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Project Summary

Environmental Implications of Changes in the Brominated Chemicals Industry

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In light of the large-scale changes occurring within the bromine-based chemicals industry, the U.S. Environmental Protection Agency (EPA) commissioned a study to investigate the potential for adverse environmental effects that might result from such changes. In particular, EPA was interested in learning if the existing excess capacity to produce bromine and ethylene dibromide has or would stimulate the industry to seek alternate uses for bromine that could result in new environmental concerns.

To accomplish the objectives of the study, an extensive literature review was conducted, followed by personal contacts with knowledgeable individuals and by independent analysis. Efforts were concentrated on present and future markets, exposure potential, and risk assessment.

The greatest potential environmental hazard is not with bromine emissions, but rather with exposure to chemicals that may be carcinogenic or teratogenic, such as ethylene dibromide, vinyl bromide, and "tris."

Many gaps exist in the information available on the bromine-based chemicals industry. Where necessary, assumptions were made to temporarily bridge the gaps. In most cases, the analyses indicate that filling the data gaps should not be a high priority in light of other pressing issues that EPA faces. In general, the environmental effects are relatively minor or the problems are already recognized and are being addressed by EPA. However, several areas do require further attention: the brominated flame retardants industry; the effect of methyl bromide on stratospheric ozone; the lack of carcinogenicity and food-residue data for methyl bromide; and the environmental effects of bromine chloride utilization.

This Project Summary was developed by EPA's Office of Exploratory Research, Washington, DC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Because of changing market conditions, much of which is attributable to various environmental considerations, substantial alterations in existing production and consumption patterns of bromine compounds have occurred. At the outset of the study, Winzler and Kelly were aware that several factors were acting to reduce the level of bromine compound demand:

- Lead phase-down. EPA's phase-down of the lead content of gasoline has already resulted in substantial reductions in lead use (and hence ethylene dibromide use) in gasoline.
- DBCP ban. EPA suspended nearly all uses of the pesticide dibromochloropropane on 29 October 1979. Future use of DBCP appears to be very limited, if not nil. DBCP is also controlled by OSHA.

- Ethylene dibromide regulation. Ethylene dibromide is under consideration by EPA for regulation under Section 112 of the Clean Air Act (NESHAP). Such regulation would result in an emission standard for ethylene dibromide, or, where this is infeasible, design, equipment, work practice, or operational standards may be imposed. The effect of such regulations on ethylene dibromide consumption is unclear. Vinyl chloride is under NESHAP regulation, and its domestic production and consumption remain very high.
- Tris ban. Tris (2,3-dibromopropyl) phosphate, a flame-retardant used in textiles, is no longer used for this purpose because of its carcinogenicity and exposure potential.
- PBB contamination. The contamination of animal feed with polybrominated biphenyls (a group of fire retardants) in 1973 in Michigan heightened the public's awareness of this group of chemicals, and their use has nearly stopped since then.
- Ethylene dibromide replacement in some fumigation. The technology for using gamma radiation for fruit fumigation has been developed, and this could replace ethylene dibromide for this purpose.

However, the investigators were also aware of other market factors increasing the demand for bromines:

- Greater use of BrCl for water disinfection. The trend toward reducing the residual chlorine demand in effluents appears to be resulting in a strong demand for bromine chloride.
- Calcium bromide use in drilling fluid. The use of calcium bromide in well-drilling fluid is expanding very rapidly.
- Fire retardants. The use of brominated compounds as fire retardants represents a strong market.
- Ethylene dibromide as fumigant. The use of ethylene dibromide as an agricultural crop and seed fumigant is increasing.
- Flame retardant not found to be carcinogenic. No carcinogenic response was observed in rats exposed to dibromoneopentyl/glycol, a reactive flame retardant widely used in unsaturated polyester resins and polyurethane foam.

The very dynamic nature of the bromine market is of interest to EPA because of the potential for new or expanded uses for bromine, which in turn might result in environmental problems from specific compounds. The objective of the proposed study was to evaluate this potential and to assess the implications for EPA's regulatory mission.

The approach to achieving the objectives of the study included the following major elements where desirable and practical:

- Identification of significant bromine compounds, their producers and users, and the quantities involved.
- Identification of future trends in production and use.
- Estimation of emission rates.
- Characterization of environmental fate of bromine compounds, including estimates of ambient concentrations.
- Review of pertinent toxicological data, with emphasis on carcinogenicity and teratogenicity.
- Identification of pollution-control technologies and analytical methods.
- Rough assessment of carcinogenic and non-carcinogenic risk.
- Evaluation of likelihood and magnitude of potential problems and the likely regulatory pathway and control strategies.

First, a literature review based upon an extensive computerized bibliographic search was conducted. The literature review was followed by a campaign of personal contacts by telephone with individuals working in industry, government, and academe, the purpose of which was to clarify the literature and to fill some of the major information gaps in the literature. Then, the tasks mentioned above were completed, and independent assumptions and calculations were made where needed. The most important compounds received the greatest attention.

Results

The major uses for bromine in the United States are for manufacturing ethylene dibromide, flame retardants, calcium bromide, methyl bromide, and bromine chloride. Despite the declining usage of ethylene dibromide (EDB) in gasoline, EDB is still responsible for nearly half of the total domestic bromine demand. At least 76 brominated organic chemicals were listed by the U.S. International Trade Commission as being produced commercially during 1978.

The salient features of the 1979 domestic bromide industry according to the U.S. Bureau of Mines were:

- The United States produced 65 percent of the world's bromine.
- U.S. exports were far greater than imports.
- Nearly half of the U.S. demand for bromine was supplied as the gasoline additive ethylene dibromide (48 percent), followed by fire retardants (29 percent), sanitation preparations (16 percent), and other uses (6 percent).

