Environment Canada
Environnement Canada

CANADA CENTRE FOR INLAND WATERS
CENTRE CANADIEN DES EAUX INTERIEURES

ANTIMONY

ITS PRODUCTION AND USE IN CANADA

- A Background Paper -

D. B. Lymburner
H. Knoll
Social Sciences Research

UNPUBLISHED REPORT
RAPPORT NON PUBLIE

DRAFT COPY

(Not for Publication)

ANTIMONY

ITS PRODUCTION AND USE IN CANADA

- A Background Paper -

D. B. Lymburner H. Knoll

Social Sciences Research

May 1973

OCCURRENCE OF ANTIMONY

Antimony ore deposits are generally small, and dispersed throughout the world. There are few deposits of antimony wherein ore is developed in advance of current mining requirements.

The primary ore mineral of antimony is stibnite, chemically named antimony trisulphide. Complex ores of stibnite containing lead, copper, silver, and mercury can be important sources of antimony. From those complex ores meagre in antimony, the antimony is usually recovered as a by-product.

In Canada lead smelting operations yield antimony as a by-product, mainly in the form of antimonial lead. Canada's estimated ore reserves are between 200,000 and 350,000 tons. These ore reserver are located in New Brunswick and in the Yukon.

In 1965 the Yukon Antimony Corporation Ltd. reported the finding of reserves in the Carbon and Chieftain hills of the Wheaton River district. The reserve comprises 250,000 tons of 5% antimony ( ).

Since 1971 Consolidated Durham Mines and Resources Ltd. has been exploiting a deposit which may yield 100,000 tons of ore containing 7% antimony ( ). This particular mine is located in the Lake George area near Fredericton, N.B.

Mexico, U.S.S.R., South Africa, and Bolivia have ore deposits similar in size to that of Canada. The largest ore findings are in China. These are as large as all those of the rest of the world combined.

PRODUCTION OF ANTIMONY

In terms of world production Canada's contribution to the antimony supply is relatively small: 200 - 400 tons annually compared with a world production of about 76,000 tons (FIG.). The world supply of antimony has been generally adequate to meet the demand; and in industrialized countries, secondary production adds significant amounts of antimony to the available supply source.

Although world production has increased approximately fourfold in the past 40 years, this increase has been irregular.

The unsteady growth rate reflects the economic cycles involving pre- and post-war activities, and the implications of increased demand for antimony during the war.

Also, there have been drastic changes in the channels of supply to the world market. China, once an important supplier of large amounts of antimony ores, metal, and antimony oxide to the U.S.S.R. and its political allies, has curbed its trade. This has led to expanded production of antimony in North and South America, and Europe, to compensate for the decreased world supply ( ). The reduction of the Chinese supply has also caused an increase in South Africa's production of antimony in recent years.

China has great domestic need for antimony now for the manufacture of antimonial lead batteries to supply power to their electric trucks and buses.

Prices have exhibited cyclic fluctuations with long intervals of relative price stability. For example, prices were unchanged for five years prior to 1969. Then, in a series of increases, prices jumped from 44.7cents per pound to $1.78.. Price increases in 1969/70 were caused by a dock strike at U.S. ports, the withdrawal of China as a foreign supply source, an increase in demand, and the depletion of antimony from the U.S. Government stockpile.

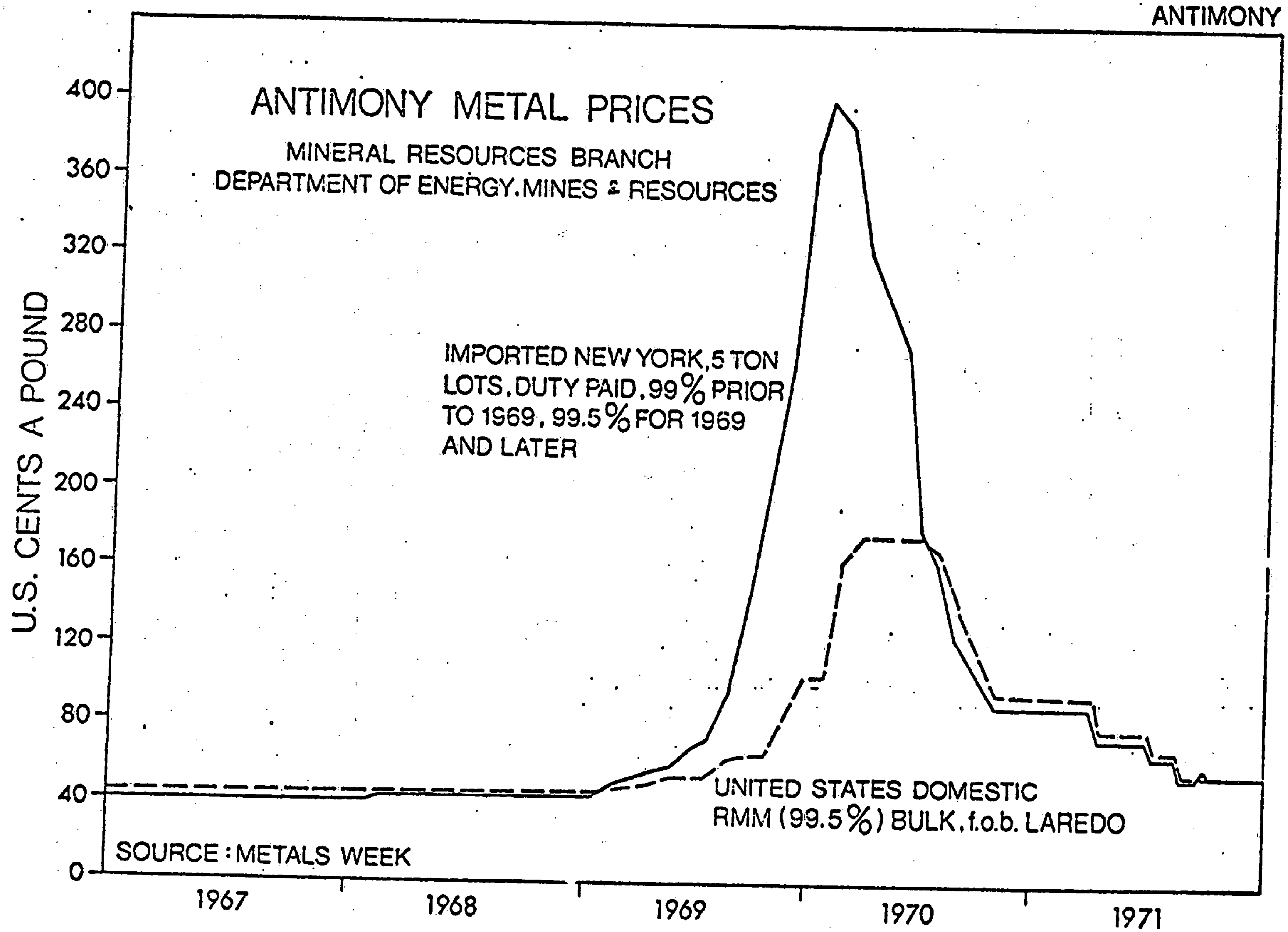
In the latter part of 1970 prices dropped: 1 lb. of antimony cost 98 cents by early 1971, and 59 cents in July 1971. The decline in price represents lower ore costs on the world market, and revisions of government stockpile objectives, which have resulted in surplus amounts of antimony on the open market. At the moment (early 1973) antimony metal costs 62 cents a pound, a price which threatens the continued operation of many mines around the world ( ) ( ).

