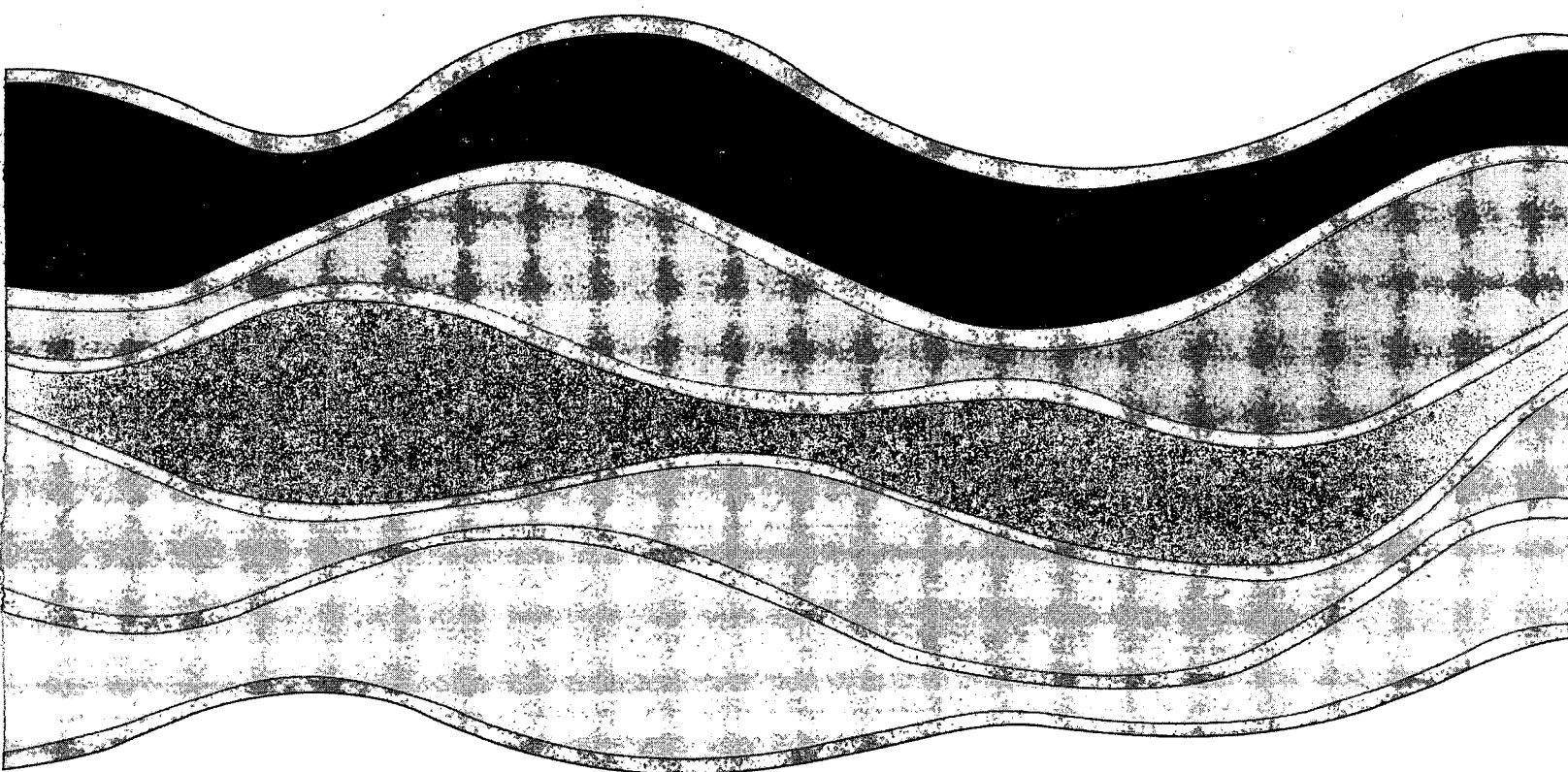
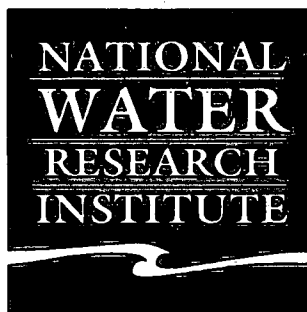


