb.	improb.	> 100
- Fire retardants	improb.	improb.	?
Hunting, shooting	16,000 ²	4,000	improb.
Sport fishing	improb.	14,000	improb.
Fireworks	improb.	improb.	(7)
Old electronic equipment	3,000 ¹	2,000	improb.
Corrosion/battery acid	? ²	?	improb.
Sewage sludge	? ¹	?	?
Household waste	8,100 ¹	?	?

¹ Soil emission in the form of dumping

² Diffuse soil emission

() : figures are calculated from the survey results and therefore may be lower than the real yearly emissions.

? : possible emissions for which no data are available

improb. = emissions thought improbable

4. OCCURRENCE, CONCENTRATIONS AND EXPOSURE

Antimony is one of the elements diffusely distributed in the earth's crust (in concentrations of 0.2-0.5 mg.kg⁻¹; it is identified in sea water, as well as water of some mineral springs (IRPTC, 1984; US EPA, 1979).

In contrast to the other heavy metals, very few data are available on occurrence and concentrations of antimony in the environmental compartments soil, water and air. Moreover, not all used measuring techniques have been validated and therefore these may not be reliable. Because of this, little is known about the environmental distribution.

4.1 SOIL AND GROUNDWATER

4.1.1 Soil

Few data on the occurrence of antimony in soil in the Netherlands are available. Average antimony levels in the Netherlands usually vary between 0.3 and 3.0 mg.kg⁻¹ d.w. It is not clear whether these data are influenced by human activities. Table 4.1 gives an overview of average antimony levels in several soil types (natural reserves and near industry).

Table 4.1 Average antimony levels in different soil types (natural reserves) in the Netherlands (mg Sb.kg⁻¹ d.w.)

Soil type	Average concentrations
Natural reserves (Van Ewijk et al., 1990)	
Sandy soil	0.3 - 1.8
Sandy clay/Loam	0.5 - 2.2
Clay-soil	1.5 - 2.2
Peaty clay/Clayey peat	1.1 - 3.0
Peat soil	1.6 - 3.0
Landside of dike (Mulder et al., 1986)	1.4
Forelands (Mulder et al., 1986)	5.5 - 6.4
Contaminated soil (Lekkerkerk) (Mulder et al., 1986)	<0.2-230***
Heel and Panheel (Brinkmann et al., 1990)*	0.2 - 1.4
Heel and Panheel (Brinkmann et al., 1990)**	1 - 1.4
Netherlands (Mulder et al., 1986)	0.6 - 2.1
Netherlands (Stuyfzand, 1991 and 1992a)	1

*: near a metal reclamation plant for processed photographic and other waste material (with antimony emission), a motorway and an electricity power plant

** : near a motorway and an electricity power plant

***: wet weight

World-wide antimony ranges from 0.1-10 mg.kg⁻¹ d.w. (Elinder and Friberg, 1986; Mulder et al., 1986).

Data on the adsorption of antimony to soil have only recently been reported. The data indicate that adsorption does occur, depending on the type and structure of the soil. In two unpolluted or only slightly polluted German forest ecosystems (approximately 0.7 mg.kg^{-1} Sb d.w. in the upper layer of the soil), more than 90% of the deposited antimony ($290 \text{ g.km}^{-2}.\text{yr}^{-1}$) was retained.

Factors enhancing the adsorption of the anionic antimony compounds are: weakly acidic (pH 4 to 5.5) conditions and the presence of iron and aluminium in the soil. In sandy soil antimony is highly mobile, in contrast to its behaviour in sandy loam soil (Mulder et al., 1986).

4.1.2 Groundwater

Table 4.2 shows antimony concentrations in groundwater in the Netherlands. Antimony concentrations range from <0.001 to $1.4 \mu\text{g.l}^{-1}$. They are correlated to degree of acidity, but because of a number of confounding factors (speciation of antimony compound, land use, soil type, use of fertilizer) the relation is not clear (Van Duijvenbooden, 1989; Stuyfzand, 1991, 1992a and 1992b).

Table 4.2 Antimony concentrations in groundwater in the Netherlands (in $\mu\text{g.l}^{-1}$)

Location	Average	Min	Max	Reference
Netherlands (60 locations)	0.07	0.005	1.3	Van Duijvenbooden, 1989
Netherlands (pH ≥ 6.2)	-	<0.001	0.1	Stuyfzand, 1991 and 1992a
Netherlands (pH < 6.2)	-	0.028	1.4	Stuyfzand, 1991 and 1992a
Natural groundwater	-	0.005	0.05	Stuyfzand, 1991 and 1992a
Groundwater polluted by				
- polluted air	-	-	1	Stuyfzand, 1991 and 1992a
- Rhine water	-	<0.001	0.5	Stuyfzand, 1991 and 1992a
- liquid manure on maize	-	<1	1.4	Stuyfzand, 1991 and 1992a
- industrial waste*	-	-	>40	Glasbergen en Kusse, 1985

- : no data available

* : catalyst with uranium antimony oxide

Distribution of antimony by groundwater is expected to be relatively unimportant because of the adsorption to soil particles (Mulder et al., 1986).

4.2 SURFACE WATER AND SEDIMENT

4.2.1 Surface water

Antimony concentrations in surface water are not monitored in the Netherlands. Table 4.3 gives an overview of some antimony concentrations in surface water. Concentrations vary between $< 1^*$ (below detection limit) and $10 \mu\text{g.l}^{-1}$.

Table 4.3 Antimony concentrations in surface water in the Netherlands (in $\mu\text{g.l}^{-1}$)

Location	Average	Min	Max	Reference
Rhine (Lobith) (1988-1989)	1	-	-	Van Ewijk et al., 1990
Rhine (1980-1983)	0.3	-	-	Stuyfzand, 1991 and 1992a
Rhine (Lobith) (1975-1980)	$< 1^*$	$< 1^*$	3	RWS, 1992
Rhine	0.1	-	-	Elinder and Friberg, 1986
Meuse (Eysden) (1975-1980)	$< 1^*$	$< 1^*$	3	RWS, 1992
Lake Yssel (1975-1980)	$< 1^*$	$< 1^*$	2	RWS, 1992
Maassluis (1975-1980)	$< 1^*$	$< 1^*$	2	RWS, 1992
Scheldt (1975-1980)**	5	2	10	RWS, 1992
Dutch coastal waters	0.2	-	-	Mulder et al., 1986
Sea	0.3	-	-	Stuyfzand, 1991 and 1992a
Pacific Ocean	0.2	-	-	Elinder and Friberg, 1986

- : no data available

* : below detection limit

** : near antimony factory in Antwerp (Belgium)

According to IRPTC (1984), antimony concentrations in natural waters range up to $10 \mu\text{g.l}^{-1}$.

The fate of antimony in the aquatic environment is determined by a number of factors including pH, Eh, sorptive interactions, and biologically mediated methylation. Due to the relatively high solubility of the antimonite and antimonate ions, most of the antimony introduced into the aquatic environment is probably transported in solution to the oceans. Coprecipitation with iron and aluminium oxides, adsorption by mineral surfaces, and bioaccumulation may, however, be responsible for removing some antimony from solution. Biologically mediated methylation (which has not been demonstrated) or reduction to stibine (SbH_3) may occur in reducing environments, resulting in remobilization of antimony. The relative importance of each of these processes varies widely among watersheds; but, in general, transport of dissolved antimony to the oceans is the most probable dominant fate (US EPA, 1979). Antimony may be volatilized when in the form of stibine or its methylated derivatives. Because of rapid oxidation processes, only a small amount of the volatile antimony compounds would be liberated to the atmosphere (US EPA, 1979).