The development of Canadian deposits had to contend with low-grade ores, lack of domestic refining, and unstable markets. The factors have not influenced efforts of primary production beneficially.

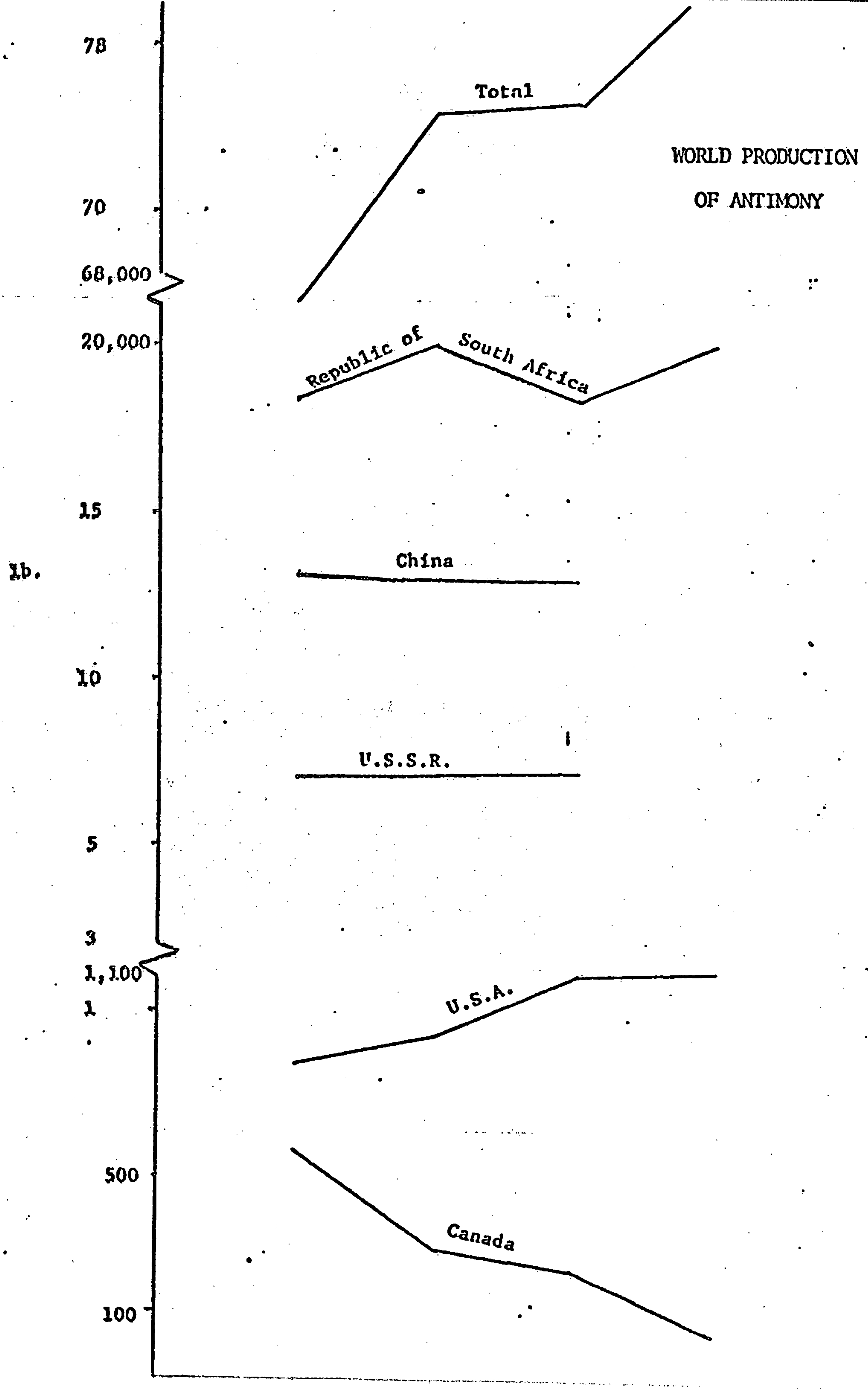
There has been no production of antimony metal or regulus in Canada between 1944 and 1971. In 1971 Consolidated Durham Mines and Resources Ltd. in New Brunswick installed facilities for concentrating 400 tons of ore daily.