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**OCCURRENCE OF ANILINE IN CANAGAGIGUE
CREEK, ONTARIO - 1995-1996**

C.A. Sullivan, D.T. Bennie and R.J. Maguire

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OCCURRENCE OF ANILINE IN CANAGAGIGUE CREEK, ONTARIO - 1995-1996

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Management Perspective

Aniline was on the first Priority Substances List (PSL1) of the Canadian Environmental Protection Act (CEPA). One of the research recommendations arising from the 1993 CEPA assessment was to determine whether it was entering the Canadian environment, since there were no data on its occurrence in surface waters in Canada. A study conducted in 1993 after the CEPA assessment showed the presence of aniline in Canagagigue Creek, downstream from Elmira, Ontario, the location of a chemical company which had used large quantities of aniline in the production of rubber chemicals. The concentrations of aniline were less than the estimated effects threshold (EET) of $1.1 \mu\text{g/L}$ derived in the CEPA assessment. Consequently, those limited data supported the CEPA assessment that aniline was not toxic to the environment. In this study, samples of Canagagigue Creek collected in 1995 and 1996 were also shown to have concentrations of aniline below the EET, lending further support to the CEPA assessment.

Before 1990, the largest use of aniline in Canada was in Elmira in the production of several rubber chemicals (antioxidants, antidegradants and vulcanization accelerators). This use accounted for 62% of aniline use in Canada in 1990. At the time of the 1993 PSL assessment, it was anticipated that this use would be curtailed soon since the company which imported the aniline to produce the rubber chemicals intended to import other intermediates instead. Consequently, it was felt that concentrations of aniline in Canagagigue Creek would decrease if they were due wholly or in large part to rubber-making, and there would be a correspondingly larger margin of safety for the most sensitive organism. Importation data obtained up to 1996 confirm a large decrease in amounts of aniline imported into Canada in the 1990s compared to amounts imported in the 1970s and 1980s. Consequently it is concluded from the results of grab sampling in 1993, 1995 and 1996, and aniline importation trends, that further determinations of aniline in Canagagigue Creek are not warranted.

Sommaire à l'intention de la direction

L'aniline a été portée sur la première liste des substances d'intérêt prioritaire (LSIP I) en vertu de la *Loi canadienne sur la protection de l'environnement* (LCPE). L'une des recommandations de recherche issues de l'évaluation 1993 aux termes de la LCPE était de déterminer si cette substance pénétrait dans l'environnement canadien puisqu'il n'existait pas de données sur sa présence dans les eaux superficielles au Canada. Une étude effectuée en 1993, dans la foulée de l'évaluation dans le cadre de la LCPE, a révélé la présence d'aniline dans l'eau du ruisseau Canagagigue, en aval d'Elmira, Ontario, soit dans le secteur où un établissement de produits chimiques avait utilisé de grandes quantités d'aniline pour la production de composés chimiques servant à la fabrication du caoutchouc. La concentration mesurée d'aniline était inférieure au seuil des effets estimés (SEE) de 1,1 mg/L déterminé lors de l'évaluation aux termes de la LCPE. Ces données restreintes confirmaient donc les conclusions de l'évaluation à l'effet que l'aniline n'est pas toxique pour l'environnement. En effet, dans cette étude, des échantillons d'eau du ruisseau Canagagigue prélevés en 1995 et en 1996 contenaient de l'aniline en concentration inférieure au SEE.

