Follow-up Report on a PSL1 Substance for Which There Was Insufficient Information to Conclude Whether the Substance Constitutes a Danger to the Environment

Styrene

Table of Contents

SYNOPSIS	4
1.0 INTRODUCTION	5
2.0 ENTRY CHARACTERIZATION	5
3.0 EXPOSURE CHARACTERIZATION	6
3.1 ENVIRONMENTAL FATE 3.1.1 Air 3.1.2 Biota 3.2 ENVIRONMENTAL CONCENTRATIONS 3.2.1 Ambient air 3.2.2 Surface water 3.2.3 Biota 4.0 EFFECTS CHARACTERIZATION 4.1 TERRESTRIAL PLANTS 4.2 WILDLIFE	
4.3 AQUATIC ORGANISMS	
5.1 ASSESSMENT ENDPOINTS. 5.2 TERRESTRIAL PLANTS 5.3 WILDLIFE. 5.4 AQUATIC ORGANISMS 5.5 DISCUSSION OF UNCERTAINTY 5.6 CONCLUSIONS.	9 10 10 10
6.0 REFERENCESAPPENDIX A. MOLECULAR STRUCTURES OF STYRENE AND ITS	12

List of Acronyms and Abbreviations

CEPA Canadian Environmental Protection Act

CEPA 1999 Canadian Environmental Protection Act, 1999

CTV Critical Toxicity Value

EC₅₀ median effective concentration EEV Estimated Exposure Value ENEV Estimated No-Effects Value kg-bw kilogram body weight

kg-bw kılogram body weight LC₅₀ median lethal concentration

NOAEL No-Observed-Adverse-Effect Level

PSL Priority Substances List PSL1 first Priority Substances List PSL2 second Priority Substances List

Synopsis

Styrene, which appeared on the first Priority Substances List (PSL1), was assessed to determine whether it should be considered "toxic" as defined under the *Canadian Environmental Protection Act* (CEPA). It was concluded that styrene was not "toxic" under Paragraphs 11(b) or 11(c) of CEPA; however, there was insufficient information to conclude whether it constituted a danger to the environment under Paragraph 11(a). Information was lacking about the potential effects of styrene on aquatic organisms, on terrestrial vegetation through atmospheric exposure, and on wildlife through media other than air.

Since 1994, additional toxicity tests have been carried out on aquatic organisms. The results of these tests indicate that aquatic organisms are unlikely to be adversely affected by the concentrations of styrene found in Canadian surface waters. No information is available about the effects of styrene on wildlife. Based on toxicity studies conducted on laboratory animals, it is unlikely that wildlife would be adversely affected by the concentrations of styrene reported in food organisms or water in Canada. No information was identified about the potential effects of styrene on plants exposed through the atmosphere. Based on toxicity information available for several PSL1 substances that are structurally similar to styrene, it is concluded that terrestrial plants are unlikely to be adversely affected by the concentrations of styrene in air reported in Canada.

Based on the information available, it is concluded that styrene is not entering the environment in a quantity or concentration or under conditions that have or may have an immediate or long-term harmful effect on the environment or its biological diversity. Therefore, styrene is not considered "toxic" as defined in Paragraph 64(a) of the *Canadian Environmental Protection Act*, 1999.

1.0 INTRODUCTION

Styrene appeared on the first Priority Substances List (PSL1) of the *Canadian Environmental Protection Act* (CEPA), which was published in the *Canada Gazette*, Part I, on February 11, 1989. Assessments were performed to determine whether the substance should be considered "toxic" as defined under CEPA and were completed in 1993 (Government of Canada, 1993a)¹. It was concluded that styrene does not constitute a danger either to the environment on which human life depends or to human life or health, and, therefore, it was not found to be "toxic" under Paragraphs 11(b) and 11(c) of CEPA. Available information was insufficient to conclude whether styrene constituted a danger to the environment under Paragraph 11(a) of CEPA. In particular, there was a lack of information about the potential effects of styrene on aquatic organisms and on wildlife through media other than air. There was also insufficient information to determine if styrene constituted a danger to terrestrial vegetation through atmospheric exposure.