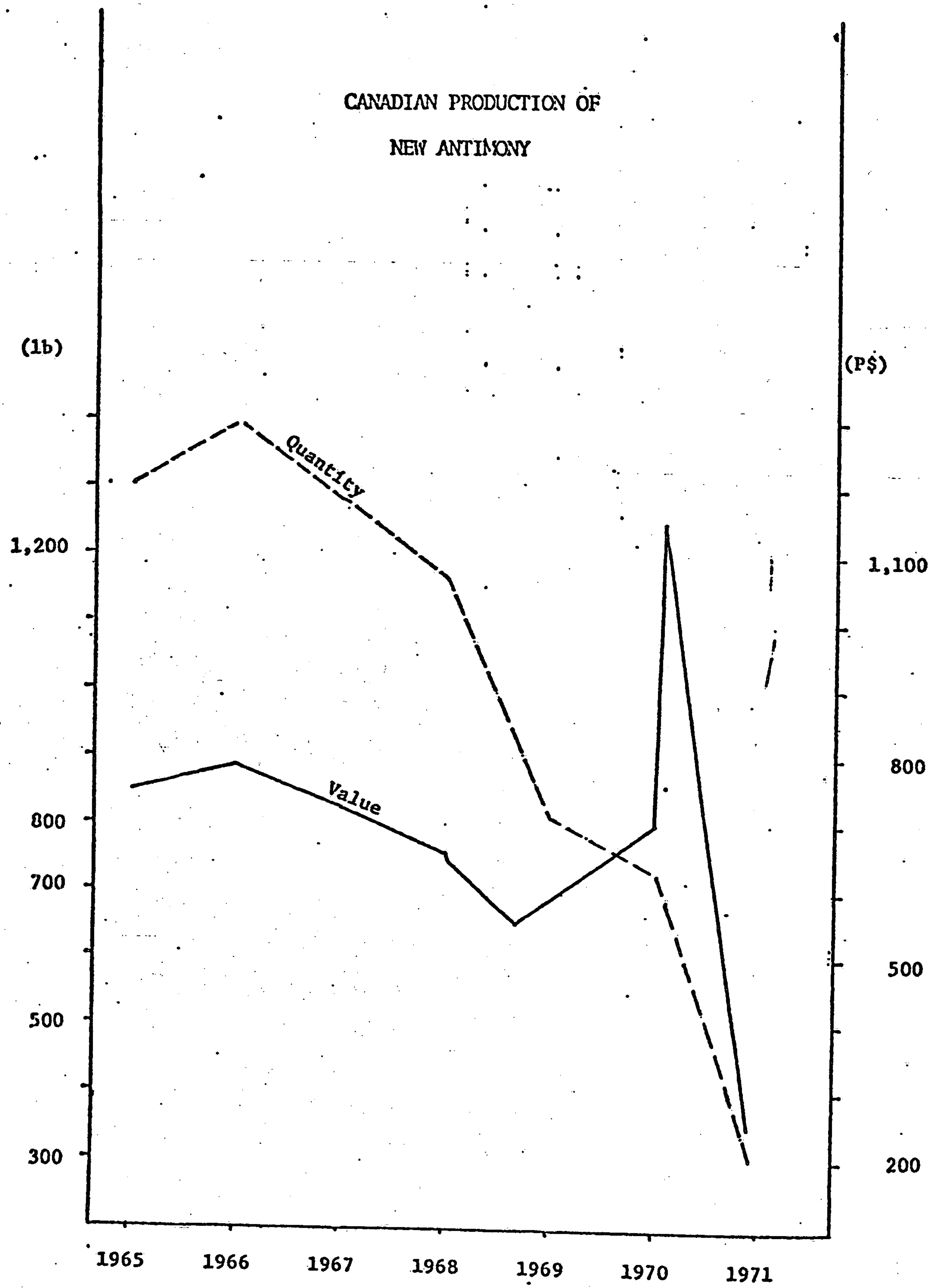
Cominco Ltd. in Trail, B.C. is the main producer of antimonial lead, which may have concentrations of antimony up to 23%. East Coast Smelting and Chemical Company Ltd. in New Brunswick, also produces antimonial lead. In both cases the antimonial lead is but a by-product of their lead and zinc smelting and refining operations

FIGURE



REPRODUCED FROM ANTIMONY BY M. GAUVIN, ANNUAL REVIEW BY THE MINERAL RESOURCES BRANCH, DEPARTMENT OF ENERGY, MINES AND RESOURCES, OTTAWA: QUEEN'S PRINTER, 1971. NO. 3.


WORLD PRODUCTION
OF ANTIMONY
Total
Republic of South Africa
China
U.S.S.R.
U.S.A.
Canada
lb.
78
70
68,000
20,000
15
10
5
3
1,100
1
500
100



CANADIAN PRODUCTION OF
NEW ANTIMONY
(1b)
1,200
800
700
500
300
(P$)
1,100
800
500
200
Quantity
Value
1965
1966
1967
1968
1969
1970
1971

EXPORTS OF ANTIMONY

Table

Possible Exports of Antimony Commodities

On the basis of the Statistics Canada classifications it is impossible to assess the actual antimony content involved in export trade, because antimony commodities are considered under more comprehensive headings.

But one may reasonably assume that not much antimony leaves the country; Canada has to import much of this metal to satisfy its own domestic needs.

With antimony mining at Lake George, N.B. being rather recent, none of the exports of concentrates from there to Belgium, Italy, Poland, and the United States would be included in current statistical reports. These countries import about 1300 tons of antimony concentrates from Canada annually for refining.

TABLE

CANADIAN PRODUCTION OF NEW ANTIMONY

YEAR	QUANTITY (POUNDS)	VALUE (DOLLARS)
1965	1,301,787	689,947
1966	1,405,681	745,011
1967	1,267,686	671,874
1968	1,159,960	614,779
1969	820,122	508,476
1970	726,474	1,104,040
1971P	330,000	249,000

SOURCE: DOMINION BUREAU OF STATISTICS (STATISTICS CANADA)

NOTE: QUANTITY REFERS TO CONTENT OF ANTIMONIAL LEAD, DORÉ SLAG AND FLUE DUST.