Avant 1990, la principale source d'utilisation de l'aniline au Canada était la synthèse de plusieurs produits entrant dans la fabrication du caoutchouc (antioxydants, agents protecteurs et accélérateurs de la vulcanisation) à Elmira. Soixante-deux pour cent de l'aniline employée au pays passait à cette production en 1990. Au moment de l'évaluation dans le cadre de la LSIP en 1993, il était prévu que l'utilisation de cette substance diminuerait beaucoup dans un proche avenir puisque la compagnie importatrice entendait passer à d'autres intermédiaires pour la fabrication du caoutchouc. On se disait donc que, si elle était attribuable en tout ou en partie à cette source, la concentration d'aniline dans l'eau du ruisseau devrait s'abaisser. Par conséquent, la marge d'innocuité pour l'organisme le plus sensible se trouverait accrue. Les données sur l'importation de l'aniline jusque en 1996 confirment qu'il s'est importé beaucoup moins de cette substance au cours des années 1990 par rapport aux niveaux atteints dans les années 1970 et 1980. Les résultats de l'analyse d'échantillons instantanés prélevés en 1993, en 1995 et en 1996, et l'examen de la courbe d'importation de l'aniline mènent à la conclusion qu'il est inutile de procéder au dosage de cette substance dans l'eau du ruisseau Canagagigue.

Abstract

In a follow-up study to a 1993 study of the occurrence of aniline in Canagagigue Creek downstream from Elmira, Ontario, the location of a chemical company that has used large quantities of aniline in the production of rubber chemicals, the concentrations of aniline in water on two occasions in 1995 and 1996 were less than the estimated effects threshold for aquatic biota of 1.1 mg/L that was established in the Canadian Environmental Protection Act (CEPA) assessment of aniline, lending further support to the assessment that aniline was not "toxic" to the environment, as defined by CEPA.

Résumé

Dans le cadre d'une étude subséquente à une évaluation, menée en 1993, de la concentration de l'aniline dans le ruisseau Canagagigue en aval d'Elmira en Ontario, où est implantée une usine de produits chimiques qui utilisait de grandes quantités d'aniline pour la synthèse de plusieurs produits entrant dans la fabrication du caoutchouc, la concentration mesurée de l'aniline dans l'eau à deux occasions, en 1995 et en 1996, était inférieure au seuil des effets estimés pour les biotes aquatiques, soit 1,1 mg/L, fixé lors de l'évaluation de cette substance dans le cadre des évaluations de substances figurant sur la liste des substances d'intérêt prioritaire aux termes de la *Loi canadienne sur la protection de l'environnement* (LCPE). Cette étude confirme que l'aniline n'est pas « toxique dans l'environnement » aux termes de cette loi.

Introduction

Aniline was on the first Canadian Environmental Protection Act (CEPA) priority substances list (PSL1), which required that it be assessed with regard to its toxicity to the environment, to human life or health, and to the environment on which human life or health depends (Government of Canada, 1988). At the time of the assessment, the main uses of aniline in Canada were in the production of rubber chemicals (62%), polymers (32%) and phenolic-based resins (6%) (Canada Department of the Environment, 1993a). Aniline was not produced in Canada, but was primarily imported from the U.S.A. into Ontario. In 1991, the last year for which such figures are available, 107 tonnes of aniline were imported into Canada.

Based on the available data, aniline was not considered to be toxic to the environment or to the environment on which human life or health depends, but there was insufficient information to conclude whether it was toxic to human life or health (Canada Department of the Environment, 1993a). One of the research recommendations arising from the CEPA assessment was to determine whether aniline was entering the Canadian environment, since there were no data on its occurrence in surface waters in Canada.

Aniline had been found in monitoring wells beneath a chemical company site in Elmira, Ontario, at concentrations up to 300 mg/L (Lesage *et al.*, 1990; CH2M Hill Engineering, 1991), and in the dense non-aqueous phase liquid beneath former containment areas on the same site at concentrations up to 2% (Dames & Moore Canada, 1992). The chemical company used to produce aniline until 1971, and, at least up to 1991, imported aniline for the production of rubber chemicals (Canada Department of the Environment, 1993a). The total amount of aniline in the groundwater and in the dense non-aqueous phase liquid at the Elmira site is not known. There are no water quality guidelines for aniline in groundwater. At the time of the aniline assessment, it was not known whether aniline was present in nearby Canagagigue Creek as a result of the migration of groundwater to the surface, or as a result of industrial discharges. A subsequent limited study described the occurrence of aniline in Canagagigue Creek, downstream from Elmira, on two dates in April and September, 1993 (Maguire and Batchelor, 1993).