Table 4.4 gives an overview of antimony concentrations in industrial waste water.

Table 4.4 Antimony concentrations in industrial waste water in the Netherlands (in $\mu\text{g.l}^{-1}$) (Van Ewijk et al., 1990; Enders et al., 1990)

Location	Average	Min	Max
Pigment industries	12,700-52,000	-	5,200,000
Textile improvements	-	10	4,500
Waste incineration (waste water)	-	200	2,300
Production of plastics	50	-	150
Production of Flu-powder	400	-	-
Production of semiconductors	7	-	-

- : no data available

4.2.2 Sediment

No data on antimony concentrations in sediment in the Netherlands are available. Data on antimony concentrations of suspended particles in fresh water in the Netherlands are given in table 4.5. They vary between 0.2 and 1.9 mg.kg^{-1} d.w.

Table 4.5 Antimony concentrations in suspended particles in fresh water in the Netherlands (in mg.kg^{-1} d.w.)

Location	Concentration	Reference
Eysden (Meuse) (1/5/91)	1.9 (n=4)	RWS, 1992
Hagestein (Lek) (10/7/91)	0.6 (n=4)	RWS, 1992
Kampen (Yssel) (24/7/91)	0.6 (n=4)	RWS, 1992
Scheldt (1/7/91)	1.0 (n=4)	RWS, 1992
Maassluis (24/6/91)	0.7 (n=4)	RWS, 1992
Lake Yssel (18/6/91)	0.2 (n=4)	RWS, 1992
Rhine (Germany) (in sediment)	8.0 - 96	Mulder et al., 1986
North Sea (in sediment)	0.9	Mulder et al., 1986

- : no data available

World-wide antimony concentrations in uncontaminated sediment vary between 0.15 and 20 mg.kg^{-1} d.w. (mean concentration 1 mg.kg^{-1} d.w.; both fresh and marine water conditions) (Coughtrey et al., 1983 (cited in Mulder et al., 1986)). Concentrations in sediments near antimony emitting industries may be much higher (up to 10,000 mg.kg^{-1} d.w. near a copper smelter in the USA).

Sorption is the most important process resulting in the removal of antimony from solution. Crecelius et al. (1975: cited in US EPA, 1979) found that in uncontaminated areas most of the antimony in sediments was bound to extractable iron and aluminium compounds. Antimony bound in such forms would probably be susceptible to remobilization via bioaccumulation, reduction, or biomethylation. On the other hand, antimony in heavily contaminated areas was found mainly in stable, unextractable forms. These forms might include the oxide or insoluble metal antimonates or antimonites. Other studies found that antimony is not being strongly bound in the sediments (US EPA, 1979).

Antimony has been found in municipal and industrial aqueous effluents (Duvoort,

1988; Van Ewijk et al., 1990; Gels et al., 1988). In the Netherlands antimony concentrations of 80-90 mg.kg⁻¹ d.w. have been found in the sludge from one municipal sewage work (Veenendaal), which receives sewage from textile improvement industries. A few years ago these concentrations were 200-300 mg.kg⁻¹ d.w. Although antimony concentrations are still decreasing, it is expected that the minimum content will not be less than 50 mg.kg⁻¹ d.w. (≥ 50 mg.kg⁻¹ antimony is chemical waste) (Duvoort, 1988; Gels et al., 1988). In other countries (Ireland, Canada, Sweden and USA), concentrations between 0.03 and 12.2 mg.kg⁻¹ were found. There is no maximum limit for the antimony concentration in sludge used in the Netherlands and it is not generally analyzed for. If antimony containing sludge is used in agriculture, the extent of adsorption to soil depends on the type and structure of the soil, but sludge application appeared not to influence the level of antimony in soil. Only in isolate cases high levels in herbage could be expected (Duvoort, 1988).

4.3 AIR

4.3.1 Air (outdoor)

The antimony content of outdoor air is not monitored in the Netherlands. Table 4.6 gives an overview of antimony concentrations in ambient air in the Netherlands and world-wide.

Table 4.6 Antimony concentrations in ambient air (in ng.m⁻³) (Brinkmann et al., 1990; Elinder and Friberg, 1986; Mulder et al., 1986)

Location	Average	Min	Max	Reference
The Netherlands (urban)	23	-	-	Evendijk, 1973
Heel and Panheel* (near industry**)	-	6	35	Brinkmann et al., 1990
Heel and Panheel* (reference point***)	-	2	9	Brinkmann et al., 1990
Urban areas (Belgium, Germany, UK, USA)	1-30	-	-	Brar et al., 1970; Dams et al., 1970; Mulder et al., 1986; Pearson et al., 1973
Rural areas (Germany, UK, USA)	<0.5-3	-	-	Mulder et al., 1986; Pearson et al., 1973
Open ocean (USA)	0.2	-	-	Crecelius, 1981
Antarctica	0.0006-0.0044			Zoller, 1984

* : measuring method has not been validated

** : near a metal reclamation plant for processed photographic and other waste material (with antimony emission), a motorway and an electricity power station

*** : near a motorway and an electricity power station

According to IRPTC (1984), antimony concentrations in ambient air result solely from anthropogenic pollution. Antimony concentrations in industrial air (pigment industry; non-ferrous industry) vary between 0.48 and 27.4 mg.m⁻³, with peaks up to 3,417 mg.m⁻³ (Ewijk et al., 1990; Mulder et al., 1986). In flue gas of an industrial waste incinerator in Germany, antimony concentrations of 0.18 to 0.31 mg.m⁻³ have been measured.

Dry and wet deposition of antimony does take place in the Netherlands, but no deposition rates have been given.

4.3.2 Rainwater

Few data on antimony levels in rainwater in the Netherlands are available. Stuyfzand (1991) found an average antimony concentration of $0.89 \mu\text{g.l}^{-1}$ in the Dutch coastal provinces. According to Stuyfzand (1992a), rainwater (contaminated by antimony) probably is the most important antimony source for shallow groundwater.

4.3.3 Air (indoor)

Except for data on occupational exposure, no data are available on the antimony content of indoor air. Because of smoking, the indoor air antimony concentrations might be higher than that of outdoor air.

4.4 FOOD AND DRINKING WATER

4.4.1 Food

Table 4.7 gives an overview of average antimony concentrations in some foodstuffs and beverages. Antimony is sometimes present in the binding coat between enamel and metal, especially in older cooking utensils, and can be dissolved by acid drinks when the enamel coating is worn (Elinder and Friberg, 1986). Especially in the past, this could be a source of acute antimony poisoning.

Table 4.7 Average antimony concentrations in food and beverages (Elinder and Friberg, 1986; Mulder et al., 1986)

Food/beverage	Concentration (mg.kg^{-1} w.w.)	Reference
Freshwater fish	3	Elinder and Friberg, 1986
Potato powder	8	Elinder and Friberg, 1986
Vegetables	0.002-0.052	Bognar et al., 1981
Vegetables	0.4-2.5*	Furr et al., 1976
Milk	3	Elinder and Friberg, 1986
Beer	0.8 (0.2-17.6)	Kallischnigg et al., 1982

w.w. : wet weight or fresh weight

* : dry weight

Antimony in cigarettes has been studied; the tobacco, on average, contained $0.1 \text{ mg Sb.kg}^{-1}$ dry weight. The amount of inhaled antimony was estimated to be 20% of the total amount of antimony in one cigarette (Elinder and Friberg, 1986).