P—PRELIMINARY

IMPORTS OF ANTIMONY

By-product smelting and secondary production constitute Canada's domestic supply of antimony, which is primarily in the form of antimonial lead.

To satisfy all the domestic demands, Canada has to import antimony commodities, as listed in Table

Table

Again, the nature of the classification, except for antimony oxide, does not allow assessment of the actual amounts of antimony involved. In 1970 Canada bought 844,500 lbs of antimony oxide. That is 7% more than the amount imported in 1969. Almost three-quarter of this commodity comes from Britain; the remainder comes mainly from the United States and China.

Since 1964, the amount and value of antimony regulus imports are implied in the Statistics Canada Classification "Non-Ferrous Metals N.E.S.". Before 1964 statistics specific for antimony regulus show that Canada imported about 1 million pounds of this metal from China and Yugoslavia every year ( ).

Reports for 1965 to 1967 - the most recent data available - show considerable imports of antimony potassium tartate during sample four-month periods of each year.

Table

Antimony Potassium Tartate

TABLE

POSSIBLE IMPORTS OF ANTIMONY COMMODITES 1970

COMMODITY CLASSIFICATION	D.B.S. CLASSIFICATION	QUANTITY (POUNDS)	VALUE (DOLLARS)
ANTIMONIAL LEAD	CLASS 453-49, LEAD FABRICATED MATERIALS N.E.S.	764,300	334,420
ANTIMONY CHLORIDE	CLASS 403-36 CHLORIDES AND OXYCHLORIDES N.E.S.	13,453,000	1,350,200
ANTIMONY OXIDES	CLASS 402-61, ANTIMONY OXIDES	844,500 1971 - 590,600P	837,542 1971-- 437,000P
ANTIMONY OR REGULUS OF	CLASS 459-79, NON FERROUS METALS - N.E.S.	2,483,169	6,839,379
ORES, ANTIMONY	CLASS 258-99, METAL BEARING ORES, CONCENTRATES AND SCRAP N.E.S.	173,798,200	21,192,505

SOURCE: DOMINION BUREAU OF STATISTICS (STATISTICS CANADA) CAT. 65-203

NOTE:

1. AVAILABLE DATA DOES NOT PERMIT AN ACCOUNT OF ACTUAL ANTIMONY CONTENT IN EACH D.B.S. CLASSIFICATION.

2. IMPORTS OF ANTIMONY OXIDES ONLY ARE FULLY ACCOUNTABLE. IMPORT DATA FOR ANTIMONY REGULUS (METAL) ARE NOT AVAILABLE AFTER 1963 when 1,036,235 LB. WERE IMPORTED. (IN 1962 - 1,275,917 LB; 1961 - 832,547 LB.)

3. AN IMPORT ANALYSIS BY THE MARKET DATA DIVISION OF INDUSTRY TRADE AND COMMERCE FOR CHLORIDES AND OXYCHLORIDES N.E.S. DURING OCTOBER 1970 AND MARCH AND JUNE OF 1971 INDICATED NO IMPORTS OF ANTIMONY CHLORIDE.

4. N.E.S. - NOT ELSEWHERE SPECIFIED; P - PRELIMINARY

TABLE

KNOWN CHEMICAL IMPORTS
1965-67

PRODUCT - ANTIMONY POTASSIUM TARTRATE

D.B.S. CLASSIFICATION - CLASS 409-99, ORGANIC ACIDS, their ANHYDRIDES, HALIDES, PEROXIDES and PERACIDS. N.E.S.

		QUANTITY (POUNDS)	VALUE (DOLLARS)
IMPORTS FOR FOUR MONTHS	1965	8,550	7,971
	1966	5,500	5,234
	1967	11,000	10,283
ANNUAL IMPORTS[1]	1965	25,650	23,913
	1966	16,500	15,702
	1967	33,000	30,849

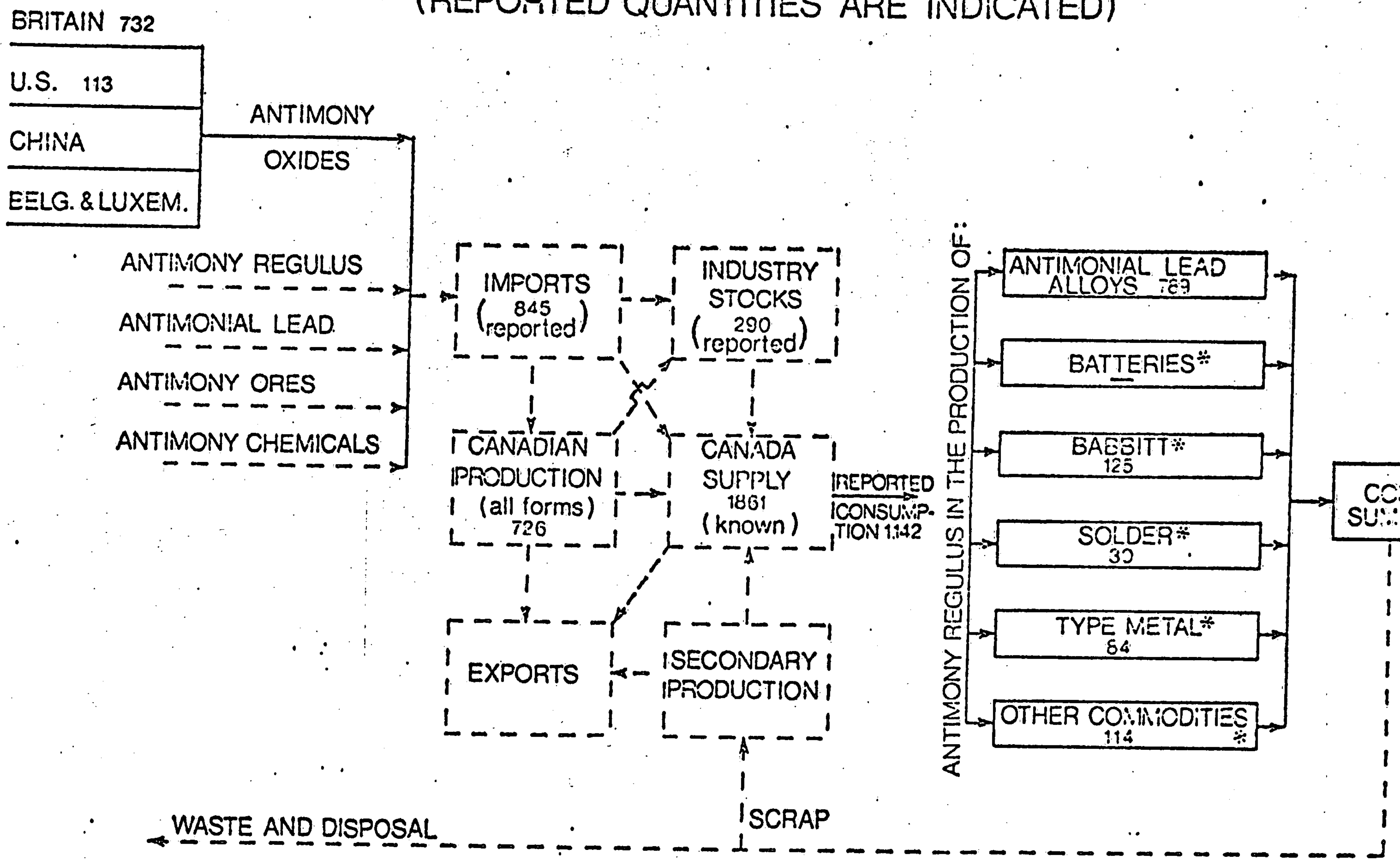
SOURCE: CHEMICAL IMPORT TRENDS 1965, 1966, 1967, CHEMICALS BRANCH, DEPARTMENT OF INDUSTRY, TRADE AND COMMERCE, OTTAWA