The concentrations were 1.0 µg/L and 0.3 µg/L, respectively, less than the estimated effects threshold (EET) of 1.1 µg/L for *Daphnia magna*. Consequently, that study supported the CEPA assessment that aniline was not toxic in the Canadian environment. This study was conducted to verify the results of the 1993 study. As before, the intent was not to conduct an intensive monitoring program for aniline, but simply to establish whether aniline was present in Canagagigue Creek.

Experimental Section

Materials

Aniline (ACS reagent grade, purity > 99.5%) was obtained from the Aldrich Chemical Co. (Milwaukee, WI, U.S.A.), and was used without further purification.

Pesticide grade dichloromethane and other solvents were obtained from different suppliers. The purity of dichloromethane was checked at 500x concentration, and that of isooctane at 10x concentration, before use. Glass fibre filters of 1 μm pore size were obtained from Gelman Sciences Inc. (Rexdale, Ont.). The sodium sulfate, aluminum foil, glass fibre filters and disposable pipets were heated to 500 °C for 24 hr before use. Hydrochloric acid and sodium hydroxide solutions used for pH adjustment were prepared from reagent grade chemicals, but were extracted with hexane before use to minimize contamination. All glassware was rinsed with pesticide grade solvents before use.

Sample Collection

The sampling site on Canagagigue Creek is 1.7 km downstream from the Elmira Water Pollution Control Plant (designated "CN-3" in the study by Carey *et al.*, 1983).

Water samples of volume 40 L were collected on February 20, 1995 and June 3, 1996 from a depth of 0.5 m. Within 4 hr of collection the water samples were filtered and were being extracted. The samples were pressure filtered through 1 μm glass fibre filters using compressed nitrogen and modified pressurized beverage containers, pressure filters and Teflon transfer lines (Fox, 1986). The filters were discarded [the log (n-octanol/water partition coefficient) for aniline of 0.9 (Chiou *et al.*, 1982) indicated that no significant amounts would be bound to suspended solids]. The water samples were extracted in these containers under acidic conditions followed by extraction under basic conditions. The extraction under acidic conditions was intended to be a clean-up step to remove acidic and neutral interferents, while the aniline would be extracted under basic conditions. Accordingly, the pH of the water sample was first adjusted to 2 with concentrated HCl. The sample was stirred with 1000 mL of dichloromethane for 30 min and the phases were allowed to separate overnight. Approximately 500 mL of dichloromethane was recovered from the first extraction. Two more extractions were performed with 500 mL of dichloromethane each time, but the phase separation time was 15-30 min. The three extracts were discarded. The pH of the water was then adjusted to 11 with 10 M NaOH. Three extractions of 500 mL of dichloromethane each time were performed, with stirring for 30 min, followed by a phase separation time of 15-30 min. These three extracts were combined, dried by passage through anhydrous sodium sulfate, and concentrated

(by rotary evaporation to 2-5 mL, followed by evaporation with a gentle stream of nitrogen), with solvent exchange, to 2.0 mL of isooctane solution. The isooctane solution was analyzed by gas chromatography without cleanup as described below. In order to minimize contamination between sampling dates, all stainless steel containers were thoroughly flushed with tap water and distilled water, and rinsed with dichloromethane, after sample handling.