Since 1994, additional toxicity tests have been carried out on aquatic organisms. A literature search was recently undertaken to identify information about the toxicity of styrene and its breakdown products to terrestrial plants through atmospheric exposure, but no such information was found. Information about releases of styrene from industrial sources and data on concentrations of styrene in air from across Canada were obtained from Canadian databases.

This report examines this new information about the entry, exposure and effects of styrene in the Canadian environment in order to determine if the substance is likely to have a harmful effect on aquatic organisms and wildlife. The report also examines information about analogues of styrene that were included in the first Priority Substances List in order to determine if styrene is likely to have a harmful effect on terrestrial vegetation through atmospheric exposure.

A draft follow-up report was made available for a 60-day public comment period (between September 28, 2002 and November 27, 2002). No comments were received.

2.0 ENTRY CHARACTERIZATION

Total on-site environmental releases of styrene reported to the National Pollutant Release Inventory amounted to 808 000 tonnes in 1996, with most, 729 000 tonnes, released into air (NPRI, 1999). Total on-site releases amounted to 731 000 tonnes in 1995 (NPRI, 1999).

The Canadian Chemical Producers' Association (1999) reported total styrene emissions of 78 tonnes from member companies in 1998 and 88 tonnes in 1997, compared with total releases of 134 tonnes in 1992.

¹ The PSL1 Assessment Report for styrene is available on the following website: <u>www.hc-sc.gc.ca/hecs-sesc/exsd/psl1.htm.</u>

3.0 EXPOSURE CHARACTERIZATION

3.1 Environmental fate

3.1.1 Air

The fate of styrene in the atmosphere is determined by its chemical and photochemical reactivity and the prevailing physical and chemical conditions in the atmosphere. Hydroxyl radicals are major reactants, and the predicted half-life for reaction with styrene is about 3.6 hours (Atkinson *et al.*, 1982). Although hydroxyl radicals are major reactants, the ozone concentrations in polluted air in cities may be sufficiently high for ozone to destroy styrene more readily than hydroxyl radicals (Alexander, 1990). The half-life of styrene due to its reaction with ozone is about 9 hours (U.S. EPA, 1984). In the atmosphere, the products of the styrene reaction with ozone are benzaldehyde, formaldehyde, benzoic acid and trace amounts of formic acid (Grosjean, 1985).

3.1.2 Biota

A bioconcentration factor of 64 was estimated for styrene (Government of Canada, 1993a) using the method presented by Veith *et al.* (1979), indicating a low bioaccumulation potential.

3.2 Environmental concentrations

3.2.1 Ambient air

Styrene was detected (detection limit $0.1~\mu g/m^3$) in 6260 (or 52%) of 12 013 24-hour samples collected from 1994 to 1998, inclusive, from rural, suburban and urban locations in seven provinces under the National Air Pollution Surveillance program (Dann, 1999). The highest 24-hour average concentration measured was 43.6 $\mu g/m^3$, in a sample collected at Toronto, Ontario, in 1995.

3.2.2 Surface water

Concentrations of styrene up to 1.7 μ g/L have been reported in Canadian surface waters (Otson, 1992).

3.2.3 Biota

There are few data available on the concentration of styrene in biota. Bonner and Meresz (1981) reported whole-body concentrations of styrene ranging up to 100 μ g/kg in fish from the St. Clair River. Assuming a bioconcentration factor of 64, biota living in surface waters having a concentration of 1.7 μ g/L would have a whole-body concentration of

109 ug/kg. This estimate is very close to the highest concentration reported for fish in the St. Clair River.

4.0 EFFECTS CHARACTERIZATION

4.1 Terrestrial plants

In August 1999, a literature search was conducted to identify information on the effects of styrene and its atmospheric breakdown products, benzaldehyde, formaldehyde and benzoic acid, on plants through atmospheric exposure. No information was identified pertaining to styrene, benzaldehyde or benzoic acid.

Information was found pertaining to formaldehyde. This substance enters the Canadian environment from natural sources (including forest fires), from direct human sources, such as fuel combustion and industrial on-site uses, and from secondary formation as a result of the oxidation of natural and anthropogenic organic compounds. Formaldehyde was included on the second CEPA Priority Substances List (PSL2) and was considered not to be "toxic" as defined in Paragraph 64(a) of the *Canadian Environmental Protection Act*, 1999 (CEPA 1999). Therefore, no further consideration will be given to this substance in the assessment of possible environmental effects of styrene.