NOTE: 1 - QUANTITIES AND VALUES ARE EXTRAPOLATED FROM FOUR MONTH FIGURES.

CONSUMPTION OF ANTIMONY

Canada consumes 1.5 - 2 million pounds of antimony every year. A very large portion of this quantity is used as antimonial lead alloy in batteries (see Appendix).

MATERIAL FLOW CHART OF ANTIMONY IN CANADA
1970 (THOUSAND POUNDS)
(REPORTED QUANTITIES ARE INDICATED)



NOTE: DASHED LINES INDICATE UNKNOWN QUANTITIES. CONSUMPTION FIGURES DO NOT INCLUDE ANTIMONY CONTENT OF PRIMARY AND SECONDARY ANTIMONIAL LEAD USED FOR THE PURPOSES NOTED - *

USES OF ANTIMONY

Hardening Agent

Suitability of antimony

Antimony provides:

1. Fluidity for high-speed casting of thin sections
2. Strength for resisting creep and fatigue in service
3. Electro-chemical stability for heavy-duty cycling of battery plates.

The largest single use of elemental antimony is as an ingredient in many lead alloys in which it hardens and strengthens lead, and inhibits chemical corrosion.

It is also used in the form of oxides and salts. Antimonial lead containing from 3% to 12% (most specifications call for 4% to 6%) antimony is used in the manufacture of lead storage batteries. In recent years the antimony content in antimonial lead has been continuously reduced. This trend is the effect of the rising prices of antimony. Some industries already look at such alternatives as age hardening and temperature treatment, rather than antimony, to overcome the softness of lead.

There are 25 manufacturers of antimonial lead batteries in Canada. In 1969 they used 39 million pounds of antimonial lead. Since this alloy has an average antimony content of 5% ( ), the antimony consumption by this industry approached 2 million pounds that year.

The antimonial lead batteries serve the communications industry in telephone, signaling, and fire alarm systems.

Metal Rolling, Casting, and Extruding

A number of alloys called babbit or "white metal" contain 5% to 18% antimony as an integral part. Other components of these so-called antifriction alloys are tin, lead, and copper.

In the tin-base group tin-antimony is included to give the antifriction quality of the alloy by attaining the force-absorbing properties from such hard-soft binary combinations. Almost the same result is obtained in the lead-base babbit where the tin-antimony is imbedded in lead.

The manufacture of antimonial lead bearings has declined because such bearings are no longer used for railroad rolling stock ( ). Antimonial lead bearings are generally employed in machines with low shaft, speeds, light loads, and low allowable cost.

Lead containing 13% antimony and minor amounts of tin is used in linotype and stereotype machines to produce accurate cast printing type. Much of the antimonial lead used by this industry is recycled, therefore the consumption of this alloy here is limited to the replenishing of supplies.

In 1970 there were 131 establishments which use antimony in their metal rolling, casting, and extruding operations. That year this industry used 1,650 tons of antimony or antimonial lead, and added a value of $104 million to the metal and its alloys by its manufacturing activity.

Electric Wire and Cable

Antimonial lead has been used for sheathing cable to increase its strength, and to inhibit its chemical corrosion. But this use of antimonial lead is lately giving way to substitution by aluminum and plastics.

However, with the many means of wireless transmission of power and communications, such as lasers and satellites, now available, the demand for cables, whatever their sheathing, is declining.

In 1969 there were 33 firms in Canada which used 573,694 lbs in their manufacture of electric wire and cables.

Flameproofing

Suitability of antimony

The heat accompanying combustion causes the release of chemical reactants from the impregnating solution composed of antimony trioxide in an organic solvent. These chemical reactants then extinguish the flames which also accompanies combustion.

The use of antimony trioxide as a flameproofing agent promises the greatest future growth potential for this substance.

The application of antimony trioxide to fabrics employed in military operations, has long been established. Now a greater public awareness of fire-safety has compelled the use of antimony trioxide as a flameproofing material domestically. Children's sleepware, work clothes, awnings, and curtains are made flame-proof in many cases with antimony trioxide. There are non-antimonious flame-retarders, but these do not seem quite so efficient.