4.4.2 Drinking water

No data are available on the antimony content of drinking water in the Netherlands. In tap-water from 94 American cities, the antimony level was (on average) less than $0.2 \mu\text{g.l}^{-1}$ (Schroeder, 1966 (cited in Mulder et al., 1986)). This supports the assumption that drinking water levels are similar to those in fresh water. In other studies concentrations of $0.6\text{-}4 \mu\text{g.l}^{-1}$ were found.

4.5 HUMAN EXPOSURE LEVELS

Data on daily intake are controversial. Reported amounts ingested range from about $10 \mu\text{g}$ in a Swedish balance study (drinking water excluded), a weekly average of $23 \mu\text{g}$ in four normal German diets to $250\text{-}1,250 \mu\text{g}$ in a USA study of institutional diets for children. There is reason to believe that the USA study may have resulted in falsely high values because of the method used (Elinder and Friberg, 1986; Mulder et al., 1986). The safe drinking water committee (1980) gives an estimated human daily intake from all sources of $100 \mu\text{g}$. According to Ewijk et al. (1990) daily dietary intake is $10\text{-}20 \mu\text{g}$. People smoking cigarettes take in an additional $0.02 \mu\text{g}$ antimony per gram tobacco (dry weight) (Elinder and Friberg, 1986; Ewijk et al., 1990). In the Netherlands in 1973 in an urban setting the total human exposure to antimony was $0.43 \mu\text{g.day}^{-1}$ (calculated by Mulder et al. (1986); based on data of Evendijk (1973)).

5. EFFECTS

5.1. HUMAN TOXICITY

Antimony is considered a non-essential metal (Elinder and Friberg, 1986; SDWC, 1990).

According to ECETOC (1991), effects on humans of antimony and antimony compounds have been evaluated by the following institutes:

- * ACGIH (American Conference of Governmental Industrial Hygienists) (1986);
- * IARC (International Agency for Research on Cancer) (1989);
- * MAK (Senatskommission zur Prüfung Gesundheitschädlicher Arbeitsstoffe der Deutschen Forschungsgemeinschaft) (1983 and 1988);
- * NIOSH (National Institute for Occupational Safety and Health) (1978);

This Chapter is mainly based on Browning (1969), Elinder and Friberg (1986), IRPTC (1984), Mulder et al. (NOTOX) (1986), NIOSH (1978) and SDWC (1980).

5.1.1 Chemobiokinetics and metabolism

Kinetics and metabolism have been determined largely from therapeutic studies (NIOSH, 1978). There appear to be important species differences with regard to the metabolism of antimony.

Absorption

* **Inhalation**

Quantitative data on the absorption of inhaled antimony compounds (dust particles, aerosols and vapour) are not available. It can, however, be deduced from the experiments on rats by Djurić et al. (1962: cited in Elinder and Friberg, 1986) that inhaled trivalent antimony is, to a great extent, absorbed from the lungs. Other studies state that absorption by inhalation is slow and limited, because of the relative insolubility of antimony and antimony compounds.

* **Ingestion**

At least 15% of a single oral dose of labelled potassium antimony tartrate (tartar emetic: trivalent) given to mice is absorbed, i.e. recovered in urine and tissues (Waitz et al., 1965 (cited in Elinder and Friberg, 1986)). Absorption may, however, be higher (up to 50%) since gastrointestinal excretion starts immediately after the metal is taken up from the gut (Elinder and Friberg, 1986). Other antimony compounds are considered to be absorbed very slowly from the gastrointestinal tract.

* **Skin absorption**

Dermal absorption is considered to be of minor importance.

Distribution

Trivalent and pentavalent antimony are differently distributed and excreted. Trivalent compounds have a great affinity for erythrocytes and, therefore, give low plasma concentrations (<5% of total amount of antimony in blood). Pentavalent compounds tend to remain in the plasma (90%) (Elinder and Friberg, 1986).

In several test animals the trivalent compounds are found in high concentration in the thyroid and liver, while the pentavalent forms are found in the liver and spleen after oral dosing. Other studies indicate that antimony is also found in the kidneys. Antimony concentrations in tissues range up to more than 10 mg.kg⁻¹ wet weight. Antimony distribution differed strongly between test species. With repeated dosage of potassium antimony tartrate (tartar emetic) antimony levels in blood, liver, urine and faeces remained fairly constant, suggesting no persistent accumulation of antimony in the body (Waitz et al., 1965 (cited in Browning, 1969)).

Abdallab and Saif (1962: cited in SDWC, 1980) in their studies of humans, showed that the highest concentrations of antimony occur in the liver, followed by the thyroid and heart. After intravenous administration, the liver, heart and thyroid retained antimony for 20 days. When three 100-mg doses of antimony were administered intramuscularly over 9 days there was still considerable antimony in these tissues 53 days later. Certain antimony compounds appeared to be retained in the lung for long periods. Gerhardson (1982: cited in Elinder and Friberg, 1986) found that former smelter-workers occupationally exposed to several different types of metals, of which antimony was one, on an average had 12 times higher lung concentrations of antimony (315 µg.kg⁻¹) when compared to persons not previously occupationally exposed (26 µg.kg⁻¹).

(Bio)transformation

No data on (bio)transformation in animals and humans are available.

Elimination

The relative excretion by the urine or faeces apparently depends to a great extent on the nature of the antimony compound. Certain species differences are also seen. Most trivalent antimony is excreted in the faeces, whereas the pentavalent forms are excreted mainly in the urine. The trivalent form is excreted at a much slower rate in the urine than pentavalent antimony probably because it collects at much lower levels in plasma (NIOSH, 1978; SDWC, 1980). After administration of a single therapeutic dose of trivalent antimony only 10% was recovered in 24 hr in urine, whereas 50% of the pentavalent form was recovered in 24 hr (Harvey, 1975 (cited in SDWC, 1980)). Other studies lead to similar conclusions (Browning, 1969; Elinder and Friberg, 1986).

Excretion of antimony after inhalation takes place in two phases. Up to 80% of the initially deposited antimony in several test animals is excreted via urine and faeces within a few days. This fast excretion phase is followed by a slow clearance with biological half-life in whole-body in the order of 20-140 days (Elinder and Friberg, 1986).

Single intravenous or intramuscular injections to volunteers produced higher 24-h urinary excretion of pentavalent (80%) than of trivalent (25%) antimony compounds, a pattern similar to the one found in animals (Elinder and Friberg, 1986).

5.1.2 Toxicity

Antimony resembles arsenic both chemically and biologically, and symptoms of acute and chronic toxicity from antimony closely resemble those induced by arsenic. Generally, the trivalent compounds are more toxic than the pentavalent.

Acute toxicity (single and short-term exposure): animal data

The lethal concentration in case of inhalatory exposure of stibine (SbH_3) for mice has been estimated as 500 mg.m^{-3} for 100 minutes (Royal Society of Chemistry, 1989). Other lethal concentrations vary between $125\text{-}150 \text{ mg.m}^{-3}$ (one week old chicken; duration not stated) and $200\text{-}225 \text{ mg.m}^{-3}$ (cat and dog; 1 hour exposure) (Shell, 1982). It is not clear from literature whether these lethal concentrations are LD_{50} s. No data on lethal concentrations of other antimony compounds in case of inhalatory exposure are available.

Lethal concentrations in case of oral, intraperitoneal and subcutaneous application are shown in table 5.1. LD_{50} s vary between 4 and $>16,700 \text{ mg Sb.kg}^{-1}$ body weight, depending on compound, test species and route of entry.