In the absence of toxicity data for styrene and its breakdown products other than formaldehyde, one approach is to use existing data for substances similar in structure to styrene. Several PSL1 substances are similar in structure to styrene: aniline, toluene, benzene and xylenes. Appendix A presents the molecular structures of these substances. A summary of their toxicity data follows:

- Aniline: Exposure of loblolly pines (*Pinus taeda* L.) to aniline at a concentration of $400\ 000 10\ 000\ 000\ \mu g/m^3$ for 21-35 days resulted in damage to the needles, including necrosis and needle drop (Cheeseman *et al.*, 1980, cited in Government of Canada, 1994).
- *Toluene:* Chlorosis and growth inhibition of terrestrial plants may occur at concentrations above 6 000 000 μg/m³ (Slooff and Blokzijl, 1988, cited in Government of Canada, 1992a). Young barley, tomato and carrot plants were damaged by toluene vapours at concentrations of 6 400 000 12 000 000 μg/m³ following a 0.25- to 3-hour exposure (Currier, 1951, cited in Government of Canada, 1992b). Barley and tomato plants were more sensitive than carrots. Damage included leaf tip darkening, loss of turgor and chlorophyll bleaching in sunlight.
- *Benzene:* Acute effects of benzene on terrestrial plants have been reported at atmospheric concentrations above 10 000 000 μg/m³ (Miller *et al.*, 1976, cited in Government of Canada, 1993b). Benzene induced a positive, negative or neutral growth response, depending upon concentration and plant species. Some degree of

recovery from sublethal effects was observed within 1–4 weeks following short-term exposures of 0.5–4 hours. Gross signs of benzene toxicity included darkening of leaf tops, loss of turgor and bleaching of chlorophyll (Currier, 1951, cited in Government of Canada, 1993b).

• *Xylenes*: Exposure of barley to xylene vapour at 20 000 000 μg/m³ for 4 hours resulted in 80% injury of leaves within 24 hours. Leaves recovered to 10% injury 4 weeks after exposure (Currier, 1951; Currier and Peoples, 1954; both cited in Government of Canada, 1993c).

4.2 Wildlife

The lowest No-Observed-Adverse-Effect Level (NOAEL) for non-neoplastic effects in animals following oral exposure to styrene via drinking water was 12 000 µg/kg-bw per day, based on reproductive effects in a three-generation study with Sprague-Dawley rats (Beliles *et al.*, 1985, cited in Government of Canada, 1993a). This value was used by Health Canada to develop a tolerable daily intake for humans (Government of Canada, 1993a).

4.3 Aquatic organisms

Before 1993, there were very few reliable studies conducted on the toxicity of styrene to aquatic organisms. Almost all studies used nominal concentrations and failed to minimize or account for losses of styrene through volatilization. Studies undertaken since then were designed to minimize volatilization and reported results based on measured concentrations of styrene. The most sensitive organism tested was the green alga, *Selenastrum capricornutum*, with a 96-hour EC₅₀ of 720 μg/L (Hoberg, 1995). Reported 96-hour LC₅₀ values for rainbow trout (*Oncorhynchus mykiss*) are 2500 μg/L (Qureshi *et al.*, 1982) and 4100 μg/L (Exxon Biomedical Sciences Inc., 1993). The fathead minnow (*Pimephales promelas*) was somewhat less sensitive, with a 96-hour LC₅₀ of 10 000 μg/L (Machado, 1995). The 48-hour LC₅₀ for the cladoceran, *Daphnia magna*, was 4700 μg/L (Putt, 1995a). *Hyalella azteca* was somewhat less sensitive, with a 96-hour LC₅₀ of 9500 μg/L (Putt, 1995b).