Antimony trioxide reduces the flammability of polyvinyl-chloride products. Estimates suggest that antimony trioxide comprises about 5% of all the compounds introduced to plastics for flameproofing. For this purpose, antimony trioxide finds unrivalled application in polypropylene and polyethylene; and it is used in unsaturated polyesters, the material which goes into the building of glass-reinforced boats, vehicle bodies, ductwork, etc.

Rubber products, some high-performance paper products, adhesives, and sealants, all contain antimony trioxide to reduce their flammability.

Paint and Varnish Manufacture

Suitability of Antimony

1. good hiding power
2. chemically stabilizing
3. flame-retarding

Antimony trioxide is used extensively in ceramic enamels where it serves as an opacifying agent, giving the white enamel a blister-free, brilliant finish. Also, it is used as a white pigment in paints. Other inorganic compounds of antimony produce pigments of black, vermilion, and yellow: vermilion is the red trisulphide precipitated from antimonial solution by hydrogen sulphide; yellow is the result of controlled oxidation of the same sulphide. Oranges, blues, and greens are produced by blending antimony compounds with other mineral pigments.

Because antimony trioxide acts as a chemical stablizing paints containing this substance do not fade over long periods of time.

The flameproofing qualities of antimony trioxide are discussed under a separate heading.

In 1969 there were 156 paint and varnish manufacturers in Canada. In that year this industry consumed 54,180 lbs of antimony oxide to which they added a value of $119.6 million through their manufacturing activity.

SUMMARY OF PRODOMINANT USES OF

ANTIMONY COMPOUNDS

Compounds \ Uses	catalyst	stabilizer	mordant	vulcanizing agent	glass decolorizer	enamel	semi-conductor	ammunition	matches, pyrotechnics	biocide	medicine
Antimony											
- (111) chloride			x								
- (111) fluoride			x								
- (111) oxide	x	x		x	x	x					
- (111) sulphide				x				x	x		
- (v) sulphide				x							
- gallium							x				
- indium							x				
- pot. tartate			x								
sodium antimonate										x	x

POSSIBLE REPLACEMENT FOR ANTIMONY

BY END-USE

There are suitable materials which could substitute for antimony in several applications, wherever and whenever substitution becomes economically feasible ( ).

Antimony possesses no properties which make it indispensible, but it does have certain technological advantages in many of its usages.

The following is a list of antimony end-uses and some possible surrogate substances for the antimony component.

Lead Hardening	-	tin, calcium, dispersion-hardened lead
Paints, pigment, enamels	-	mercury, titanium, lead, zince chromium, tin zirconium
Flame proofing	-	zincborate, chlorinated paraffin, mono-ammonium phosphate
Ceramics	-	tin oxide, titanium dioxide, zircon
Glass	-	tin oxide, titanium dioxide arsenic trioxide, barite, fluorspar, manganese dioxide
Catalyst		
Acrylonitrile	-	bismuth phospho-molybdate
Polyesters	-	various metal organics
Miscellaneous	-	numerous
Colour Stabilizer	-	other metallic oxides
Dye Fixative	-	numerous
Ammunition, matches, etc.	-	numerous

SOURCES: Compiled from information in Trends in Usage of Antimony, p.52. and Antimony by James Paone.

ANTIMONY IN THE ENVIRONMENT

Levels of antimony in the natural environment have been detected, although their concentrations are generally quite small. Antimony invariably occurs with arsenic, and often both are associated with sulphur.

The terristrial abundance of arsenic and antimony is 3 ppm and 0.7 ppm respectively, with the greatest concentrations in igneous rocks. Solution and mechanical weathering of rocks can account for the movement of antimony to the soil, atmosphere, and water. Certain antimony minerals, especially those which give an acid reaction, are slightly soluble in natural waters. (See Appendix)

Data on atmospheric levels of antimony are scarce. Where ever antimony occurs in the atmosphere, it can usually be related to volcanic activity, the burning of coal and petroleum products, or the smelting of antimoniferous ores.

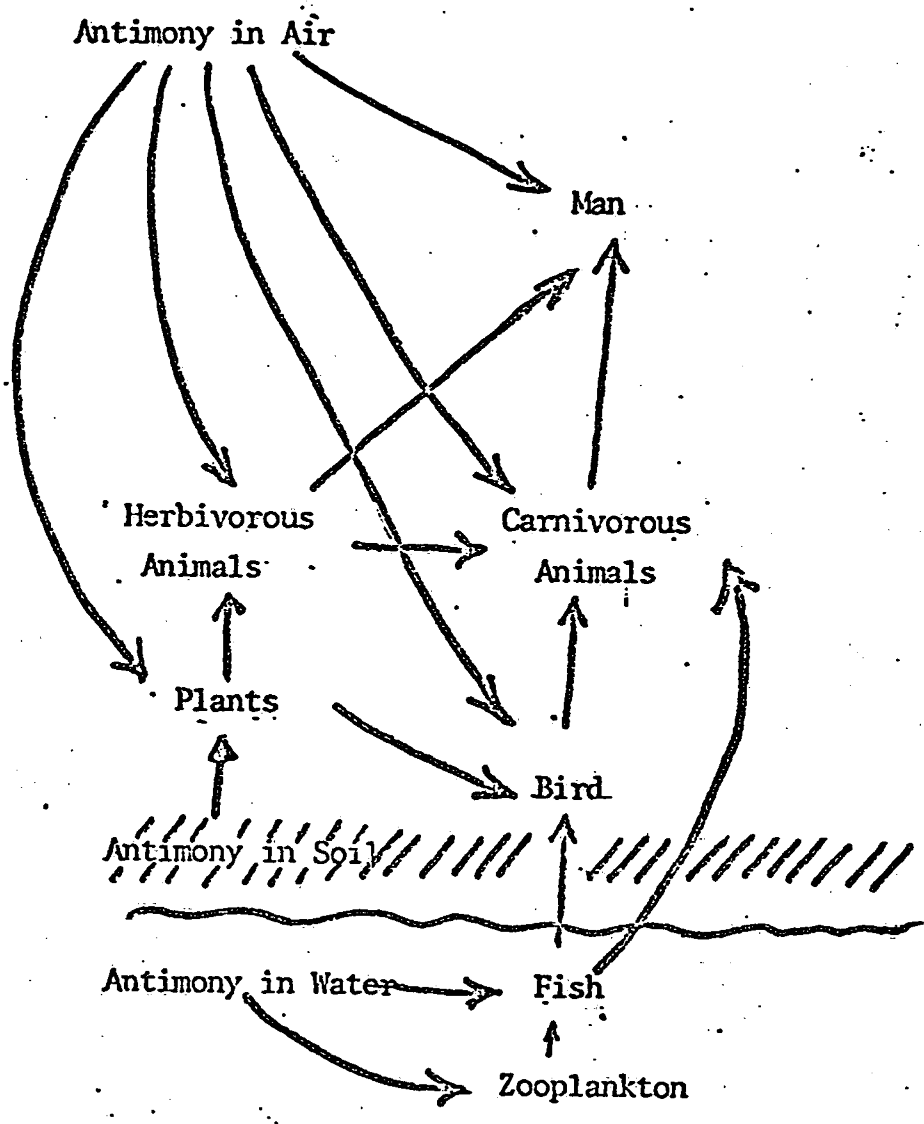
The antimony mining operations at Lake George, N.B., for example, are under close scrutiny by the Environmental Protection Service, the New Brunswick Department of Fisheries and Environment, and the New Brunswick Water Authority. Natural concentrations in spring water and sediments have been monitored, and a treatment system was designed to minimize the antimony content in the effluents and settling ponds at the mine. The water used by the mine for processing the ores represents a potential emission source of antimony, in that it contained an average 10 - 20 ppm antimony solids, and 10 - 20 ppm dissolved antimony.

