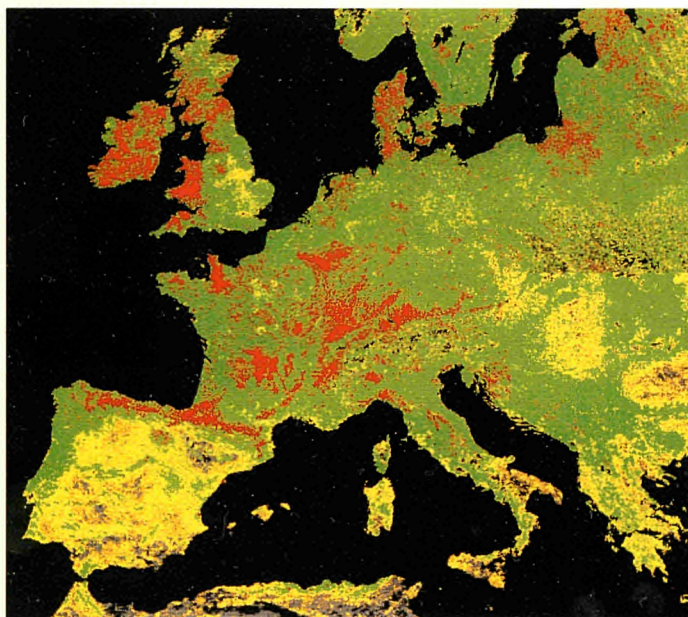

ENVIRONMENT INSTITUTE

ANTIMONY (Sb) IN URBAN AND INDUSTRIAL WASTE AND IN WASTE INCINERATION

by
D. van Velzen and H. Langenkamp



ENVIRONMENT INSTITUTE

ANTIMONY (Sb) IN URBAN AND INDUSTRIAL WASTE AND IN WASTE INCINERATION

by

D. van Velzen and H. Langenkamp

Joint Research Centre
Environment Institute
I-21020 Ispra (VA) Italy



JOINT
RESEARCH
CENTRE

EUROPEAN COMMISSION



1996

EUR 16435 EN

LEGAL NOTICE

Neither the European Commission nor any person acting on behalf of the Commission is responsible for the use which might be made of the following information

Cataloguing data can be found at the end of this publication

Contents

1. Introduction	5
2. Physical and chemical properties	6
3. Toxicological and hazardous properties	7
4. Occurrence and production	8
5. Applications	9
6. Flame retardants	10
7. Antimony in waste and in waste incineration	13
8. The Bamberg study	15
9. Antimony balances	18
9.1 Flame retardants - construction industry	18
9.2 Flame retardants - electrical/electronic industry	18
9.3 Flame retardants - automobile industry and miscellaneous	18
9.4 Metal products	19
9.5 Non-metal products.....	19
9.6 A tentative balance.....	19
10. Conclusions	21
11. References	22

1. Introduction

Nowadays, there is a particular concern that the concentration of antimony (Sb) in the feed of waste incinerators may substantially increase in the near future. This apprehension was expressed in a recent study of Jekel et al. [1].

The reason for this concern is that one of the major applications of antimony is in flame retardants for consumer electronics. It was assumed that the share of this kind of refuse in urban waste will increase in the future due to the discarding of obsolete electronic equipment. This could lead to increased concentrations of antimony in the feed to waste incinerators and, consequently, in the various product streams from incinerators, notably in the waste water from the wet scrubbers.

The flue gas from waste incinerators is usually passed through a series of wet scrubbers to remove gaseous pollutants like SO₂, HCl, HF etc. During this operation, a certain amount of heavy metals (Hg, As, Sb ...) is also dissolved in the washing liquid. Before disposal, the scrubbing liquid is treated for purification. This process includes precipitation of heavy metals in the form of hydroxides. Jekel et al. [2, 3] found in 1990 that only 60% of the antimony was removed by precipitation.

At present, the Sb concentrations in waste water from incineration plants are between 2.3 and 4.0 mg/l, which does not cause any problem in the treatment of spent scrubber liquids. However, with increased concentrations in the future, problems could arise in the waste water treatment due to insufficient removal of antimony.

There is some evidence that antimony is hazardous, due to carcinogenic properties of some of its compounds. In the Council Directive 91/689/EEC antimony and its compounds are classified as hazardous waste.

There is only very poor basic information available about the sources of antimony in municipal waste and about the consequences of the presence of antimony in waste incineration.

This report will try to fill this gap. The following items will be covered:

- a summary of the most important properties of antimony and its compounds,
- quantitative data about the production and the applications of antimony,
- a critical survey of the fate of antimony compounds during waste incineration,
- projections and recommendations for future developments.

2. Physical and chemical properties

Antimony (Sb), atomic number 51, belongs to group 15 of the periodic table which contains also the elements As and Bi. It is placed in the second long period between Sn and Te. It may exhibit valences of +5, +3, 0 or -3 and is classified as a metalloid, although it shows certain metallic characteristics in the trivalent state. There are two stable antimony isotopes with masses of 121 (57.25%) and 123 (42.75%). The relative atomic weight of Sb is 121.76.