Acute toxicity (single and short-term exposure): human data

No data are available on lethal concentrations in case of inhalatory exposure. Acute symptoms in case of inhalation are cough, headache and sore throat (Breteler, 1990; CEC, 1990).

Stibine, like arsine, when inhaled, damages the red blood cells and causes haemolysis. Signs of poisoning include symptoms of shock and haemoglobinuria (Elinder and Friberg, 1986). Exposure to $50,000 \text{ mg.m}^{-3}$ is rapidly fatal and that a few hours exposure to 500 mg.m^{-3} may be followed by death (Shell, 1982).

According to IRPTC (1984), after oral exposure to potassium antimony tartrate, death occurred when the doses ranged from 0.12 to 1.0 gram per person. Acute toxicity symptoms of antimony and antimony compounds are abdominal pain, colics, cough, sore throat, loss of appetite and vomiting (IARC, 1989; Royal Society of Chemistry, 1989). The taste threshold for either trivalent or pentavalent antimony is 0.6 mg.l^{-1} (Arzamastsev, 1964 (cited in SDWC, 1980)).

Furthermore, contact with antimony compounds may lead to painful or itchy redness in skin and eyes, blisters, blurred vision and conjunctivitis (Breteler, 1990; CEC, 1990; Royal Society of Chemistry, 1989).

Table 5.1 Acute toxicity studies: oral, intraperitoneal and subcutaneous exposure (Browning, 1969; IARC, 1989; IRPTC, 1984; Mulder et al., 1986; NIOSH, 1978; Royal Society of Chemistry, 1989; SDWC, 1980)

Compound	LD ₅₀ (average) (mg.kg ⁻¹ bw)	LD ₅₀ (average) expressed as Sb (mg.kg ⁻¹ Sb bw)	References
Oral exposure:			
Rat			
Sb	100	100	Sax, 1979
Sb ₂ O ₃	>20,000	>16,700	Smyth and Carpenter, 1948
SbCl ₃	675	360	Arzamastsev, 1964
SbCl ₅	1,115	455	Arzamastsev, 1964
K-antimony tartrate	300	110	Bradley and Fredrick, 1941
Mouse			
SbFl ₃	804	550	Bradley and Fredrick, 1941
Guinea pig			
SbCl ₃	574	305	Arzamastsev, 1964
SbCl ₅	900	365	Arzamastsev, 1964
SbFl ₃	100	70	Sax, 1979
Rabbit			
K-antimony tartrate	115	40	Oelkers, 1937
Intraperitoneal application:			
Rat			
Sb	100	100	Bradley and Fredrick, 1941
Sb ₀₀₀	112	112	IRPTC, 1984
Sb ₀	100	100	IRPTC, 1984
Sb ₃	129	125	IRPTC, 1984
Sb ₂ S ₃	1,000	720	Bradley and Fredrick, 1941
Sb ₂ O ₃	2,250	1,880	Bradley and Fredrick, 1941
Sb ₂ S ₅	1,500	900	Bradley and Fredrick, 1941
Sb ₂ O ₅	4,000	3,000	Bradley and Fredrick, 1941
Tartar emetic	11	4	Bradley and Fredrick, 1941
Mouse			
Sb ₀	90	90	IRPTC, 1984
Sb ₃	80	78	IRPTC, 1984
SbCl ₃	25	13	IRPTC, 1984
Sb ₂ S ₃	240	172	IRPTC, 1984
Sb ₂ O ₃	250	209	IRPTC, 1984
Sb ₂ S ₅	760	458	IRPTC, 1984
Sb ₂ O ₅	1,300	978	IRPTC, 1984
Guinea pig			
Sb	150	150	Bradley and Fredrick, 1941
Subcutaneous administration:			
Mouse			
SbFl ₃	15	10	Izmerov et al., 1982
SbFl ₃	22.9	16	Bromberger-Barnea and Stephens, 1965
SbFl ₃	50	35	Levina and Chekunove, 1965

Sb₀₀₀ : metallic antimony: < 0.001% impurities

Sb₀ : metallic antimony: < 0.1% impurities

Sb₃ : metallic antimony: up to 1.5% lead and 0.14% arsenic

Subacute and (sub)chronic toxicity (long-term exposure): animal data

An overview of NO(A)ECs and NO(A)ELs of antimony and antimony compounds is given in table 5.2.

Exposure by inhalation

Few data are available on subacute and (sub)chronic toxicity of inhalatory exposure to antimony compounds (mainly antimony trioxide and antimony trisulphide). Carcinogenicity and toxicity studies resulted in NO(A)EC-values varying between $<1,600$ and $<37,500 \mu\text{g}\cdot\text{m}^{-3}$. Especially female rats seemed to be susceptible to antimony compounds. Differences in susceptibility between males and females are also found in other animals (mice) (Schroeder et al., 1968 (cited in Mulder et al., 1986)) No inhalatory data on other antimony compounds are available.

Oral exposure

Few data on the long-term toxicity effects of oral exposure are available. The lowest NO(A)EL is $0.0013 \text{ mg}\cdot\text{kg}^{-1}$ body weight for guinea pigs (6 months exposure). Effects (probably blood effects) and other details are, however, not specified. Because of these limitations this study can not be evaluated. In a limited long-term study, rats given $5 \text{ ml Sb}\cdot\text{l}^{-1}$ ($0.43 \text{ mg Sb}\cdot\text{kg}^{-1}$ b.w.) as antimony potassium tartrate in drinking water showed a significantly shortened average length of life (about 15%) compared to controls. Altered blood chemistry was found (increased serum cholesterol levels in males and decreased in females and altered blood glucose levels compared to controls) (Schroeder et al., 1970 (cited in Elinder and Friberg, 1986)).

Furthermore, reduced weight gain, a slight reduction in absolute weight of the spleen and the heart and a slight increase in absolute and relative weight of the lungs were observed in rats given 1% antimony trioxide in the diet for 12 weeks (Hiraoka, 1986 (cited in IARC, 1989)). Rats given a diet containing 0.5 to 2% antimony or antimony trioxide had a decreased weight gain, and after 24 weeks the most exposed animals had elevated serum levels of a liver enzyme (GOT) (Sunagawa, 1981 (cited in Elinder and Friberg, 1986)).

No data on oral exposure of animals to elemental antimony and other antimony compounds are available.

Table 5.2 Subacute, subchronic and chronic toxicity NO(A)EC's ($\mu\text{g Sb.m}^{-3}$) and NO(A)EL's (in mg Sb.kg^{-1} body weight.day⁻¹) of antimony and antimony compounds (Browning, 1969; IARC, 1989; NIOSH, 1978; SDWC, 1980)