The treatment system for this water involves ferric chloride and lime in aqueous solution at pH 4.5. Pre-operational tests showed that such treatment can reduce the antimony level in effluents to 0.2 ppm ( ). Now that it is in operation, the New Brunswick Water Authority reports an antimony level of 0.1 ppm. This compares favorably with a recommended antimony limit of $\leq$ 0.1 ppm in water. Although, the unofficial limit for antimony in water is 0.05 ppm ( ).

All plants and animals probably ingest some antimony from the biosphere. Concentrations of antimony in fish livers and whole fish caught in Lakes Michigan, Erie, and Superior ranged from 5 - 100 ppb ( ). Some researchers have even found an average antimony content of 160 ppb in marine animals ( ). Such contaminated fish could possibly be the principal source of antimony in part of the food chain.

diagram of food chain

How Antimony Reaches Man



TOXICITY OF ANTIMONY

Antimony and its compounds are toxic; doses as low as 100 mg have been fatal.

Yet, one compound, antimony potassium tartate, is used for medicinal purposes - as an emetic - in human without signs indicative of antimony poisoning following such treatment.

Antimony poisoning can cause eczematous eruptions of the skin, inflammation of mucous membranes, gastro-intestinal upset, and various nervous complaints. The last sign is perhaps the most fundamental one because antimony has an inhibitory effect on the cerebral cortex which in turn influences the autonomic nervous system. This and the hyperexcitability, which antimony can induce, explain the electrocardiograph abnormalities prompted by cardiac arrhythmia ( ).

The degree of poisoning depends somewhat on the manner in which the body comes into contact with the antimony, whether by ingestion, inhalation, or touch.

Exposures to antimony are most likely while mining, smelting, and refining its ores, in the production of alloys, in the manufacture of abrasives, and in type-setting in the printing industry.

But there are few recorded cases of severe poisoning from the industrial use of antimony and its compounds.

Stibine, or antimony trihydride, is a colourless gas which is produced when certain antimony alloys reacts with acid, as in the charging of storage batteries. Although no chronic stibine poisonings have been reported, there were cases of poisoning from a mixture of gases of which stibine was one ( ).

The safety limit to stibine exposure over an 8-hour working day is 0.1 ppm ( ). For most other antimony compounds the safety limit is 0.5 mg/m^3 of air ( ); for antimony (V) fluoride it is 0.3 mg/m^3 of air ( ).

RECYCLING AND WASTE DISPOSAL

In Canada secondary production provides 40 - 70% of the antimony supply; in the United States secondary production accounts for 30 - 60% of the available antimony there.

The fairly efficient recycling processes are typical of industrialized countries, and primarily so because antimony is applied to products that lend themselves to recycling.

98% of all antimonial lead storage batteries in Canada are recycled. Most of the antimony derived from secondary production is usually used for antimonial lead.

Recycling of chemicals, pigments, and plastics is less common or non-existent, so that their disposal may present a source of potential input of antimony into the environment.

APPENDIX Sb-A

WORLD MINE PRODUCTION OF ANTIMONY 1968-71
(short tons)

	1968	1969	1970P	1971e
REPUBLIC OF SOUTH AFRICA	18,514	20,080	18,841	20,000
BOLIVIA	12,276	14,484	12,724	13,700
PEOPLE'S REPUBLIC OF CHINA	13,200	13,000	13,000	*
U.S.S.R.	7,200	7,300	7,400	*
MEXICO	3,819	3,557	4,925	5,400
TURKEY	3,446	3,495	3,053	*
YUGOSLAVIA	1,935	2,278	2,200	2,300
MOROCCO	1,336	1,551	2,175	*
ITALY	865	1,272	1,381	*
PERU	900	*	*	*
UNITED STATES	856	938	1,130	1,130
AUSTRALIA	931	933	833	*
THAILAND	*	827	2,598	*
CZECHOSLOVAKIA	*	660	660	*
CANADA	580	410	363	165
OTHER COUNTRIES	1,879	2,259	1,924	33,935
TOTAL	67,737	73,044	73,207	76,630

SOURCES: DOMINION BUREAU OF STATISTICS (STATISTICS CANADA). MINERALS YEARBOOK, U.S. DEPT. OF INTERIOR. COMMODITY DATA SUMMARIES 1971, U.S. BUREAU OF MINES.
* - INCLUDED IN "OTHER COUNTRIES".
P - PRELIMINARY; e - ESTIMATED