Pure antimony is a silvery white, brittle crystalline solid and a poor conductor of electricity and heat. Its melting point is 630.8 °C and its boiling point 1753 °C. It is quite stable and not readily attacked by air or moisture.

Under certain conditions of pH and temperature in the presence of oxidizing agents, dissolution of Sb in aqueous systems can occur with the formation of soluble tri- and pentavalent compounds. These are generally complexes in the form of HSbO_2 , SbO_2^- and SbO_2^+ and are all scarcely soluble.

Antimony reacts with chlorine to form tri- and pentachlorides. Both compounds are very hygroscopic and hydrolyse in aqueous solutions to oxychlorides of various compositions. These compounds are slightly soluble in water and SbOCl can be recovered as a precipitate. The solubility is much higher in alkaline solutions. The antimony chlorides are among the most volatile Sb compounds: SbCl_3 boils already at 283 °C.

Antimony reacts with sulphur to form compounds like antimony red (Sb_2S_3) and golden antimony (Sb_2S_5). Both products are applied in the pyrotechnical industry, in the production of matches and in galvano-technology.

The antimony oxides (Sb_2O_3 , Sb_2O_4 , Sb_2O_5) are white crystalline compounds, soluble in acids and alkaline solutions. Antimony trioxide is frequently used in flame retardants. It represents at present the largest single application of antimony in industry.

Standard text books [4,5] give more detailed information about the chemistry of antimony and its compounds.

3. Toxicological and hazardous properties

An excellent survey of the present knowledge on toxicity effects of antimony and its compounds was given by Slooff et al. in 1992 [6]. They report that the most recent evaluations of the effects of antimony and antimony compounds on humans have been carried out by:

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

Only very few cases of acute and chronic poisoning by antimony, antimony trioxide or antimony hydride have been reported. A more recent study was made in 1994 by Kennntner & Leinemann [7].

The most toxic antimony compound is SbH_3 , which is an inflammable gas with a boiling point of $-17\text{ }^\circ\text{C}$. However, this compound is certainly not present in waste or during waste incineration and, consequently, will not be considered in this report.

Acute toxicity symptoms of antimony and its compounds are abdominal pain, colic, cough, sore throat, loss of appetite and vomiting [8]. There are very few data available on lethal concentrations or on subacute and long term toxicity effects of antimony.

Slooff et al. [6] conclude that, as yet, the risk of antimony in food and drinking water is either small or not present at all. The tolerable daily intake for humans is set at $0.86\text{ }\mu\text{g/kg bw}$ (bw= body weight), whereas the actual estimated daily intake is 0.17 to $0.33\text{ }\mu\text{g/kg bw}$.

Standards and guidelines for antimony concentrations in force in Europe are given below:

- Indoor air (work space MAC) 0.5 mg/m^3 (as Sb dust)
- In flue gases 0.5 mg/m^3 (combined parameter for As, (17. BImSchV - Germany) Co, Ni, Pb, Cu, Sn, Sb, V)
- Drinking water $10\text{ }\mu\text{g/l}$
- Chemical waste 50 mg/kg (dry weight, Sb and Sb compounds)

4. Occurrence and production

Antimony is one of the rarest elements on earth, its abundance in the earth crust is estimated as approximately 0.2 g/t [4] or 0.3 g/t [5]. The most important natural occurrence of antimony is rhombic antimony trisulphide (antimonite or stibnite Sb_2S_3) with 71.7% Sb. Other antimony ores are antimonite oxide (valentinite, senarmonite Sb_2O_3), antimonite hydroxide (stibiconite), antimony oxysulphide (kermesite, pyrostibite $2Sb_2S_3 \cdot Sb_2O_3$). Over one hundred different naturally occurring minerals of antimony have been identified.

The main reserves of antimony are in China, South Africa, Bolivia, Russia and Mexico. The world reserves are estimated to be between 4.5 and 6 million tons, the Chinese reserves being 3.0 - 3.5 million tons.

Data about the world production of Sb are rather inaccurate. Crowson [9] reports that during the 80s the world production was relatively stable at approximately 70 thousand t/y, whereas from 1990 on the production has been decreasing to 53 thousand t/y. Recent data [10] confirm this trend. Table 1 gives a survey of the production by the most important countries over the years 1990 - 1992 [10]. The tendency to a decreasing production rate is evident.

Moreover, China and the former Soviet Union offer antimony to the international market at considerably reduced prices, which tends to cause an overproduction in respect to the needs of the market and stockpiling of the excess. Indeed, there are considerable quantities of antimony stockpiled in various countries, in the USA mainly under the responsibility of the Defence Logistics Agency (DLA). In 1994 sales of stockpiled antimony took place for the first time since 1988 [10]. DLA brought some 3500 tons of antimony on the market from its stockpiles.

A considerable amount of antimony in metal alloys (usually lead) is recycled. For example, in the Netherlands recycling amounts to 375 tons per year, compared with a net import of the order of 1300 t/y [6]. In the U.S. about 20 thousand tons were recycled in 1990 on a total consumption of approximately 39 thousand t/y [9]. The percentage of recycled Sb is gradually decreasing because of the increased use of low maintenance batteries, which use lead alloys containing less or no antimony and the downsizing of automotive batteries which requires less antimony per battery.