Test species	Exposure time	NO(A)EC NO(A)EL	LO(A)EC LO(A)EL	Effects	References
Exposure by inhalation:					
antimony trioxide					
Rat	13m, 5d.w ⁻¹ , 6h.d ⁻¹	<1,600	1,600	1/17 bronchioalveolar adenoma, increased lung weight, focal fibrosis, adenomatous hyperplasia, multinucleated giant cells and pigmented macrophages in females	Watt, 1983
Rat	52w, 5d.w ⁻¹ , 7h.d ⁻¹	<37,500	37,500	Non-neoplastic lesions in lungs of both males and females (less severe in males)	Groth et al., 1986
Minipig	52w, 5d.w ⁻¹ , 6h.d ⁻¹	4,200	>4,200	No effects	Watt, 1983
antimony ore (mainly antimony trisulphide)					
Rat	6w	<2,200	2,200	Electrocard. changes dilated hearth, focal haemorrhage and congestion in lungs	Brieger et al., 1954
Rat	52w, 5d.w ⁻¹ , 7h.d ⁻¹	<17,000	17,000*	Non-neoplastic lesions in lungs of both males and females (less severe in males)	Groth et al., 1986
Rabbit	6w	<4,000	4,000	Electrocard. changes dilated hearth, focal haemorrhage and congestion in lungs	Brieger et al. 1954
Dog	10w	<4,000	4,000	Cardiotoxic changes	Brieger et al. 1954
Dog	7w	3,800	>3,800	No cardiotoxic effects at tested concentrations	Brieger et al. 1954
Oral exposure:					
antimony metal					
Rat	1 yr	<100	100	Myocardial damage	Bradley and Fredrick, 1941
antimony trioxide					
Dog	daily (duration not given)	<125	125	Vomiting and gastrointestinal disturbances	Flury, 1927
Cat	daily (duration not given)	<125	125	Vomiting, weight loss	Flury, 1927
antimony trichloride					
Rat	10d	<72	72	Myocardial degeneration	Arzamastsev, 1964
Guinea pig	6m	0.0013	>0.0013-1.3	Toxic effects not stated	Arzamastsev, 1964
Guinea pig	10d	<6.5	6.5	Blood changes (decreased haemoglobin, increased reticulocyte count)	Arzamastsev, 1964
potassium antimony tartrate					
Rat	lifetime	<0.43	0.43	15% shortened lifespan, altered blood chemistry	Schroeder et al., 1970
Rat	12m	<36	36	Consistent injury of the hart	Bradley and Fredrick, 1941
Mouse	lifetime	<0.5	0.5	Shortened lifespan (most shortened in females)	Schroeder et al., 1968

< : based on LO(A)EC and LO(A)EL

* : measured as 36,000-40,000 $\mu\text{g.m}^{-3}$ antimony ore (see also Chapter 5.1.3 carcinogenicity)

** : measured as 0.0025 mg.kg^{-1} SbCl_3

Subacute and (sub)chronic toxicity (long-term exposure): human data

Antimony acts by inhibiting some enzymes, disturbing protein and carbohydrate metabolism and glycogen production, by binding to sulphhydryl groups of serum proteins. Systemic intoxication due to industrial exposure appears rare, although causal antimony poisoning may be hard to establish because of the possible arsenic content of antimony used (Royal Society of Chemistry, 1989).

Exposure by inhalation

Few data on subacute and (sub)chronic inhalatory exposure in human beings are available from occupational studies.

Among a group of workers exposed to 600-5,500 $\mu\text{g}\cdot\text{m}^{-3}$ antimony trisulphide for 8 to 24 months several deaths occurred, possibly related to heart disease. In the department where the deaths occurred, 37/75 workers had electrocardiographic changes. After cessation of exposure, the changes persisted in 12/56 workers who were re-examined. Gastrointestinal disturbances were also reported (Brieger et al., 1954 (cited in IARC, 1989 and Mulder et al., 1986)). It must be noted that population data (history, smoking) and confounding factors have not been taken into account. Electrocardiographic changes were also observed in smelter workers in other studies and in people who were given antimony containing drugs (parenterally) (NIOSH, 1978).

Antimony trioxide causes pneumoconiosis (silicoantimoniosis) in humans, which is symptomless in general (IARC, 1989). The degree of abnormalities (rounded opacities) was correlated with the amount of antimony retained in the lungs and with duration of exposure (McCallum, 1963 (cited in IARC, 1989)). Other studies on smelter workers led to similar results. Environmental concentrations were reported to vary between 300 and 248,000 $\mu\text{g}\cdot\text{m}^{-3}$ antimony metal, antimony compounds or antimony ore dust. Contaminants have included silica and arsenic materials as well as particulates and gases characteristic of smelter operations (NIOSH, 1978).

Smelter workers exposed to antimony trioxide frequently complained of symptoms related to mucous membrane irritation, such as rhinitis (with cases of septal perforation and loss of smell), pharyngitis, laryngitis, bronchitis and pneumonitis. Other symptoms, less often encountered, included weight loss, nausea, vomiting, abdominal cramps and diarrhoea (Renes, 1953 (cited in IARC, 1989)). In other studies, only skin irritation or no indication of systemic toxicity was found in smelter workers.

Chronical poisoning of stibine has never been reported (Royal Society of Chemistry, 1989; Shell, 1982).

Oral exposure

In chemical safety data sheets of several antimony compounds is stated that chronic exposure may cause nausea, headaches, sleeplessness, loss of appetite and weight, dizziness, anaemia and degenerative changes in the liver and kidneys (Royal Society of Chemistry, 1989). No further data on chronic oral exposure have been reported (Browning, 1969).

Data on subacute exposure (probably parenteral administration) originate from clinical studies on the use of antimony compounds as therapy in case of schistosomiasis (bilharzia). Antimony was found to cause severe cardiotoxic effects (see exposure by inhalation). The ECG changes have been associated with both tri- and pentavalent antimony, though more with trivalent compounds. Women may be

more susceptible to the effects of antimony than man (NIOSH, 1978).

5.1.3 Genotoxicity and carcinogenicity

Genotoxicity

In a spot test antimony trioxide was not mutagenic to Escherichia coli B/r WP2 or to Salmonella typhimurium (TA1535, TA1537, TA1538, TA98 or TA100) (Kanematsu et al., 1980 (cited in IARC, 1989 and Mulder et al., 1986)). Antimony sodium tartrate significantly induced chromosome aberrations in human leucocytes in vitro (Paton and Allison, 1972). Potassium antimony tartrate (36.5% antimony) and piperazine antimony tartrate (36.9% antimony) induced chromosome aberrations in bone marrow cells of rats treated intraperitoneally (El Nahas et al., 1982).

A number of indicator tests were conducted. The Sb(III) compounds, antimony trichloride and antimony trioxide, significantly induced SCE's in V79 Chinese hamster cells, whereas antimony pentachloride and antimony pentoxide gave negative results (Kuroda et al., 1991). Antimony trioxide, antimony trichloride and antimony pentachloride were strongly positive in the Bacillus subtilis rec-assay (Kuroda et al., 1991). However, antimony trichloride and antimony pentachloride have also been reported to be only mildly positive (Kanematsu et al., 1980, cited by Kuroda et al., 1991) or even negative in the rec-assay (Nishioka, 1975, cited in Kuroda et al., 1991). $Sb(C_2H_3O_2)_3$ significantly enhanced transformation of Syrian Hamster embryo cells by SA7 adenovirus in a concentration of 0.003 mM (Casto et al., 1979 (cited in Mulder et al., 1986)). Further data on genotoxicity are not available.

Carcinogenicity

Animal data

Exposure by inhalation

Groups of 49-51 female Fischer rats, 19 weeks old, were exposed by inhalation to 0, 1,600 ($\pm 1,500$), or 4,200 ($\pm 3,200$) $\mu\text{g.m}^{-3}$ commercial grade antimony trioxide (measured as antimony: purity 99.4%; arsenic 0.02%) for 6 h per day on five days per week for 13 months. After cessation of exposure, the animals were observed for one year. Lung tumours localized in the bronchioloalveolar region occurred in 14/18 high-dose rats (three adenomas, nine scirrhous adenomas and two squamous-cell carcinomas). One bronchioloalveolar adenoma occurred in a low-dose rat, and no lung tumour was observed in the control group. There was evidence of local invasion, but no metastasis was observed. No data on survival of treated and control groups are available. There was no significant difference in the number of other tumours occurring in treated and control groups (Watt, 1983 (cited in Elinder and Friberg, 1986 and IARC, 1989)).