APPENDIX Sb-B

CONSUMPTION AND STOCKS OF ANTIMONY 1969-71 (POUNDS)

		1969	1970	1971
ANTIMONY REGULUS (METAL) IN THE PRODUCTION OF:	ANTIMONIAL LEAD ALLOYS	814,754	788,747	..
	BABBITT	145,779	124,451	..
ANTIMONY HELD BY CONSUMERS	SOLDER	22,127	30,272	..
Dec. 31. 1970 - 289,909	TYPE METAL	198,777	84,158	..
1971 - 248,809	OTHER USES	124,305	114,381	..
	TOTAL	1,305,742	1,142,009	1,461,763
ANTIMONY CONTENT OF PRIMARY AND SECONDARY ANTIMONIAL LEAD ALLOYS USED FOR:	BATTERIES	2,155,677	1,283,478	..
	TYPE METAL	105,019	16,421	..
CONTAINED ANTIMONY HELD BY CONSUMERS	BABBITT	14,111	66,125	..
Dec. 31, 1970 - 188,319	SOLDER	3,818	9,348	..
	OTHER USES	43,145	25,030	..
	TOTAL	2,321,770	1,400,402	1,856,685

SOURCE: DOMINION BUREAU OF STATISTICS (STATISTICS CANADA), MANUFACTURING AND PRIMARY INDUSTRIES DIVISION

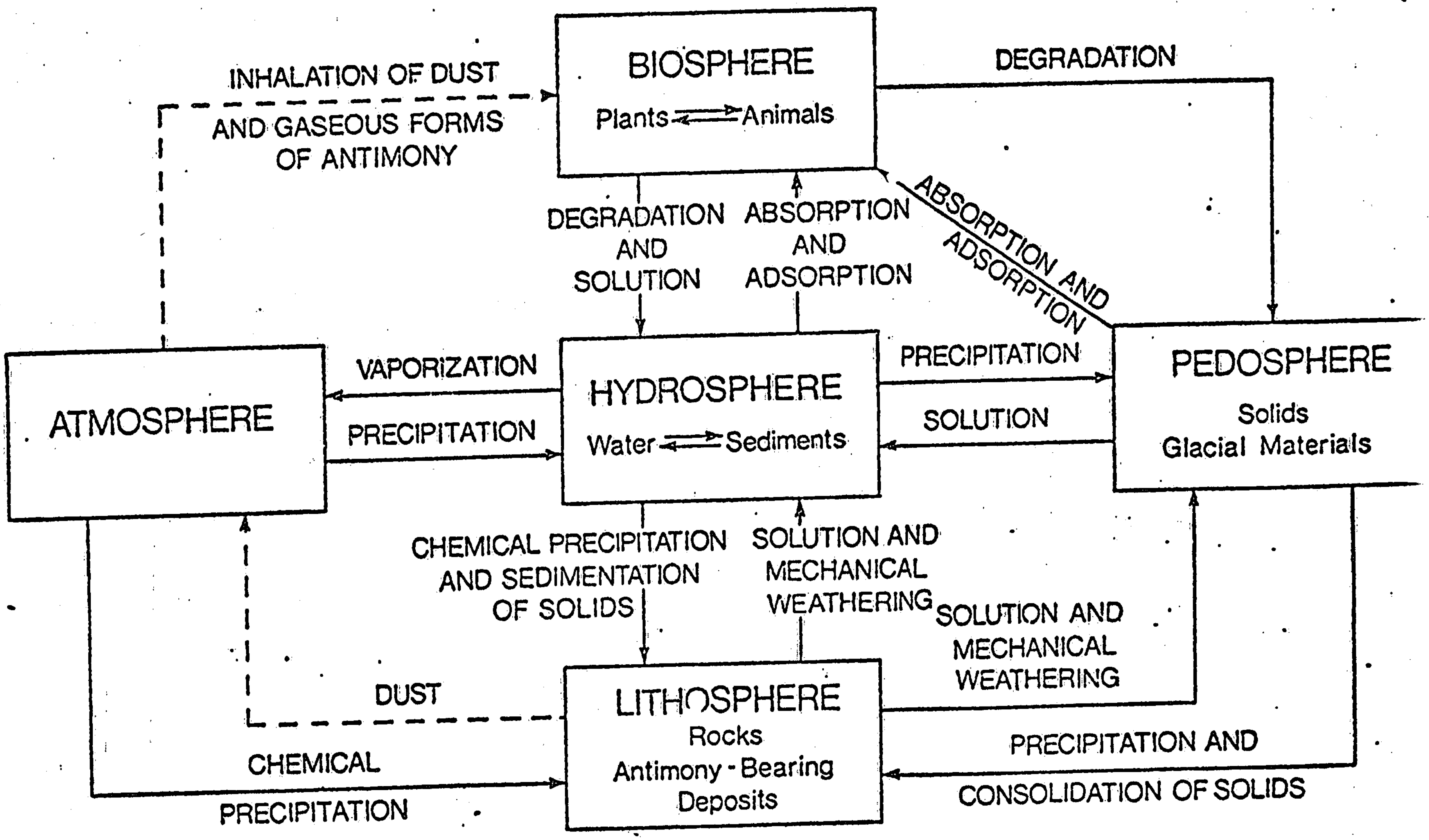
NOTE: QUANTITIES REPRESENTED BY REGULUS CONSUMPTION AND CONTAINED METAL CONSUMPTION ARE INSEPARABLE

i.e. CONTAINED ANTIMONY USES INCLUDE SOME REGULUS USES

.. NOT AVAILABLE

FIGURE

GENERALIZED GEOCHEMICAL CYCLE OF ANTIMONY



SOURCE: REPRODUCED FROM GEOCHEMISTRY OF ARSENIC AND ANTIMONY BY R.W. BOYLE AND I.R. JONASSON, GEOLOGICAL SURVEY OF CANADA, DEPT. OF ENERGY, MINES AND RESOURCES, OTTAWA, 1973, p. 25