It is evident that the general tendency of antimony market during the last decades is towards a decreasing production and consumption.

Table 1: World Antimony Production (t/y).

Country	1990	1991	1992
China	22 000*	15 000*	15 000*
Bolivia	8 454	7 287	6 022
Ex Soviet Union	5 100	4 800	5 000*
South Africa	5 258	4 485	4 400*
Mexico	2 614	2 752	2 500*
TOTAL	43 426	34 324	32 922*

* = Estimate

5. Applications

The applications of antimony can be roughly divided into three categories:

- Metal products
- Non-metal products
- Flame retardants.

Metal products comprise the use of antimony alloys, mainly lead alloys. Antimonial lead is the name of a frequently used Pb/Sb alloy with a concentration of up to 25% Sb. The largest application in this field is as a grid metal in lead acid storage batteries. In the U.S., the second of importance in the category “metal products” is ammunition. Minor applications are bearing metals, cable covering, solder, sheet and pipes etc.

Non-metal product applications of antimony consist of catalysts for polyester manufacture, semiconductors, applications in the production of specialty glasses as decolorizers and opacifiers and in the use of pigments.

The largest single application of antimony compounds today is in *flame retardants*. The main product used is antimony trioxide, nearly always in combination with other chemicals, especially organic bromine compounds. We will discuss the application of flame retardants in a separate chapter, because it is assumed that this is the main source of antimony in waste incinerators.

The distribution of the consumption of primary antimony over the various categories for the years 1975-90 in the U.S. is given in Table 2 [4].

For Europe, the distribution figures are in the same order of magnitude. As an example, Van Ewijk et al. [11] reports that in the Netherlands in 1990 the total antimony consumption was 1055 t/y, divided into the following categories:

Metal products	110 t/y	(10%)
Non-metal products	289 t/y	(27%)
Flame retardants	656 t/y	(62%)

It follows clearly that more than 60% of the total Sb applications is in flame retardants.

Table 2: Consumption of primary antimony in the U.S. in thousands of tons/y [4].

	1975	1980	1985	1986	1987	1988	1989	1990
Metal products	5.13 (43%)	1.50 (15%)	1.49 (14%)	1.44 (14%)	2.31 (22%)	2.78 (23%)	3.02 (22%)	3.13 (25%)
Nonmetal products	3.21 (27%)	3.53 (35%)	2.29 (22%)	2.25 (22%)	2.38 (23%)	2.53 (21%)	2.67 (20%)	2.59 (20%)
Flame retardants	3.45 (29%)	5.17 (51%)	6.83 (64%)	6.43 (64%)	5.68 (55%)	6.76 (56%)	7.74 (58%)	7.02 (55%)
TOTAL	11.79	10.20	10.61	10.12	10.37	12.07	13.43	12.74

6. Flame retardants

The ever increasing application of thermoplastic materials in a large number of industries is accompanied by the necessity of reducing the risk of fires caused by the inflammability of these materials. Typical applications of thermoplastics are the electrical and electronic industry, car manufacture, construction of buildings, furniture and textiles. The inflammability of thermoplastics can be drastically reduced by the incorporation of flame retardants.

The major market areas for flame retardants in Western Europe are plastics, rubber and elastomers, textiles and nonwovens, insulation material, paper and paperboard, in declining order of importance.

A large variety of products is used as flame retardants, depending on the matrix in which they have to be applied and on their influence on the mechanical properties of the basic material. Table 3 gives a survey of the estimated Western European consumption of flame retardants in 1989 and 1994 [12, 13].

There is a large market with a certain tendency to increase with time. The expected average growth rate is in the order of 2.8%/y. The total consumption is in the order of 160 thousand tons per year. Antimony oxide ranks fifth with 12.5 thousand tons per year.

Antimony oxide does not have any notable flame retardant properties itself, but enhances the properties of other products, especially halogenated organic compounds. This synergistic effect is explained by the formation of volatile halogen compounds during combustion. This also explains the fact that antimony trioxide has flame retardant properties without additives when used in standard PVC: the chlorine contained in the PVC serves to form the volatile antimony trichloride.

It follows that antimony oxide is mainly used in combination with brominated or chlorinated organic flame retardants. The most frequent ratios of retardant compound to antimony trioxide are 3:1 for brominated and 5:1 for chlorinated compounds. Organobromine compounds are usually applied in higher quality products, in cheaper products chlorinated paraffins are often sufficient.

In 1989 the quantity of antimony oxide consumed in flame retardants in Western Europe was estimated at approximately 12500 metric tons. This figure corresponds with an antimony consumption pro capita of approximately 25 g/y.cap over a population of about 400 million persons. About 60% of this amount is used in the construction and building industry, 30% in the electrical and electronic industry and 10% in the automobile industry and other less important applications [14].

Table 3: Western European Consumption of Flame Retardants (thousands of tons/y).