5.0 ASSESSMENT OF "TOXIC" UNDER CEPA 1999

The environmental risk assessment of a PSL substance is based on the procedures outlined in Environment Canada (1997). Analysis of exposure pathways and subsequent identification of sensitive receptors are used to select environmental assessment endpoints (e.g., adverse reproductive effects on sensitive fish species in a community). For each endpoint, a conservative Estimated Exposure Value (EEV) is selected and an Estimated No-Effects Value (ENEV) is determined by dividing a Critical Toxicity Value (CTV) by an application factor. A conservative (or hyperconservative) quotient (EEV/ENEV) is calculated for each of the assessment endpoints in order to determine whether there is potential ecological risk in Canada. If these quotients are less than one, it

can be concluded that the substance poses no significant risk to the environment, and the risk assessment is completed. If, however, the quotient is greater than one for a particular assessment endpoint, then the risk assessment for that endpoint proceeds to an analysis where more realistic assumptions are used and the probability and magnitude of effects are considered. This latter approach involves a more thorough consideration of sources of variability and uncertainty in the risk analysis.

5.1 Assessment endpoints

The assessment endpoints for this report are adverse effects on terrestrial plants exposed to styrene through the air, on wildlife and on aquatic organisms.

5.2 Terrestrial plants

For a hyperconservative risk characterization for terrestrial plants, the EEV is $43.6 \,\mu\text{g/m}^3$, the highest 24-hour average concentration of styrene reported in the Canadian atmosphere from 1994 to 1998, inclusive.

No internationally accepted protocols are available for testing the effects of chemicals on plants through atmospheric exposure, nor are there any other plant effects data for styrene using any other test methods. There are, however, some terrestrial plant data on substances which are close chemical analogues of styrene, which were examined on a case-by-case basis and deemed to be acceptable.

The CTV is 400 000 μ g/m³, the lowest concentration of compounds structurally similar to styrene (aniline, toluene, benzene and xylenes) that caused adverse effects in terrestrial plants. Dividing this CTV by a factor of 100 (to account for the uncertainty associated with using aniline toxicity as a surrogate for styrene toxicity, extrapolation from laboratory to field conditions, and interspecies and intraspecies variations in sensitivity) gives an ENEV of 4000 μ g/m³.

The hyperconservative quotient (EEV/ENEV) is then 43.6/4000 = 0.01. Styrene is therefore unlikely to cause significant harm to terrestrial vegetation in Canada as a result of atmospheric exposure.

The review of the existing information shows that there is no indication of concern for plants exposed to styrene. At the same time there are no accepted international protocols for testing the effect of chemicals on plants via atmospheric exposure. Indeed such data is not required in other international programs such as the Organization for Economic Co-operation and Development Screening Information Data Set (OECD SIDS) program to screen chemicals for hazard to environment or humans. It is considered that this route of exposure not be considered further for this substance.

5.3 Wildlife

For wildlife, the EEVs are $100 \mu g/kg$, the highest whole-body concentration of styrene reported for fish from the St. Clair River, and $1.7 \mu g/L$, the highest concentration of styrene reported for Canadian surface waters.

The CTV is 12 000 $\mu g/kg$ -bw per day, the lowest NOAEL in a three-generation oral exposure study using rats, based on reproductive effects. Dividing the CTV by a factor of 10 (to account for the extrapolation from laboratory to field conditions and interspecies and intraspecies variations in sensitivity) gives an ENEV of 1200 $\mu g/kg$ -bw per day.

To reach the ENEV of 1200 μ g/kg-bw per day, an animal would each day have to eat 12 times its own weight of food containing styrene at a concentration of 100 μ g/kg (1200 μ g/kg-bw per day divided by 100 μ g/kg = 12) or drink more than 700 times its own weight of water containing 1.7 μ g styrene/L (1200 μ g/kg-bw per day divided by 1.7 μ g/L = 706), assuming that all of the styrene in the food and water was assimilated. In its original assessment, the Government of Canada (1993a) concluded that the maximum concentration of styrene measured in air from a rural site in Canada was over 800 times lower than the effects threshold estimated for wild mammals exposed by inhalation. It is therefore unlikely that wildlife would be adversely affected by the concentrations of styrene occurring in the Canadian environment.

5.4 Aquatic organisms

For a hyperconservative risk characterization for aquatic organisms, the EEV is $1.7 \mu g/L$, the highest concentration of styrene reported for Canadian surface waters.

The CTV for aquatic organisms is 720 μ g/L, the 96-hour EC₅₀ for the green alga, *Selenastrum capricornutum*. Dividing this CTV by a factor of 10 (to account for the extrapolation from laboratory to field conditions and interspecies and intraspecies variations in sensitivity) gives an ENEV of 72 μ g/L. This study was also used by the Canadian Council of Ministers of the Environment to set an interim Canadian water quality guideline of 72 μ g/L for the protection of aquatic life (CCME, 1999).