Groups of 90 male and 90 female Wistar rats, eight months old, were exposed by inhalation to 0 or 45,000 $\mu\text{g.m}^{-3}$ antimony trioxide (purity $\geq 95\%$; arsenic 0.004%) or to 0 or 36,000-40,000 antimony ore concentrate (containing 46% antimony, principally as antimony trisulphide; titanium $< 4\%$; aluminium 0.5%; tin 0.2%; lead 0.3% iron 0.3%, arsenic 0.08%) for 7 h per day on five days per week for 52 weeks. After cessation of exposure, the animals were observed for 4 months. 27% of with antimony trioxide treated females developed lung tumours.

The lung tumours found were nine squamous-cell carcinomas, five scirrhous carcinomas and eleven bronchioloalveolar adenomas or carcinomas. 25% of with antimony ore concentrate treated females developed lung tumours (nine squamous-cell carcinomas, four scirrhous carcinomas and six bronchioloalveolar adenomas or carcinomas). No significant differences in survival between treated and control groups were found. No lung tumour was seen in treated males or in male or female controls. The incidence of other tumours was not different between treated and control rats (Groth et al., 1986 (cited in Elinder and Friberg, 1986 and IARC, 1989)).

No data on carcinogenicity in case of inhalation of other antimony compounds are available.

According to IARC (1989), there is sufficient evidence for the carcinogenicity of antimony trioxide in experimental animals. There is limited evidence for the carcinogenicity of antimony trisulphide in experimental animals. It may be concluded that female rats are more susceptible to antimony compounds than male rats.

Oral exposure

Lifetime administration of antimony tartrate ($5 \text{ mg Sb.l}^{-1} = 0.43 \text{ mg.Sb.kg}^{-1} \text{ b.w.}$ (rat) or $0.5 \text{ mg.Sb.kg}^{-1} \text{ b.w.}$ (mouse)) in drinking water) did not induce an increase in tumour incidence in mice or rats (Kanisawa and Schroeder, 1969; Schroeder et al., 1968 and Schroeder et al., 1970 (cited in Mulder et al., 1986 and NIOSH, 1978)).

Human data

The ACGIH (1983: cited in Elinder and Friberg, 1986) refers to unpublished data on mortality among workers in a large antimony smelter in the United Kingdom. In the 1960s, exposure to antimony, mainly in the form of antimony trioxide, ranged from 0.5 to 4 mg.m^{-3} . Apart from antimony, the workers were also exposed to zirconium. The data cited are difficult to interpret, but there appears to be an increased proportional mortality in lung cancer among the most heavily exposed men. Smoking habits were not reported. Davies (1973: cited in NIOSH, 1978) found similar results, but the absence of pertinent information, including community and factory population descriptions, data analysis and environmental, blood, and urine antimony concentrations make it impossible to accept the findings without further scientific evaluation and confirmation (NIOSH, 1978).

According to IARC (1989), there is inadequate evidence for the carcinogenicity of antimony trioxide and antimony trisulphide in humans. Other antimony compounds have not evaluated. According to CEC (1989), epidemiological studies suggest that occupational exposure to antimony trioxide could be associated with an excess of lung cancer. The ACGIH concluded that antimony oxide should be regarded as a suspected carcinogen.

5.1.4. Reproductive and developmental toxicity

Few data are available on reproductive effects of antimony and antimony compounds (metallic antimony, antimony trioxide and mixed dusts) in animals and humans.

Animal data

Female rats were exposed by inhalation for 4 h per day for 1.5-2 months to 0 or 250,000 $\mu\text{g}\cdot\text{m}^{-3}$ antimony trioxide (Belyaeva, 1967 (cited in IARC, 1989 and NIOSH, 1978)). They were then mated, and exposure continued until days 3-5 before expected delivery. Pregnancy was obtained in 16/24 treated females and in 10/10 controls. Litter size and weight of offspring at birth and weaning were not altered by exposure to antimony trioxide. Experimental animals that became pregnant produced fewer offspring per animal than controls. Microscopic studies of all treated animals showed uterine and ovarian changes. Gross inspection of the placentas and newborns, and microscopic examination of several fetuses showed no morphological changes. According to NIOSH (1978) however, a definitive interpretation of Belyaeva's work is not possible without further evidence.

Pregnant female rats (six to seven per group) were exposed by inhalation to 0, 27, 82 or 270 $\mu\text{g}\cdot\text{m}^{-3}$ antimony trioxide (0, 22, 69 or 220 $\mu\text{g Sb}\cdot\text{m}^{-3}$) for 24 h per day for 21 days (Grin et al., 1987 (cited in IARC, 1989)). Fetal growths and viability were assessed at the end of gestation. Maternal body weight gain was not effected by exposure, but, at the high-dose level, increased pre- and postimplantation loss of embryos was observed. At the mid-dose level, preimplantation loss and fetal growth retardation were evident. These (no) effect concentrations are, however, difficult to interpret. The data were derived from a Russian article, which is very short and does not present detailed information. Compared to other studies the observed (no) effect concentrations are very low. Further, in contrast to the quotation by IARC only biochemical alterations in the blood were observed at the mid-dose level. Therefore this study can not be evaluated.

Bradley and Fredrick (1941: cited in NIOSH, 1978) noted frequent abortions in rabbits given repeated high oral doses ($>55 \text{ mg}\cdot\text{kg}^{-1}$ every other day for a period of more than 90 days) of metallic antimony. In other studies on antimony compounds no reproductive effects were observed.

Human data

Evidence of effects of antimony on reproduction is confined to a single report. Belyaeva (1967: cited in NIOSH, 1978 and IARC, 1989) observed reproductive disorders among women working at an antimony metallurgical plant. A group of 318 antimony-exposed (mixed dusts of antimony metal, trioxide and pentasulphide) female workers was stated to have had higher incidences than controls of late-occurring spontaneous abortions (12.5% vs 4.1%) and premature births (3.4% vs 1.2%). The average birth weights of the 70 children of the exposed women were similar to those of the 20 children of the control women (3,360 g and 3,350 g, respectively); however, at one year of age, the children of the exposed women were significantly lighter than the control children (8,960 g and 10,050 g respectively).

5.2 ECOTOXICITY

5.2.1. Bioaccumulation and biomagnification

Antimony has a low to moderate potential for bioaccumulation in both freshwater and marine species (EPA, 1979; Mulder et al., 1986). Bioconcentration factors (BCF: ratio of the Sb-concentration in the organism in mg per kg (wet weight)

divided by the concentration of the Sb-concentration in water in mg per l) vary from 40 up to 27,000 (Chapman et al., 1968; Mulder et al., 1986). In table 5.3 the average BCF are presented as estimated for the various species). Taking into account the moderate bioaccumulation potential and the finding of lower Sb-levels in higher organisms biomagnification will not occur.

Table 5.3 Bioaccumulation factors of antimony (based on wet weight unless specified otherwise) (Mulder et al., 1986; Chapman et al., 1968)

Biota	Bioaccumulation factor	
Plants		
- freshwater	1,000	
- marine	50 - 100,000	(dry weight)
Crustaceans	200	
	1,000	(dry weight)
Molluscs	1,000	(dry weight)
Fish	80	
	400	(dry weight)

5.2.2. Aquatic species

Aquatic toxicity data on antimony are scarce. In table 5.4 a summary is given of the available toxicity data. Large differences have been observed, the LC₅₀-96 hr ranging from 0.3 up to 1,100 mg.l⁻¹. Partly, these differences can be explained by differences in test species and life-stages. It should be noted, however, that some data are inconsistent. For example, Mulder et al. (1986) presented results of Denuit et al. (1982), showing LC₅₀-values increase with exposure time for the same species. Further large differences have been observed between LC50 values for fish, ranging from 0.0006 mg.l⁻¹ for C. carpio (Marking and Bills, 1981; in Nikunen et al., 1990), which is at the level of environmental background values, up to 1,100 mg.l⁻¹ for L. idus (Juhnke and Lüdemann (1978), which level likely exceeds the solubility limit in water.