Type	1989	1994*
Alumina trihydrate	50.0	58.0
Organophosphorus compounds - nonhalogenated	30.9	32.5
Brominated compounds	28.1	32.1
Chlorinated compounds	19.6	22.7
Antimony oxide	12.5	14.5
Organophosphorus compounds - halogenated	8.6	9.5
Boron compounds	1.7	2.0
Ammonium polyphosphates	1.5	2.0
Red phosphorus	1.0	1.3
Magnesium hydroxide	0.7	2.1
TOTAL	154.5	177.1

* = Estimate

It has been mentioned before that antimony oxide is predominantly used in combination with halogenated chemicals. One of the main applications is in PVC, which requires approximately 25 thousand tons of various flame retardants per year. Flame retardant PVC is used in the building, construction, transportation, wire and cable and packaging industries. The demand for flame retardant PVC is expected to decrease in Western Europe because of substitution trends in building and construction (floor covering) as well as in wire and cable industries (insulation). Several European countries (Austria, Denmark and Switzerland) are considering banning PVC completely from the list of materials to be used in the construction industry.

The other category of flame retardants using Sb are the brominated compounds. There are a number of different groups of these compounds:

- brominated hydrocarbons (mainly aromatic and cycloaliphatic)
- brominated alcohols and phenols (including polyols)
- brominated ethers (mainly aromatic)
- brominated acids and their derivatives

The brominated organic flame retardants generally are very effective, requiring relatively small quantities of flame retardant in the final product. Their activity is considerably enhanced by the use of antimony oxide as a synergist. The most effective products are polybrominated diphenyl ethers, especially decabromodiphenyl ether. This product has been successfully used in the electrical/electronics industry and in polyurethane foam for car seats and upholstered furniture.

The main advantage of the polybrominated diphenyl ethers is their effectiveness. Due to the small quantities needed per unit of product, they have little influence on the physical and mechanical properties of the basic material. On the other hand, polybrominated diphenyl ethers gave rise to considerable concern in environmental authorities in Germany. In 1989, Prof. Hutzinger at the University of Bayreuth [21, 22] discovered dioxins in the combustion products of plastic materials treated with brominated flame retardants pyrolyzed in laboratory equipment. This led to a controversy about the risk of using of decabromodiphenyl ether and a voluntary suspension of the use of the material by a number of companies.

There is a tendency in Germany to replace the brominated flame retardants by other ones, like phosphorus compounds and alumina trihydrate or magnesium hydroxide. Unfortunately, the substitute flame retardants are much less effective than the brominated compounds and, consequently, higher concentrations are needed, which has negative effects on the mechanical and physical properties of the matrix material.

The main conclusion of the foregoing chapter is that there are forces at work which have a negative effect on the production and consumption of halogen containing flame retardants and, evidently, also on the consumption of antimony oxide in this market sector.

7. Antimony in waste and in waste incineration

Relatively little is known about the origins and presence of antimony in waste and in waste incineration. During the last three years there has been an increasing interest in that topic. The thermal treatment of municipal waste is a useful tool for the study of the presence of antimony in waste, as the various product streams of waste incineration can be chemically analyzed and material balances prepared.

Several studies about the Sb content in various waste streams are available. In 1987, van der Beek et al. [15] studied the Sb concentrations in collected municipal waste in Amsterdam, Arnhem and Rotterdam in the Netherlands. The study is concerned with typical small household waste (vegetables, fruits, paper, plastics, glass, bread and carpets), in which an average concentration of 2.9 mg/kg for wet and 5.2 mg/kg for dry waste was determined.

Nakamura et al. [23] reported a Sb concentration of 7.6 mg/kg in household waste in Japan. More than 80% of this figure comes from flame retardants (clothes, curtains, textiles and plastics).

Much higher values are reported by Hesseling [16] for a mixed waste fed to a Dutch Waste Incineration Installation. Here an average input concentration of 20 mg/kg is calculated. Antimony is found in the bottom ash, in the residues of the electrostatic precipitator (electrofilter) and in the fly ash. The concentrations are reported in Table 4, expressed in mg Sb per kg of original dry waste. The individual concentrations in the various fractions can be estimated, taking into account that the bottom ashes normally amount to 280 g/kg original dry waste and the solids from the electrofilter to approximately 25 g/kg.

In this context, the work of Reimann [17, 18] is of great importance. The author carried out extensive chemical analyses of the various residues from the waste incineration plant at Bamberg, preparing mass balances for every single component [17]. In 1995 a special study was dedicated to antimony [18]. The total average antimony concentration of the incoming waste is found to be 38 mg/kg, which is considerably higher than the 20 mg/kg reported by Hesseling in 1987 [16].

Other sources report average Sb concentrations of 42 ± 2 mg/kg [19] and a range of 10-60 mg/kg [20]. All reported values are in the same order of magnitude, but there are important deviations from case to case. The data of the various sources are summarized in Table 4.

The different composition of the various input waste streams is most probably the reason for the discrepancies: The material burned in the waste incinerator at Bamberg is well defined and consists of a mixture of 44% municipal waste, 43% industrial waste and 13% dewatered sludge.