The conservative quotient (EEV/ENEV) is 1.7/72 = 0.02. Therefore, styrene concentrations in water in Canada are unlikely to cause adverse effects on populations of aquatic organisms.

5.5 Discussion of uncertainty

The ENEV for terrestrial plants was based on the toxicity of aniline. The uncertainty of using a surrogate substance was taken into account in determining the ENEV. Styrene could be a more or less potent toxicant than aniline.

Despite some limitations in the data relating to the environmental effects and exposure of styrene, data available at this time are considered adequate for reaching a conclusion on the environmental risk of styrene in Canada.

5.6 Conclusions

CEPA 1999 64(a): Based on available data, it is concluded that styrene is not entering the environment in a quantity or concentration or under conditions that have or may have an immediate or long-term harmful effect on the environment or its biological diversity. Therefore, styrene is not considered "toxic" as defined in CEPA 1999 Paragraph 64(a).

6.0 REFERENCES

- Alexander, M. 1990. The environmental fate of styrene. The SIRC Review, April 1990. Styrene Information and Research Center, Washington, D.C. pp. 33–42.
- Atkinson, R., S.M. Aschman, D.R. Fitz, A.M Winer and J.N. Pitts, Jr. 1982. Rate constants for the gas-phase reactions of ozone with selected organics at 296 Kelvin. Int. J. Chem. Kinet. 14(1): 13–18.
- Beliles, R.P., J.H. Butala, C.R. Stack and S. Makris. 1985. Chronic toxicity and three-generation reproduction study of styrene monomer in the drinking water of rats. Fundam. Appl. Toxicol. 5: 855–868.
- Bonner, R.F. and O. Meresz. 1981. St. Clair River organics study: identification and quantitation of organic compounds. Organic Trace Contaminants Section, Laboratory Services Branch, Ontario Ministry of the Environment. 219 pp.
- Canadian Chemical Producers' Association. 1999. Reducing emissions 7. 1998 emissions inventory and five year projections. A Responsible Care Initiative. The Canadian Chemical Producers' Association, Ottawa, Ontario.
- CCME (Canadian Council of Ministers of the Environment). 1999. Canadian water quality guidelines for the protection of aquatic life: Styrene. *In*: Canadian environmental quality guidelines, 1999. Canadian Council of Ministers of the Environment, Winnipeg, Manitoba.
- Cheeseman, J.M., T.O. Perry and W.W. Heck. 1980. Identification of aniline as an air pollutant through biological assay with loblolly pine. Environ. Pollut. 21: 9–22.
- Currier, H.B. 1951. Herbicidal properties of benzene and certain methyl derivatives. Hilgardia 20: 383–406.
- Currier, H.B. and S.A. Peoples. 1954. Phytotoxicity of hydrocarbons. Hilgardia 23: 155–173.
- Dann, T. 1999. Personal communication. National Air Pollution Surveillance program data for styrene. Pollution Measurement Division, Environmental Technology Centre, Environment Canada, November 1999.
- Environment Canada. 1997. Environmental assessments of Priority Substances under the *Canadian Environmental Protection Act*. Guidance manual version 1.0 March 1997. Chemicals Evaluation Division, Commercial Chemicals Evaluation Branch, Hull, Quebec (EPS 2/CC/3E).