Additionally, Mulder et al. (1986) reported on a study by LeBlanc and Dean (1984), stating that the hatching of fathead minnows (P. promelas) embryos and survival and growth of the larvae was unaffected by exposure to an Sb concentration of 7.5 µg.l⁻¹. No information however was presented as to the lowest effective concentration and so there is doubt whether this level could be considered to be a NOEC.

Table 5.4. Acute and chronic toxicity data on antimony in mg.l⁻¹ (chemical form SbCl₃, Sb₂O₃ or K[Sb(OH)₆) derived from laboratory experiments with various freshwater and marine species

Species	Exposure time	Criterion	L(E)C50 NOEC	Reference
Bacteria				
M. aeruginosa	8 d	growth	33	Bringmann and Kühn (1978)
Algae				
S. capricornutum	4 d	growth	0.63	US EPA (1978)
S. costatum*	4 d	growth	> 4.2	
Protozoa				
E. sulcatum	3 d	growth	120	Bringmann (1978)
Crustaceans				
D. magna	2 d	mortality	19	LeBlanc (1984)
C. maenas *	4 d	mortality	1.3	Denuit et al. (1982)
Worms				
T. tubifex	4 d	immobility	680	Khangarot(1991)
Amphibians				
G. carolinensis	4 d	mortality	0.3	Birge et al. (1979)
Fish				
C. variegatus *	4 d	mortality	6.2-8.3	Heitmuller et al. (1981)
L. idus	2 d	mortality	1,100	Juhnke and Lüdemann (1978)
P. promelas	?	mortality	22	LeBlanc (1984)

* : marine species

5.2.3. Terrestrial species

No toxicity data are available for soil organisms.

5.3 TOXICOLOGICAL LIMIT VALUES

5.3.1. Humans

Epidemiological studies among smelter workers indicate an increased mortality due to lung cancer among the most heavily, mainly to antimony trioxide, exposed persons. Most studies had some inadequacies and simultaneous exposure to other substances occurred. Therefore, it is concluded that there is inadequate evidence for carcinogenicity of antimony trioxide and antimony sulphide in humans.

There is sufficient evidence for carcinogenicity of antimony trioxide after inhalation in experimental animals. From the carcinogenicity experiments with rats it appeared that the development of tumours was clearly accompanied by toxicity in the target organ (the lungs). There is limited evidence for carcinogenicity of antimony trisulphide in experimental animals after inhalation. From limited oral studies there are no indications of carcinogenicity.

The major toxic effects in humans involve the gastrointestinal tract, heart, respiratory tract, skin and liver. Most effects have also been reported in animal studies. Trivalent compounds generally are more toxic than pentavalent. Females seem to be more susceptible than males.

One epidemiological study on women working at an antimony metallurgic plant suggest some effect on reproduction, but these data do not allow a definite conclusion. In experimental studies with rats it appeared that antimony compounds cause reproductive and/or embryotoxic effects. No teratogenicity studies were carried out, but from the conducted reproductive studies no indications for teratogenic effects were obtained.

No induction of gene mutations was found in two test systems. Antimony tartrate induced chromosome aberrations in human leucocytes in vitro and in bone marrow cells of rats treated intraperitoneally. A number of indicator tests were carried out. In the rec-assay both positive and negative results were obtained. Trivalent antimony substances were able to induce SCE in vitro, whereas pentavalent compounds did not.

Antimony compounds (like arsenic compounds) inhibit enzymes by binding to SH-groups of proteins.

Antimony is chemically (see periodic system) and biologically closely related to arsenic. Symptoms of acute and chronic toxicity from antimony closely resemble those induced by arsenic. The available data on genotoxic effects of antimony also indicate that the genotoxic profile of antimony compounds resembles that of arsenic compounds, for which there are clear indications that the mechanism of genotoxic action is indirect*. Therefore, and because of the correlation between carcinogenicity and toxicity it seems as yet justified to use a threshold extrapolation method for risk assessment. The assessment of toxicological limit values will be based on experimental studies.

* Note: Arsenic appeared to be quite potent in inducing chromosome aberrations and SCE, and is only very weakly active in inducing gene mutations. A large number of special studies (emphasizing on co-mutagenicity) clearly indicated that the mechanism of action of arsenic is indirect.

Oral exposure

In rats, long-term exposure primarily resulted in effects on the heart, gastrointestinal disturbances and blood changes. In a limited lifetime study rats exposed to 5 ml Sb.l⁻¹ in drinking water (corresponding to 0.43 mg.kg⁻¹ bw) showed decreased longevity and altered blood chemistry (serum cholesterol levels and blood glucose levels). In establishing a limit value, a safety factor of 500 instead of 100 was used to reflect the use of a LO(A)EL. This results in a tolerable daily intake of 0.86 µg.kg⁻¹ bw (WHO, 1992 draft, final document in press).

Inhalatory exposure

Exposure to antimony compounds by inhalation primarily resulted in effects on the lungs. In a carcinogenicity study, in which rats were exposed for 13 months, a lowest observed effect concentration of 1,600 µg.m⁻³ was found. In establishing a limit value a safety factor of 500 was used to reflect the use of a LO(A)EL. This results in a tentative toxicological limit value of 3.2 µg Sb.m⁻³.

5.3.2. Ecosystems

Surfacewater

The reliability of various aquatic toxicity data is uncertain. Yet, some data will be used to derive a indicative maximum permissible concentration in water.

Since there are less than four chronic NOEC values the preliminary effect assessment procedure is applied as described in Slooff (1992). Since acute toxicity data are available for (green) algae, crustaceans and fish, a factor of 100 is applied to the lowest acute L(E)C50-value (approx. 0.3 mg.l⁻¹), the result being compared with 1/10 of the lowest chronic NOEC-value (33 mg.l⁻¹). The lowest value is taken as the tentative maximum permissible concentration: 3 µg.l⁻¹.

Soil

No data are available (toxicity data or partition coefficients) to derive an indicative maximum permissible concentration of antimony in soil.

6. EVALUATION

Antimony is a naturally occurring but non essential element, resembling arsenic both chemically and biologically. In contrast to the other heavy metals few data are available on the environmental concentrations which hampers a sound risk evaluation in general.

6.1 RISKS TO HUMANS

On the basis of all data (epidemiological studies, experimental studies, genotoxicity tests, metabolism studies) it was concluded (see section 5.3.1) that, with regard to the carcinogenic effects of antimony, there are insufficient arguments to use a "non-threshold" extrapolation method for risk assessment. The toxicological limit values are based on experimental data on rats for both oral and inhalatory exposure.

In establishing a limit value for oral exposure a safety factor of 500 was applied to the lowest observed adverse effect level (decreased longevity and altered blood chemistry) found in a drinking water study, resulting in a tolerable daily intake of $0.86 \mu\text{g}\cdot\text{kg}^{-1}$ bw. Data on daily intake are controversial but are estimated at 10 to $20 \mu\text{g}$, corresponding to 0.17 to $0.33 \mu\text{g}\cdot\text{kg}^{-1}$ bw based on a body weight of 60 kg. Therefore the risks of antimony in food and drinking water for humans is considered to be small, if present at all.