Table 4: Antimony flows and concentrations in several urban/industrial waste incinerators. Data given in mg/kg original dry waste

Waste stream	The Netherlands [16]	Bamberg [18]	Switzerland (EAWAG) [19]	IAWG (Internat.) [20]
Bottom ash	13 ± 6	1 - 37	6 ± 2	3 - 24
Electrofilter precipitate	6 ± 5	2 - 29	36 ± 2	7 - 36
Fly ash	1 ± 1	<0.1	<0.5	<0.5
TOTAL (input)	20 ± 11	3 - 65	42 ± 2	10 - 60

The exact composition of the other wastes in the Netherlands [16], in Switzerland [19] and the one from an international source [20] was not reported, but it is likely that the share of industrial waste in Bamberg and in the Swiss example is higher than in the other two cases.

The antimony concentration in industrial waste is considerably higher than in urban waste, which yields an adequate explanation for the different Sb concentrations found in the various input waste streams. Additionally, it must be noted that the range of variation of all measured concentrations is very large. Reimann reports a bandwidth of 3-65 mg/kg for his average of 38 mg/kg Sb. This very large range is probably caused by the continuously changing composition of the solid refuse which is offered for incineration.

8. The Bamberg study

A detailed study about the fate of antimony in waste incineration was carried out at the waste incineration power plant (Müllheizkraftwerk=MHKW) at Bamberg by Reimann [18]. This study can be considered exemplary and of general validity.

The MHKW Bamberg is a modern waste incineration plant with a capacity of approximately 125 thousand tons of mixed refuse per year, equivalent to 400 thousand inhabitants equivalent. Simultaneously, 100 000 m³ of sewage sludge, containing 3 wt% of dry material is treated in the plant. The sewage sludge is concentrated in two centrifuges to approximately 30% dry material, which is mixed with the solid waste before incineration. The waste burned in the MHKW Bamberg consists of a mixture of 44% municipal waste, 43% industrial waste and 13% of sludge. The total water content is 20-25%.

The maximum capacity of the installation is 18 t/h of refuse with an average caloric value of 8500 - 10000 kJ/kg. The thermal energy of the waste is utilized in three separate boilers, each with a production of 18 tons per hour of saturated steam of 26 bar at a temperature of 225°C, i.e. a total of 54 tons per hour of steam. The steam produced can be used for the production of 7.2 MW electrical energy in a condensation turbine or to feed a district heating network with a maximum heating capacity of 45 MW. The combination of heat and power generation is also possible.

The combustion takes place in a moving grate incinerator with an air ratio of 1.6 - 2.0, which requires a flow of combustion air of 4000 - 5000 m³/t of waste. The produced flue gas is 5000 - 5500 m³/t of waste. The oxygen content of the flue gas is normally between 8 and 10 vol%. The temperature of the gases in the post combustion chamber is >1000°C and the temperature of the burning solid bed is much lower, 300-700°C.

The amount of bottom ash is 296 kg/t of waste, including the iron content. After removal of the iron 284 kg/t remain. The ashes are cooled down and at the same time washed with 150 litres of water per ton of input waste. After the treatment the water has a temperature of 50-60°C and a pH of 12-13. The waste water from the washing is fed to the flue gas purification section. The Sb content of the washing water is a good yardstick for the leachability of antimony from the bottom ash. The experimentally found concentration ranges from 0.002 to 0.5 mg/l, which means that the leachability of Sb from the slags is very low.

The hot flue gases pass through the boiler section where they are cooled down from >1000°C to 230-300°C. Then they pass through the particulate removal section, which consists of an electrostatic precipitator. In this electrofilter approximately 24 kg of filter dust is collected per ton of waste. The concentration of fly ash in the gases leaving the electrostatic precipitator is about 60 mg/m³.

The final flue gas purification consists of two wet scrubbers, which remove HCl, SO₂, HF, HBr and remnants of heavy metals and fine fly ash. The first scrubber is an acid scrubber with a pH of 0.5-1.0, where HCl, HF and heavy metals are absorbed. The specific production of waste water in this scrubber is 210 l/t of waste.

The second scrubber is operating at a pH of 8 by addition of caustic soda and serves mainly for the removal of SO₂. The waste water production of this scrubber is 52 l/t of waste. The two final waste water streams are unified and fed to the municipal sewer system. Before final disposal the waste water is treated with slaked lime and TMT-15 for the precipitation of bivalent heavy metals (Hg!).

The flue gases are reheated to 80-85°C and leave the plant through the stack. During the measuring campaign in Bamberg in 1994-1995, the particulate concentration in the final flue gas was 5-10 mg/m³. At present, after a latest plant modification, these values are considerably lower, 1-3 mg/m³.

The Sb concentration of every single process stream is determined by the methods described in DIN 3844414-S7 and DIN 38406-E22. Samples of the ashes and electrofilter dust are taken every hour, mixed and homogenized. The final samples are used for the daily Sb analysis. The results of the study are based on measuring campaigns carried out during the years 1994-1995. The results of the study are shown in Table 5.

The data for the different waste water streams refer to the untreated streams to avoid errors caused by the addition of additives. The final treated waste water leaving the plant had a Sb concentration of <0.5 mg/l, which represents a Sb load of <0.13 g/t of input waste.

Table 5: Average antimony flows and concentrations in the MHKW Bamberg study [18].