Analysis

(1) For the 1995 sample

Tentative identification of aniline in the sample extracts was done with a Hewlett-Packard 5890A-II gas chromatograph (GC) equipped with a 7673A autosampler (1 μ L injections), flame ionization detector (FID), nitrogen-phosphorus detector (NPD) and 5895A ChemStation for data handling. A single splitless injector - dual column - dual detector (FID/NPD) technique was used. The dimensions of the DB-5 columns [polymethyl(5% phenyl)siloxane] (J & W Scientific - Chromatographic Specialties Inc., Brockville, Ont.) were 0.25 mm i.d. x 30 m length, with 0.25 μ m film thickness. Injector and detector temperatures were 200 and 300 $^{\circ}$ C, respectively. The column temperature program was 50 $^{\circ}$ C for 1 min, then 10 $^{\circ}$ /min to 120 $^{\circ}$ C, then 20 $^{\circ}$ /min to 280 $^{\circ}$ C, with a 1 min final hold. The helium carrier gas, nitrogen make-up (FID), and helium make-up (NPD) flow rates (at 50 $^{\circ}$ C) were 1.3-1.5, 28, and 32 mL/min, respectively. Detector flow rates for hydrogen and air were 33 and 450 mL/min, respectively, for the FID, and 3.7 and 115 mL/min, respectively, for the NPD. The splitless injector was purged with helium 0.75 min after injection. Standard solutions of aniline in the expected concentration range were used to calibrate retention times and detector responses. The presence of aniline was taken to be tentatively confirmed if it occurred within a retention time window of 0.04 min for a known standard of aniline (at a retention time about 6 min) and if its peak height was at least three times the noise level. Measurement precision at the limit of quantitation was about 20%. Solvent, reagent and procedural blanks were performed for each sampling date. At no time was contamination evident.

Confirmation of the identity of aniline was done by gas chromatography - selected ion monitoring mass spectrometry (GC-SIM-MSD) with a Hewlett-Packard 5890A-II GC, 7673 autosampler (1 μ L injections), 5971A mass selective detector and MS ChemStation for data handling. Injector (splitless) and detector temperatures were 250 and 190 $^{\circ}$ C, respectively. A DB-5 column was used, with the same dimensions as those used for the GC-FID/NPD analyses. The column temperature program was 50 $^{\circ}$ C for 1 min, then 10 $^{\circ}$ /min to 280 $^{\circ}$ C, with a 1 min final hold. The helium carrier gas flow rate was 1 mL/min, and the inlet pressure was 15 psig. The splitless injector was purged with helium 0.75 min after

injection. The MSD was operated in electron impact mode with an ionization potential of 70 eV. The four ions monitored, and their relative intensities, were: target (T), 93.05 amu (100%); qualifier 1 (Q1), 66.10 amu (30%); Q2, 65.10 amu (13.3%); and Q3, 94.05 amu (6.7%). A peak was confirmed as aniline if it occurred within the retention time window of 0.04 min for a known standard of aniline, and if the ratios of qualifying ions to the target ion were within 20% of the ratios for the external standard.

(2) For the 1996 sample

Tentative identification of aniline in the sample extracts was done with a Hewlett-Packard 6890 gas chromatograph (GC) equipped with a HP 6890 Series injector/autosampler (1 μ L injections), nitrogen-phosphorus detector (NPD) and electron capture detector (ECD), and 1656A rev 04.01 Asterix ChemStation for data handling. A single splitless injector - dual column - dual detector (NPD/ECD) technique was used, although only data collected from NPD contained information on aniline. The dimensions of the HP-5 columns [polymethyl(5% phenyl)siloxane] (Hewlett-Packard, Mississauga, Ont.) were 0.25 mm i.d. x 30 m length, with 0.25 μ m film thickness. Injector and detector temperatures were 225 and 300 $^{\circ}$ C, respectively. The column temperature program was 60 $^{\circ}$ C for 1.20 min, then 5 $^{\circ}$ /min to 80 $^{\circ}$ C, then 8 $^{\circ}$ /min to 280 $^{\circ}$ C, with a 5 min final hold. The helium carrier gas in constant flow mode, and helium make-up (NPD) flow rates (constant make-up flow rate) were 3.0 and 5.0 mL/min, respectively. Detector flow rates for hydrogen and air were 4.0 and 60 mL/min, respectively, for the NPD. The splitless injector was purged with helium 1.0 min after injection, at a rate of 10.9 mL/min. Standard solutions of aniline in the expected concentration range were used to calibrate retention times and detector responses. The presence of aniline was taken to be tentatively confirmed if it occurred within a retention time window of 0.04 min for a known standard of aniline (at a retention time about 5.5 min) and if its peak height was at least three times the noise level. Measurement precision at the limit of quantitation was about 20%. Solvent, reagent and procedural blanks were performed for each sampling date. At no time was contamination evident.