In establishing a limit value for inhalatory exposure a safety factor of 500 was applied on the lowest observed adverse effect level (lung toxicity) in a 13-months study with rats, resulting in a tentative maximum tolerable concentration of $3.2 \mu\text{g Sb}\cdot\text{m}^{-3}$. An average exposure concentration in urban areas of $23 \text{ ng Sb}\cdot\text{m}^{-3}$ has been reported (see table 4.6). These data, however, refer to the situation of 20 years ago and may need updating. More recent data mention concentration levels between 2 and $9 \text{ ng Sb}\cdot\text{m}^{-3}$ for rural areas and between 6 and $35 \text{ ng Sb}\cdot\text{m}^{-3}$ near industry. Based on these data the risk of current antimony concentrations in outdoor air is considered to be small.

6.2 RISKS TO ECOSYSTEMS

Based on the available aquatic toxicity data in section 5.3.2. a tentative maximum tolerable concentration of $6 \mu\text{g.l}^{-1}$ was derived (as "dissolved" Sb; $< 0.45 \mu\text{m}$). The average antimony concentrations in Dutch surface waters are usually below $1 \mu\text{g.l}^{-1}$ (which is the detection limit of most measuring results presented) with peak levels of $3 \mu\text{g.l}^{-1}$. Locally higher levels however may occur, for instance in the vicinity of pigment industries, the average Sb concentrations (total) in the waste water ranging from 12,700 to 52,000 $\mu\text{g.l}^{-1}$. Therefore the risk of antimony to aquatic organisms is within acceptable limits for Dutch surface waters, possibly excepted localities in the vicinity of waste water outlets (pigment and light bulb industry; see table 3.8 and table 4.4).

There are no data on the toxicity on sediment inhabiting organisms, whereas information on the partitioning coefficient water/sediment is also lacking. Therefore no (tentative) maximum tolerable concentration in sediment has been proposed. Data on antimony concentrations in uncontaminated sediments, however, indicate that the risks in the top layer of the sediment in the Netherlands are probably negligible in general: world-wide these concentrations vary between 0.15 and 20 mg.kg^{-1} dw, whereas antimony concentrations in suspended particles in Dutch fresh waters vary between 0.2 and 1.9 mg.kg^{-1} dw. Localities in the vicinity of outlets of municipal and industrial waste (concentrations up to 50 mg.kg^{-1} dw) very well could be at risk.

A point that needs attention is the amount of antimony that lands up in the sediment as result from hunting and sport fishing (18,000 kg Sb each year).

No data are available to derive a maximum tolerable concentration in soil. Average antimony levels in the Netherlands usually vary between 0.3 and 3 mg.kg^{-1} dw, which is probably in the range of naturally occurring levels. Locally historical dump sites show much higher concentration levels. A point that needs attention is the amount of antimony that lands up in the soil as result from shooting and hunting (16,000 kg Sb each year).

7. RECOMMENDATIONS

For man the current antimony levels in food and drinking water as well as in the air seem to be within the tentative toxicological limits.

Also the risk of antimony to aquatic organisms is generally within acceptable limits for Dutch surface waters and sediments. However, in the vicinity of waste water outlets (pigment and light bulb industry) the tentative proposed maximum tolerable concentration may be exceeded. Confirmation by a single measuring programme is proposed, indicating also the extent of exceeding the proposed limit values.

The risks to soil organisms is believed to be within acceptable range (historical dumping sites excepted) and at this stage no priority should be given to ecotoxicological effect studies.

Antimony needs further attention as to the contamination of soil and surfacewater due to shooting, hunting and sport fishing (diffuse pollution with 34,000 kg Sb yearly). It is recommended to evaluate the effects of these activities as such, including the harmful effects of other contaminants such as lead (Janus et al., 1992).

It is recommended not to initiate an evaluation activity at the level of an integrated criteria document.

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APPENDIX A

PHYSICAL/CHEMICAL CHARACTERISTICS OF ANTIMONY AND SOME ANTIMONY COMPOUNDS

Antimony (Lide, 1990; Royal Society of Chemistry, 1989)

chemical formula:	Sb
atomic number:	51
atomic weight:	121.75
physical form:	metal, crystalline (hexagonal)
colour:	silver-white
melting point:	630.5°C
boiling point:	1,750°C
density:	6.684 at 25°C
vapour pressure:	1 mm Hg at 886°C
oxidation states:	+5, +3 or -3
solubility:	insoluble in water
CAS registry number:	7440-36-0
common names:	antimony regulus, regulus of antimony, stibium

Antimony trioxide (IARC, 1989; Lide, 1990; Mulder et al., 1986; NIA, 1990)

chemical formula:	Sb ₂ O ₃
molecular weight:	291.5
physical form:	crystalline: cubic (senarmontite); rhombic (valentinite)
colour:	white (senarmontite); colourless (valentinite)
melting point:	656°C
sublimation point:	1,550°C
density:	5.2 (senarmontite); 5.67 (valentinite)
solubility:	0.014 g.l ⁻¹ water at 30°C; soluble in KOH, HCl, tartaric acid and acetic acid; insoluble in organic solvents
CAS registry number:	1309-64-4; (12412-52-1 senarmontite); (1317-98-2 valentinite)
common names:	antimonous oxide, antimony(III)oxide, antimony sesquioxide, antimony bloom, antimony oxide, antimony white, diantimony trioxide, exitelite, flowers of antimony, weisspies-glanz

Antimony trisulphide (IARC, 1989; Lide, 1990; Mulder et al., 1986)

chemical formula:	Sb ₂ S ₃
molecular weight:	339.68
physical form:	crystalline: rhombic; amorph
colour:	black (rhombic); yellow red (amorph)
melting point:	550°C
boiling point:	1,150°C
density:	4.64 (rhombic); 4.12 (amorph)
solubility:	0.00175 g.l ⁻¹ at 18°C; soluble in ethanol, NH ₄ HS.K ₂ S, HCl
CAS registry number:	1317-98-2
common names:	antimonous sulphide, antimony black, antimony glance, antimony needles, antimony orange, antimony sesquisulphide, antimony trisulphide colloid, antimony vermilion, black antimony, crimson antimony sulphide, diantimony trisulphide, gray antimony, sulphuret of antimony, stibnite

Potassium antimony tartrate (Lide, 1990)

chemical formula:	$K(SbO)C_4H_4O_6 \cdot 1/2H_2O$
molecular weight:	333.93
physical form:	crystalline
colour:	colourless
melting point:	100°C
boiling point:	-
density:	2.6
solubility:	83 g.l ⁻¹ (cold water); 333 g.l ⁻¹ hot water
CAS registry number:	-
common names:	tartar emetic

Stibine (Elinder and Friberg, 1986; Hommel, 1987; Lide, 1990; Sax and Lewis, 1989)

chemical formula:	SbH_3
molecular weight:	124.77
physical form:	gas (inflammable)
colour:	colourless
odour:	odourless (Elinder and Friberg), disagreeable odour (Sax and Lewis, 1989), unpleasant rotting odour (Hommel, 1987)
melting point:	-88°C
boiling point:	-17.1°C (Lide, 1990); -18.4 (Royal Society of Chemistry, 1989)
density:	4.36 at 15°C (gas); 2.204 at -18.4°C (liquid)
solubility:	200 ml gas in 1,000 ml water; 4.1 g.l ⁻¹
CAS registry number:	7803-52-3
common names:	antimonous hydride, antimony hydride, antimony trihydride, hydrogen antimonide, stilbene