Waste stream	Specific flow rate	Sb content	Specific Sb flow rate (g/t waste)	Sb flow (%)
Bottom ash (dry and free of Fe)	284 kg/t	65 mg/kg	18.4	48.3
Electrofilter precipitate	24 kg/t	808 mg/kg	19.4	50.9
Water from ash washing	100 l/t	<0.05 mg/l	<0.005	<0.01
1st wet scrubber	210 l/t	1.24 mg/l	0.26	0.68
2nd wet scrubber	52 l/t	0.042 mg/l	0.002	<0.01
Fly ash in flue gas	5200 m ³ /t	0.005 mg/m ³	0.026	0.07
TOTAL (input)			38.1	100.0

The results of the study can be summarized in a number of conclusions:

- About 50% of the Sb input remains in the bottom ash. This part of the antimony consists of metallic Sb or Sb_2O_3 . The bed temperature of the incinerator is not sufficiently high to evaporate these compounds.
- The leachability of the slags in the alkaline washing water is below the detection limit.
- Nearly all of the other half of the Sb is found in the particulate, separated in the electrostatic precipitator. This means that an effective particulate removal at temperatures of about 180 °C will be sufficient for a complete Sb removal. If electrostatic precipitators will not be sufficiently effective, bag filters can be used for this purpose.
- The amount of antimony found in the first wet scrubber is 0.26 g/t. To all probability, this is caused by fly ash which is not precipitated in the electrofilter. The solids are then partly absorbed in the acidic scrubbing water. We assume that the Sb concentration in the fly ash having passed the electrofilter is equal to the value found in the dust from the electrostatic precipitator (808 mg/kg). The fly ash concentration is 60 mg/m³ and the flue gas rate 5200 m³/t of input waste. This means that the calculated amount of Sb entering into the acid scrubber is 0.25 g/t of input waste, which is very near to the value experimentally found.
- The Sb concentrations in the various waste water streams are very near or below the detection limit. This is a strong indication that there are no volatile Sb compounds present in the flue gas.

Separate analyses have shown that the Sb content of the sewage sludge, which forms part of the feed to the incinerator, is very low, namely about 3 mg/kg. By means of this figure the calculation of the average Sb content of the solid waste input can be corrected. Including this correction, the antimony concentration of the *solid waste fed to the MHKW Bamberg* is estimated to be in the range of 5-70 mg/kg, with an average of 40-45 mg/kg.

9. Antimony balances

According to Table 2 in Chapter 5 the antimony consumption can be roughly divided into three categories:

- 60% flame retardants
- 20% metal products
- 20% nonmetal products.

The flame retardants are again subdivided into three application fields:

- 60% construction (36% of the total Sb)
- 30% electrical-electronics (18% of the total Sb)
- 10% automobile industry and miscellaneous (6% of the total Sb).

Moreover, a huge part of the Sb consumed in metal products is recycled.

It is of interest to estimate the fate of the antimony of the various categories, especially with the view on the maximum quantity to be expected in the feed streams to waste incinerators.

9.1 *Flame retardants - construction industry*

The main application of this category is in piping, insulation and floor covering inside buildings. These materials have a very long life time (several decades). In case of demolition of the building, the larger part of the material is landfilled or treated as special waste. Only a minor quantity of the antimony used in this sector is offered to waste incinerators.

It can be estimated that at maximum about 15% of the antimony used in this sector will end up in the feed for waste incinerators.

9.2 *Flame retardants - electrical/electronic industry*

This is the category which causes the main concern. Indeed, all the material is in principle consumer material with a life time of less than a decade, excepted the electrical wiring used in buildings. Conservatively we assume that all (100%) of the antimony used in this sub-sector is found sooner or later in domestic and industrial refuse.

9.3 *Flame retardants - automobile industry and miscellaneous*

The average life time of modern cars is about ten years. At the end of this period the used cars are demolished. In the best of cases a certain amount of the material is recycled. Generally, the upholstery, carpets etc. is disposed of as special and/or toxic waste. It is highly improbable that a considerable amount of this category will be mixed with municipal and/or industrial waste. The contribution of this category to waste incineration can thus be neglected.

The use of flame retardants in the textile industry is included in the sector automobiles/miscellaneous. The share is relatively small, not more than 30%, i.e. 3% of the total amount of antimony. However, the totality of this sub-sector ends up in the domestic or industrial waste streams. Therefore we assume that 30% of the antimony used in the sector automobiles/miscellaneous in the feed of waste incinerators.

9.4 Metal products

A large quantity of the antimony belonging to this sector is recycled and thus does not end up in the refuse. Another significant part of the alloys becomes chemical waste and does not belong to urban waste. Moreover, a significant part of the alloys is used for hunting and fishing. This part of the flow of antimony ends up directly in the environment.

Finally, there is also an important amount of antimony from metal products ending up in the urban waste. According to a conservative estimation a maximum of about 50% of this category is of interest for domestic and industrial waste.

9.5 Non-metal products

This category contains applications such as glass manufacture, catalysts, pigments, fireworks etc. At the end of their useful life, the greater part of the glass and pigments are found in urban and industrial waste. All the catalysts are collected and partly recycled. The Sb used in fireworks is, in the nature of things, directly sent into the environment. There are no exact data available, but it may be assumed that a maximum of about 60% of the Sb from this sector is found in the urban and industrial refuse.