- Exxon Biomedical Sciences Inc. 1993. Acute fish toxicity test: Rainbow trout. Exxon Biomedical Sciences Inc., East Millstone, New Jersey. 30 pp. (Project No. 140358).
- Government of Canada. 1992a. *Canadian Environmental Protection Act*. Priority Substances List assessment report. Toluene. Environment Canada and Health and Welfare Canada, Ottawa, Ontario. 26 pp.
- Government of Canada. 1992b. *Canadian Environmental Protection Act*. Priority Substances List supporting document. Toluene (unedited version). Health and Welfare Canada and Environment Canada, Ottawa, Ontario, December 14, 1992. 80 pp + tables.
- Government of Canada. 1993a. *Canadian Environmental Protection Act*. Priority Substances List assessment report. Styrene. Environment Canada and Health Canada, Ottawa, Ontario. 47 pp.
- Government of Canada. 1993b. *Canadian Environmental Protection Act*. Priority Substances List supporting document. Benzene. Environment Canada and Health Canada, Ottawa, Ontario. 137 pp.
- Government of Canada. 1993c. *Canadian Environmental Protection Act*. Priority Substances List assessment report. Xylenes. Environment Canada and Health Canada, Ottawa, Ontario. 32 pp.
- Government of Canada. 1994. *Canadian Environmental Protection Act*. Priority Substances List assessment report. Aniline. Environment Canada and Health Canada, Ottawa, Ontario. 30 pp.
- Grosjean, D. 1985. Atmospheric reactions of styrenes and peroxybenzoyl nitrate. Sci. Total Environ. 46: 41–59.
- Hoberg, J.R. 1995. Styrene Toxicity to the freshwater green alga, *Selenastrum capricornutum*. Submitted to Styrene Information and Research Center, Washington, D.C., by Springborn Laboratories, Inc., Wareham, Massachusetts, September 14, 1995. 123 pp. (SLI Report No. 95-6-5933).
- Machado, M.W. 1995. Styrene Acute toxicity to fathead minnow (*Pimephales promelas*) under flow-through conditions. Submitted to Styrene Information and Research Center, Washington, D.C., by Springborn Laboratories, Inc., Wareham, Massachusetts, September 14, 1995. 128 pp. (SLI Report No. 95-6-5862).
- Miller, T.A., R.H. Rosenblatt, J.C. Darce, J.G. Pearson, R.K. Kulkarni, J.L. Welch, D.R. Cogley and G. Woodard. 1976. Problem definition studies on potential environmental pollutants. IV. Physical, chemical, toxicological and biological properties of benzene, toluene, xylenes and *p*-chlorophenyl methyl sulfide,

- sulfoxide and sulfone. U.S. Army Medical Research and Development Command, Fort Netrick, Frederick, Maryland (NTIS AD/A-040 435).
- NPRI (National Pollutant Release Inventory). 1999. NPRI database. *Canadian Environmental Protection Act*. Environment Canada, Ottawa, Ontario.
- Otson, R. 1992. Personal communication. Environmental Health Directorate, Health and Welfare Canada, Ottawa, Ontario.
- Putt, A.E. 1995a. Styrene Acute toxicity to water fleas (*Daphnia magna*) under flow-through conditions. Submitted to Styrene Information and Research Center, Washington, D.C., by Springborn Laboratories, Inc., Wareham, Massachusetts, September 14, 1995. 125 pp. (SLI Report No. 95-6-5945).
- Putt, A.E. 1995b. Styrene Acute toxicity to amphipods (*Hyalella azteca*) under flow-through conditions. Submitted to Styrene Information and Research Center, Washington, D.C., by Springborn Laboratories, Inc., Wareham, Massachusetts, September 14, 1995. 126 pp. (SLI Report No. 95-7-5997).
- Qureshi, A.A., K.W. Flood, S.R. Thompson, S.M. Janhurst, C.S. Inniss and D.A. Rokosh. 1982. Comparison of a luminescent bacterial test with other bioassays for determining toxicity of pure compounds and complex effluents. *In*: J.G. Pearson, R.B. Foster and W.E. Bishop (eds.), Aquatic toxicology and hazard assessment: Fifth conference. American Society for Testing and Materials, Philadelphia, Pennsylvania.
- Slooff, W. and P.J. Blokzijl (eds.). 1988. Integrated criteria document toluene. Research for Man and Environment, National Institute of Public Health and Environmental Protection (RIVM), Bilthoven, The Netherlands (Report No. 758473010).
- U.S. EPA (Environmental Protection Agency). 1984. Health and environmental effects profile for styrene. Environmental Criteria and Assessment Office, U.S. Environmental Protection Agency, Cincinnati, Ohio. 94 pp. (NTIS/PB88-182175).
- Veith, G.D., D.L. DeFoe and B. Bergstedt. 1979. Measuring and estimating the bioconcentration factor of chemicals in fish. J. Fish. Res. Board Can. 36: 1040–1048.

APPENDIX A. MOLECULAR STRUCTURES OF STYRENE AND ITS ANALOGUES