Confirmation of the identity of aniline was done by gas chromatography - selected ion monitoring mass spectrometry (GC-SCAN-MSD) with a Hewlett-Packard 6890 GC, 6890 Series autosampler (1 μ L injections), 5973 mass selective detector and MS ChemStation for data handling. Injector (pulsed splitless) and MSD Transfer Line heater were 250 $^{\circ}$ C and 290 $^{\circ}$ C, respectively. A HP-5MS column was used, with the same dimensions as those used for the GC-NPD/ECD analyses. The column temperature program was 100 $^{\circ}$ C for 1.20 min, then 8 $^{\circ}$ /min to 280 $^{\circ}$ C, with a 5 min final hold. The helium carrier gas flow rate was 1.2 mL/min, in constant flow mode and the inlet pulse pressure was 25 psig. The

pulsed splitless injector was purged with helium 1.50 min after injection at a rate of 50 mL/min. The MSD was operated in electron impact mode with an ionization potential of 70 eV. The four ions monitored, and their relative intensities, were: target (T), 93.05 amu (100%); qualifier 1 (Q1), 66.10 amu (30%); Q2, 65.10 amu (13.3%); and Q3, 94.05 (6.7%). A peak was confirmed as aniline if it occurred within the retention time window of 0.04 min for a known standard of aniline, and if the ratios of qualifying ions to the target ion were within 20% of the ratios for the external standard.

Results and Discussion

Aniline was tentatively identified in the 1995 sample and confirmed by mass spectrometry in the 1996 sample, at concentrations of 27 and 43 ng/L, respectively. These concentrations were significantly less than the concentrations of 1.0 µg/L in April, 1993 and 0.3 µg/L in September, 1993.

In the CEPA assessment of priority chemicals, effects thresholds for the most sensitive aquatic biota were estimated by dividing the lowest-observed-effects-concentration in toxicity tests by various factors that accounted for the limited data available (Canada Department of the Environment, 1992). Emphasis was placed on ecologically relevant test results (e.g., mortality rather than Microtox endpoints). The estimated effects thresholds (EET) were then compared to the mean environmental concentrations (EC) observed in Canada. If the EET/EC ratio was ≤ 1 for a given compound, then the potential existed for that compound to cause harmful effects to aquatic biota.

For aniline the most sensitive aquatic species identified in the CEPA assessment was *Daphnia magna*, with a 14-day lowest-observed-effects-concentration (for mortality) of 22 µg/L (Gersich and Milazzo, 1990). Dividing this value by a factor of 20 to convert to a no-observed-effects-concentration, to account for interspecies differences and to extrapolate laboratory results to the field, yielded an estimated effect threshold of 1.1 µg/L. Because there were no data on the occurrence of aniline in surface water, the level III fugacity model of Mackay and Paterson (1991) was used with importation data to predict a steady-state concentration of about 9×10^{-3} ng/L aniline in surface water in southern Ontario. This concentration was about 1.3×10^5 times less than the estimated effects threshold. Consequently, aniline was considered not to be toxic to the environment (Canada Department of the Environment, 1993a). In this study, the concentrations of aniline found in Canagagigue Creek were 25-40 times less than the EET. Therefore these limited data are in agreement with the CEPA assessment of aniline. It is not known whether the aniline that was found arose from current industrial activity in Elmira or from the surfacing of groundwater.

At the time of the 1993 PSL1 assessment (Canada Department of the Environment, 1993a), it was anticipated that aniline importation into Canada would decrease significantly because the company which imported most of the aniline to produce the rubber chemicals intended to import other intermediates instead. Consequently, it was felt that concentrations of aniline in Canagagigue Creek would decrease if they were due wholly or in large part to rubber-making, and there would be a correspondingly larger margin of safety for the most sensitive organism. Importation data obtained up to 1996 (see Figure 1) confirm that there has been a large decrease in amounts of aniline imported into Canada in the 1990s compared to amounts imported in the 1970s and 1980s. Consequently it is concluded from the results of grab sampling in 1993, 1995 and 1996, and aniline importation trends, that further determinations of aniline in Canagagigue Creek are not warranted.

Acknowledgement

We thank E.D. Brien of the Commercial Chemicals Evaluation Branch, Environmental Protection Service, Environment Canada, for obtaining some of the data on importation of aniline and its salts into Canada.