The percentages presented above are, naturally, speculative. A factor that has not been taken into consideration is that the various categories are including only the end products, whereas the consumption figures are referring to the total input of material. All losses during manufacture are not considered. This adds another few percents of antimony discharged to the sewage system, dumped or recycled and decreases the assumed maximum load figures.

The tentative antimony balance for the urban and industrial waste is made up in Table 6.

From the data given in Table 6, it can be concluded that maximally about 47% of the antimony production may end up in urban and industrial waste. Approximately 50% of this quantity originates from flame retardant applications.

9.6 A tentative balance

The total consumption of antimony of the European Community (1990) was 20500 t/y [9]. Taking into account that the total population is about 360 millions, the *specific antimony consumption per capita* is calculated at 57 g/y.cap.

Other data [6, 11] quote an antimony consumption of approximately 1000 t/y in the Netherlands for a population of 15 millions. This gives a specific antimony consumption of 67 g/y.cap.

Table 6: Tentative antimony material balance.

Category	Application	To urban waste	Maximum Sb load to urban waste
Flame retardants - construction	36%	15%	5%
Flame retardants - electrical	18%	100%	18%
Flame retardants - automobiles	6%	30%	2%
FLAME RETARDANTS - TOTAL	60%	38%	25%
METAL PRODUCTS	20%	50%	10%
NON METAL PRODUCTS	20%	60%	12%
TOTAL (input)	100%		47%

This figure includes the amount of Sb exported later, which is approximately 20% of the total. A correction made for the export reduces the figure for the specific antimony consumption in the Netherlands to 53 g/y.cap.

Since it is based on data valid for the whole European Community, the figure of 57 g/y.cap is adopted as the average antimony consumption in the Community and used in the following balance calculations.

The analysis summarized in Table 6, shows that maximally about 47% of the antimony production ends up in urban and industrial waste. The expected flow of antimony to waste incineration plants is therefore approximately equal to 47% of 57 g/y.cap, i.e. 27 g/y.cap.

The contribution of Sb in flame retardants of the electronics industry is not more than 10 g/y.cap (18% of 57 g/y.cap). The estimate is based on the assumption that all flame retardants used in this sector are ending up in the urban waste. This assumption is conservative, the real figure is certainly lower. It follows that the contribution of the electronic equipment is important, but certainly does not represent the principal source of Sb to waste incinerators.

In chapters 7 and 8 we have shown that the average Sb concentration of the feed stream to waste incinerators is approximately 42 mg/kg. The average waste production per capita in Europe is approximately 400 kg/y.cap. Consequently, the present load of antimony in municipal waste is somewhere about 17 g/y.cap.

This figure is rather close to the conservative estimation of the maximum expected load calculated in the third paragraph of this chapter. An increase of the share of electronic waste has only a minor influence on the total Sb concentration in urban refuse. Therefore it is not likely that a dramatic increase of the antimony load in waste incinerators due to an increase of electronic waste will occur in the near future.

10. Conclusions

The present study is intended to give topical information about the sources of antimony in municipal waste and about the consequences of the presence of antimony in waste incineration. The conclusions of this study can be summarized as follows:

- The main source of antimony in the feed to municipal waste incinerators is originating from flame retardant applications.
- There are no signs that the market for antimony in general and for antimony in flame retardants in particular will be significantly increasing in the near future. On the contrary, there is a certain tendency to the application of antimony free flame retardants and to a decreasing consumption in the sector of antimony alloys.
- There are no indications that a strong increase in the feed of antimony to urban waste incinerators has to be anticipated in the near future. The present antimony load is already covering a large part of the expected maximum possible feed rate. The results of our study do not support the concern of Jekel et al. [1].
- During the waste incineration process the antimony compounds are found in the residue (bottom ash) and as solid products in the fly ash. It follows that modern waste incinerators, equipped with efficient dust removal systems such as electrostatic precipitators or bag filters *before the wet scrubbing section*, have no difficulties to meet the requirements of the European legislation concerning the quality of the waste products from waste incineration.

The last statement may not apply to a minority of waste incinerators, which do not cool down the flue gases to 230-300 °C, but apply direct quenching of the hot flue gases before particulate removal. In this case, a considerable part of the antimony, present in the fly ash, is collected in the acid quenching liquid. This liquid has to be purified before final disposal and has to meet the Sb concentration limits for waste water.

It is concluded that there seems to be no urgent need for actions in the field of waste management in connection with a future increase of the load of antimony to waste incinerators. However, data about antimony in waste are very scarce. Also reliable data on the toxicity and the carcinogenic properties of antimony compounds are largely outstanding. There is certainly an open field for further research on these items.