Several significant changes have occurred in the bromine industry over the last several years, the most important of which has been the decline in ethylene dibromide utilization as a gasoline additive.

Since the EPA's gasoline lead phasedown program began in 1973, and its ban against the use of leaded gasoline in automobiles equipped with catalytic converters began some time later, the use of ethylene dibromide as a combustion-exhaust lead scavenger has declined substantially — roughly 25% between 1974 and 1979 — resulting in 60 x 10^6 lb less bromine being used for EDB production in 1979 than in 1974. This situation, plus the addition of 200 x 10^6 lb bromine production capacity (nameplate) during 1975 and 1976, left the bromine industry with a large excess production capacity for ethylene dibromide and bromine. No other sizeable products exist for which the excess EDB capacity can be used.

Bromine-based fire-retardant chemicals have shown a moderately strong and steady increase in demand over the years. However, great uncertainty exists regarding the actual rates of production and consumption. Because of the increasing demand for fire retardants, the virtual elimination of the production and use of the brominated flame retardants "tris" and polybrominated biphenyls in the United States during the 1970's did not cause a dip in the overall demand for fire retardants.

The demand for calcium bromide has grown tremendously since its introduction as a well-drilling fluid in 1972. Since 1976, domestic production increased from nearly zero to over 100 x 10^6 lb (42% bromine content) in 1978. This increased demand stems from the oil and gas industry's efforts to increase production.

"Sanitation preparations," a group designation of the Bureau of Mines that includes bromine chloride and elemental bromine used as water disinfectants and methyl bromide and ethylene dibromide used as fumigants, experienced a diminishing demand until 1979, when domestic demand increased 73 percent over the 1978 level. Virtually all of the "sanitary preparations" group can be accounted for by the fumigants methyl bromide and ethylene dibromide through 1978. In 1979, a new facility with a production capacity for bromine chloride of 30×10^6 lb/yr (21×10^6 lb bromine per yr) began operating, helping to account for the large increase in demand.

The historical data show a gradual increase in production and demand for bromine; a widening in the difference between production and demand, indicating increased exports in the 1970's; a moderately high increase in the demand for fire retardants and a decrease for EDB; and sharp increases in production capacity during 1975 and 1976.

A crude forecast of EDB demand between 1973 and 1979, assuming that leaded gasoline consumption had not been diminished by EPA regulations, indicated that there would likely have been only a small excess bromine production capacity by 1979, rather than the large excess that exists now.

Domestic bromine demand is expected to increase at a rate of 2 to 5 percent annually (compounded annually) to 1985, driven by demand increases for flame retardants (4 to 8%/yr), bromine chloride (15%/yr), calcium bromide (15%/yr), and methyl bromide (4 to 5%/yr). Demand for ethylene dibromide will continue declining, perhaps at a rate of 15 percent per year. The overall demand for bromine will depend heavily on the demand for calcium bromide.

While bromine production in the United States has increased modestly over the years, production in Israel has more than doubled since 1976, although U.S. production was still five-fold greater than Israel's in 1979. Moreover, in an effort to boost exports, Israel plans on doubling its bromine production from 53,000 tonnes (116×10^6 lb) in 1980 to 100,000 tonnes (220×10^6 lb) per year by 1984.

Imports increased greatly during 1978 and 1979, although they are still only 1% or less of domestic consumption. During 1979, approximately 99% of the accounted-for imports were from Israel.

Exports increased significantly over 1977, although declining 6% from 1978 to 1979. Exports represented approximately 18 percent of the bromine produced in the United States during 1979. Israel is aggressively pursuing a program of increased production of bromine and bromine-based chemicals for foreign markets. Because bromine in its lead-lined shipping containers is heavy, and therefore costly to transport, Israel will likely be able to capture a portion of U.S. exports to areas that are closer to Israel than to the United States. Nevertheless, U.S. producers feel that their foreign markets will remain strong. The strength of the recent export market is thought to be due to the approval of a lightweight container for shipping bromine. Also, to increase profits and safety, producers tend to ship bromine derivatives rather than bromine itself, according to a major producer.

Conclusions and Recommendations

The greatest potential environmental hazard is not with bromine emissions, but rather with exposure to chemicals that may be carcinogenic or teratogenic, such as ethylene dibromide, vinyl bromide, and "tris."

Many gaps exist in the information available on the bromine-based chemicals industry. Where necessary, assumptions were made which tentatively bridged the gaps. In most cases, the analyses indicate that filling the data gaps should not be a high priority in light of other pressing issues that EPA faces. In general, the environmental effects are relatively minor or the problems are already recognized and are being addressed by EPA. However, several issues do require further attention:

- Better definition of the brominated flame retardants industry and associated environmental effects is needed. A current EPA-sponsored study strives to achieve this goal.
- The effect of methyl bromide on stratospheric ozone deserves greater attention.
- The lack of carcinogenicity and food-residue data for methyl bromide may hamper EPA's planned review under the Federal Insecticide, Fungicide, and Rodenticide Act.
- Additional research into the environmental effects of bromine chloride utilization would be useful to further substantiate the evidence that bromochlorination is less environmentally damaging than chlorination.

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***Robert Barles** is the EPA Project Officer (see below).*
The complete report, entitled "Environmental Implications of Changes in the Brominated Chemicals Industry," (Order No. PB 82-247 594; Cost: $13.50, subject to change) will be available only from:
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Telephone: 703-487-4650
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