References

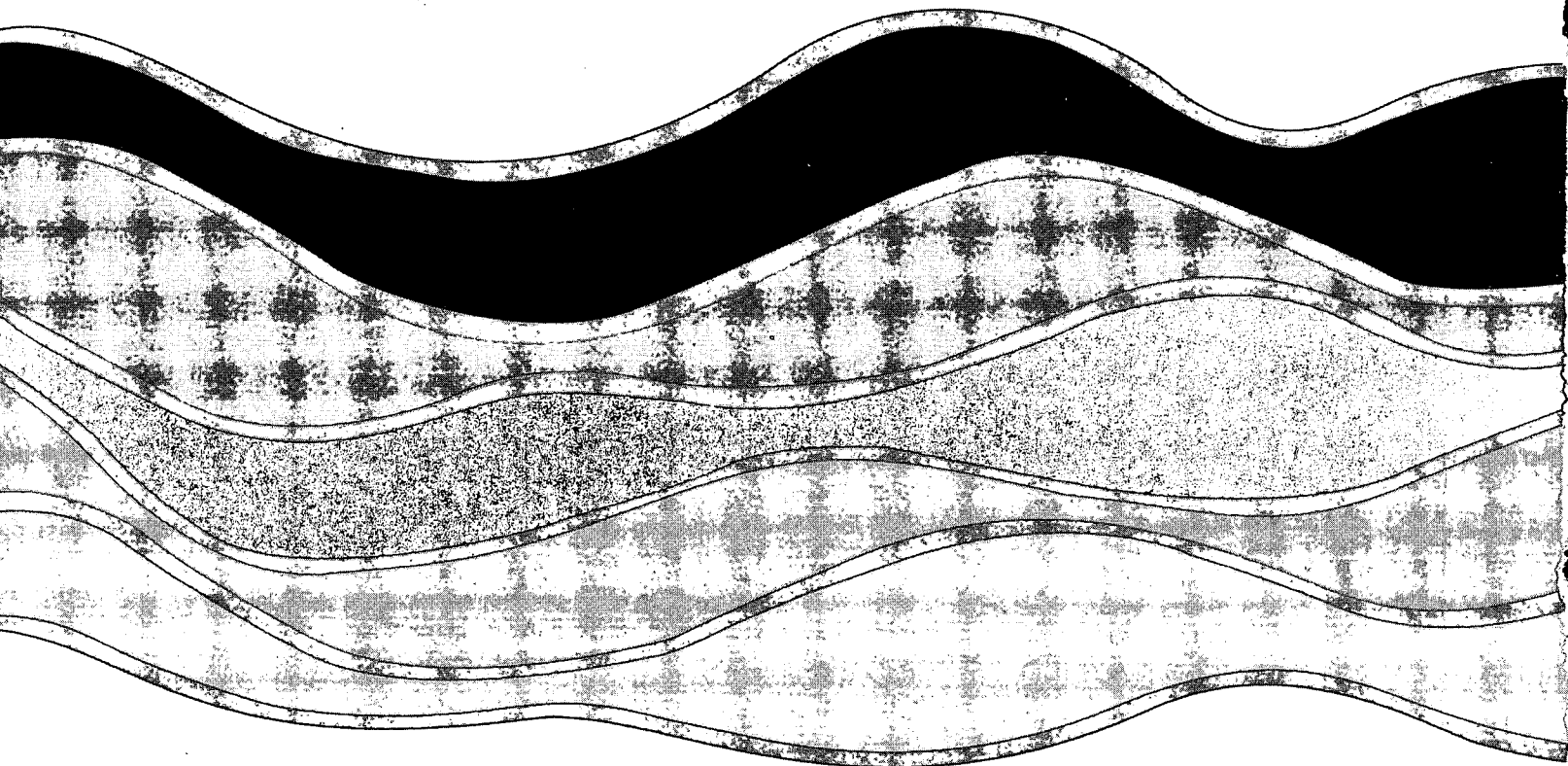
- Canada Department of the Environment (1992). Guidelines for conducting assessments under the Canadian Environmental Protection Act. Commercial Chemicals Branch, Department of the Environment, Hull, Québec K1A 0H3.
- Canada Department of the Environment (1993a). Canadian Environmental Protection Act priority substances list assessment report - aniline. Commercial Chemicals Branch, Department of the Environment, Hull, Québec K1A 0H3, ISBN 0-662-20719-X, 32+ pp.
- Canada Department of the Environment (1993b). Canadian Environmental Protection Act priority substances list supporting documentation - aniline. Commercial Chemicals Branch, Department of the Environment, Hull, Québec K1A 0H3, 42+ pp.
- Carey, J.H., Fox, M.E., Brownlee, B.G., Metcalfe, J.L., Mason, P.D. and Yerex, W.H. (1983). The fate and effects of contaminants in Canagagigue Creek. 1. Stream ecology and identification of major contaminants. Department of the Environment, Inland Waters Directorate Scientific Series No. 135, National Water Research Institute, Burlington, Ontario L7R 4A6, ISBN 0-662-12929-6, 37+ pp.