11. References

- [1] M. Jekel, R. Enders, J. Ritz, C. Vater & A. Grohmann, "Ganzheitliche Untersuchung des Reststoffproblems bei Abfallverbrennungsanlagen: Nassverfahren ohne Abwassereinleitung", Abschlussbericht zum Vorhaben des Bundesministeriums für Forschung und Technologie, No. 1450548 3, Berlin Juli 1993
- [2] M. Jekel, J. Ritz & C. Vater, "Abwässer und deren Behandlung" in K.J. Thomé-Kozmiensky (Ed.) "Müllverbrennung und Umwelt 5", p. 375, EF Verlag, Berlin 1990
- [3] R. Enders, C. Vater & M. Jekel, "Antimon im Abwasser von Abfall-verbrennungsanlagen", Müll und Abfall 22 (12) 784 (1990)
- [4] Kirk-Othmer Encyclopedia of Chemical Technology, 4th Edition, Volume 3, pp. 367-407, John Wiley & Sons, New York 1992
- [5] Ullmanns Encyclopädie der technischen Chemie, 4^o Auflage, Band 8, "Antimon und Antimon-Verbindungen", pp. 1-17, Verlag Chemie, Weinheim 1974
- [6] W. Slooff, P.F.H. Bont, J.M. Hesse & B. Loos, "Exploratory Report Antimony and Antimony Compounds", Dutch National Institute of Public Health and Environmental Protection (R.I.V.M.), Report No. 710401020, October 1992
- [7] M. Kenntner & M. Leinemann, "Umwelt- und arbeitsmedizinische Bedeutung von Antimon und seinen wichtigsten Verbindungen", Zbl Arbeitsmed. 44 (1994)
- [8] "IARC Monograph on the evaluation of carcinogenic risks to humans. Some organic solvents, resin monomers and related compounds, pigments and occupational exposures in paint manufacturing and painting", International Agency for Research on Cancer, Lyon 1989, ISBN 92 832 1247 9, pp. 291-305
- [9] P. Crowson "Minerals Handbook 1992 - 1993", Stockton Press, New York 1992
- [10] Metals & Minerals Annual Review - 1994, The Mining Journal Ltd, London 1994, pp 76-77
- [11] M. van Ewijk, C.J.M. Koning & J.P.M. Ros "Toepassingen en emissies van de aandachtstof antimoon", Dutch National Institute of Public Health and Environmental Protection (R.I.V.M.), Report No. 736301004, December 1990
- [12] Frost & Sullivan "The European Market for Flame Retardants Chemicals" (E1488 P, February 1991)
- [13] Specialty Chemicals - SRI International "Flame Retardants" June 1991
- [14] Personal communication with Mr. P. Rooze of Campine S.A. Brussels, 28.11.95
- [15] A.I.M. van de Beek, A.A.J. Cornelissen & T.G. Aalders, "Fysisch en chemisch onderzoek aan huishoudelijk afval van 1987, inclusief batterijen", Dutch National Institute of Public Health and Environmental Protection (R.I.V.M.), Report No. 738505007, 1989
- [16] W.F.M. Hesseling, "Onderzoek emissies afvalverbrandingsinstallaties", TNO/MT Reports No. 87726-16068 and 8726-13611, November/December 1987
- [17] D.O. Reimann, "Heavy metals in domestic refuse and their distribution in incinerator residues", Waste Management and Research 7, 57-62 (1989)
- [18] D.O. Reimann, "Antimon (Sb) - im Abfall sowie quantitativer Vergleich zu weiteren Restabfallinhaltsstoffen" Kurzbericht UO1/539A/AM, December 1995
- [19] H. Belevi, "Dank Spurenstoffen ein besseres Prozessverständnis in der Kerichtverbrennung", EWAG News 40^D, November 1995
- [20] IAWG, "An international perspective on characterization and management of residues from municipal solid waste incineration", Final Document, International Ash Working Group (1995)
- [21] O. Hutzinger, R. Dumler, H. Thoma & D. Lenoir, "Thermal formation of polybrominated benzodioxins (PBDD) and dibenzofurans (PBDF) from bromine containing flame retardants", Chemosphere 19, 305-308 (1989)
- [22] O. Hutzinger, R. Dumler, H. Thoma & D. Lenoir, "PBDF and PBDD from the combustion of bromine containing flame retarded polymers - a survey", Chemosphere 19, 2023-2031 (1989)
- [23] K. Nakamura, S. Kinshita & H. Takatuki, "The origin and behaviour of lead, cadmium and antimony in MSW incinerators. Seminar on cycle and stabilization technologies of MSW incineration residues", 5-8 March 1996, Kyoto Research Park, Japan.

European Commission

EUR 16435 – Antimony (Sb) in urban and industrial waste and in waste incineration

D. van Velzen, H. Langenkamp

1996 – 24 pp. – 16.2 x 22.9 cm

Environment and quality of life series

Catalogue number CL-NA-16435-EN-C

The sources of antimony in municipal waste and the consequences of the presence of antimony in input of waste incinerators were investigated. It is concluded that more than 50% of the antimony is originating from all types of flame retardants and that about 35% of the antimony stream is coming from flame retardants from consumer electronics.

The remainder is coming from metal and miscellaneous applications of antimony.

There is a tendency to decrease the application of halogenated products (and thus of antimony) in flame retardants. Also the other fields of application of antimony show a decreasing trend.

There are no indications that a substantial increase of the concentration of antimony in the feed to municipal waste incinerators will occur in the near future.

During the incineration process, the antimony compounds are only found in the bottom ash and in the fly ash. No volatile Sb compounds are present in the flue gas. This means that efficacious particle removal systems are sufficient for a complete Sb removal during incineration.