- CH2M Hill Engineering Ltd. (1991). Research and development of permanent onsite solutions for contamination of groundwater at waste disposal and industrial sites in Canada. Final report. A report to Supply and Services Canada in fulfilment of DSS Contract KE405-7-6557/01-SE. Suite 600, 180 King Street South, Waterloo, Ontario N2J 1P8.
- Chiou, C.T., Schmedding, D.W. and Manes, M. (1982). Partitioning of organic compounds in octanol-water systems. *Environ. Sci. Technol.* **16**, 4-10.
- Dames & Moore, Canada (1992). Study of DNAPL occurrence beneath former operating ponds of Uniroyal Chemical Ltd., Elmira. A report prepared for Uniroyal Chemical Ltd. in compliance with Part IV, Section 6 of the Ministry of the Environment Amended Control Order (1991). Project 19377-013, 7560 Airport Road, Mississauga, Ontario L4T 2H5.
- Fox, M.E. (1986). A practical sampling and extraction system for the quantitative analysis of sub-ng/L organochlorine contaminants in filtered water and suspended solids. In: *Methods for Analysis of Organic Compounds in the Great Lakes, Vol. II*, W.C. Sonzogni and D.J. Dube (eds.), University of Wisconsin Sea Grant Institute, Madison, WI, U.S.A., Vol. II, 27-34.
- Gersich, F.M. and Milazzo, D.P. (1990). Evaluation of a 14-day static renewal toxicity test with *Daphnia magna* Straus. *Arch. Environ. Contam. Toxicol.* **19**, 72-76.
- Government of Canada (1988). An act respecting the protection of the environment and of human life and health. *Hansard*, Chapter 22, pp. 1-96, Queen's Printer, Ottawa, Ont.
- Lesage, S., Ritch, J.K. and Treciokas, E.J. (1990). Characterization of groundwater contaminants at Elmira, Ontario, by thermal desorption, solvent extraction GC-MS and HPLC. *Water Pollut. Res. J. Can.* **25**, 275-292.
- Mackay, D. and Paterson, S. (1991). Evaluating the multimedia fate of organic chemicals: a level III fugacity model. *Environ. Sci. Technol.* **25**, 427-436.
- Maguire, R.J. and Batchelor, S.P. (1993). Occurrence of aniline in Canagagigue Creek, Ontario. National Water Research Institute Contribution No. 93-140, Environment Canada, Canada Centre for Inland Waters, Burlington, Ontario L7R 4A6, 14+ pp.

Year	Total (tonnes)
1976	332
1977	560
1978	334
1979	679
1980	544
1981	610
1982	513
1983	1353
1984	1239
1985	879
1986	620
1987	570
1988	677
1989	354
1990	65
1991	107
1992	22
1993	30
1994	35
1995	25
1996	33



Figure 1. Imports of aniline and its salts into Canada, 1976-1996. Data were obtained from Canada Department of the Environment (1993b) and from a 1997 on-line search of Statistics Canada data (<http://www.gc.ca>)



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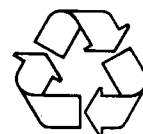


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