

**SILICA GEL COLUMN CLEANUP FOR PESTICIDES,
PCBS AND PAHS IN WATER,
SEDIMENT AND BIOTA SAMPLES FROM THE
YAMASKA RIVER, QUEBEC**

by

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**February 1990
NWRI Contribution #90-56**

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ABSTRACT

A silica gel column cleanup method was developed for 143 PCB congeners, PAHs, and organochlorine, organophosphate, triazine, amide and carbamate pesticides which features a five-fraction elution in solvents of increasing polarity. The elution pattern of each chemical was tested, and in some cases the elution pattern can provide additional information in the gas chromatographic identification of certain pesticides.

RÉSUMÉ

Une méthode d'épuration sur colonne de gel de silice a été mise au point pour 143 congénères des BPC, les HAP, et les pesticides organochlorés, organophosphatés, triazine, amide et carbamate. Cette méthode comporte une élution en cinq fractions à l'aide de solvants de polarité croissante. Le patron d'élution pour chacun des produits chimiques a été testé et dans certains cas, ce dernier pouvait fournir de l'information additionnelle pour l'identification de certains pesticides par chromatographie en phase gazeuse.

MANAGEMENT PERSPECTIVE

This silica gel column cleanup method has been developed for the analysis of water, sediment and biota samples from the Yamaska River for a wide range of pesticides and industrial chemicals.

PERSPECTIVE-GESTION

Cette méthode d'épuration sur colonne de gel de silice a été mise au point pour l'analyse d'échantillons d'eau, de sédiments et de biota de la rivière Yamaska dans le but de détecter une grande variété de pesticides et de produits chimiques industriels.

INTRODUCTION

The Yamaska River basin in Quebec (cf. Fig. 1) is the focus of intensive agricultural activity. In 1982, 26% of all agricultural pesticides (excluding oils) sold in Quebec were sold in the Yamaska River basin, more than in any other basin (Reiss et al., 1984). The main pesticide classes used in the Yamaska River basin were triazines and triazoles (38% of total, excluding oils), amides (18%), carbamates (16%) and organophosphates (7%). In addition, there are several textile mills and other light chemical industries in the Yamaska River basin, with the potential for contamination of the river by dyes and other industrial chemicals.

The water quality (C,N,P) of the Yamaska River has been studied extensively (Campbell et al., 1976, 1982; Belanger, 1980). In addition, over the past fifteen years occasional surveys have been conducted for metals (Mongeau, 1979; Belanger, 1980), herbicides (Caille et al., 1975; Muir et al., 1978; Duval and Gauthier, 1986; Forrest and Caux, 1989; Maguire et al., 1989), PCBs and chlorinated pesticides (Harvey, 1979; Goulet and Laliberte, 1982; Laliberte and Goulet, 1983; Croteau et al., 1984; Paul et al., 1984; Maguire et al., 1989). In a more intensive study of contamination of the Yamaska River during the period 1985-1987, which incidentally corresponded to the time that municipal sewage treatment plants were installed on major towns on the river, we were interested in determining 143 pesticides, PCB congeners and PAHs (in addition to dyes) in samples of water, suspended solids, bed sediment and biota. For such an extensive series of chemicals it was anticipated that the cleanup of sample extracts would be critical for successful determinations. This report describes

the five-fraction silica gel column cleanup which was developed. The results of the sample analyses will be reported later.

EXPERIMENTAL SECTION

Materials

Most chemical standards were obtained from chromatographic supply companies. Sets of PCB congeners were obtained from the National Research Council of Canada, Halifax. These PCB congeners represent, by weight, 3% of Aroclor 1221, 44% of Aroclor 1242, 48% of Aroclor 1248, 38% of Aroclor 1254 and 60% of Aroclor 1260; therefore the sum of these PCB congeners should not be regarded as "total PCBs". Pesticide grade dichloromethane and other solvents were obtained from different suppliers and their purity (at 1000x concentration) was checked before use. HPLC grade solvents from different suppliers were used in the high performance liquid chromatographic determination of carbamate pesticides and dyes. The sodium sulfate was heated to 500 °C for 24 h before use. Silica gel (Merck Kieselgel 60) was obtained from BDH Chemicals (Toronto). All glassware was rinsed with pesticide grade solvents before use. ACRO LC13 disposable filters with Luer inlets were obtained from Gelman Sciences (Montreal).

Silica gel fractionation

Individual standards and mixtures of standards were prepared in toluene

or isooctane and their elution behaviour was tested in a five-fraction silica gel column cleanup. The silica gel was activated at 200 °C for 24 hours, then deactivated with 5% Milli-Q (Millipore-Waters, Mississauga) water and mixed overnight. Columns (10.5 mm i.d.) were packed with 2 cm of anhydrous sodium sulfate above and below 8 cm of silica gel, and rinsed with hexane. The standards were applied to the columns and fractionated as follows:

Fraction 1: 60 mL hexane

Fraction 2: 60 mL hexane/dichloromethane (80/20, v/v)

Fraction 3: 60 mL dichloromethane

Fraction 4: 200 mL acetone

Fraction 5: 100 mL methanol

All five fractions were solvent-exchanged with isooctane and reduced to 1 mL for analysis as described below in order to determine in which fraction each chemical eluted.

Methods of determination

(a) PCBs and chlorinated pesticides

Analyses for PCBs and chlorinated pesticides were performed with a Hewlett-Packard 5890A gas chromatograph with a single splitless injector - dual column - dual electron capture detector technique. One column was DB5 and the other was DB1701. Column dimensions were 0.25 mm i.d. x 30 m in length, with 0.25 µm film thickness. Injector and detector temperatures were 250 and 300°C,

respectively. The initial column temperature was 120°C, and the program rate was 2°/min to 280°C. The hydrogen carrier gas and argon/methane (5%) make-up flow rates were 1 - 1.5 and 30 mL/min., respectively. The identities of the 67 chlorinated insecticides and PCB congeners sought are shown in Table 1. Standard mixtures of all of these compounds in the expected concentration ranges were prepared and used to calibrate retention times and detector responses. The presence of a compound was taken to be confirmed if it occurred within the appropriate chromatographic "window" on both columns. Chromatographic windows were typically 0.04 min. at their widest at 80 min. retention time.

(b) Organophosphorus, triazine, and amide pesticides

Analyses for organophosphorus, triazine, and amide pesticides were performed in splitless mode with a Varian 3400 gas chromatograph and a thermionic specific detector. A 25 m x 0.32 mm i.d. Ultra-2 column (0.17 μ m film thickness) (Hewlett Packard) was programmed from 80 to 280°C at 1.5°/min., followed by a 5 min. hold. The inlet and detector temperatures were 250 and 300°C, respectively. The helium carrier gas, nitrogen make-up, air and hydrogen flow rates were 1 - 1.5, 29, 175 and 4.5 mL/min., respectively. The identities of the 43 organophosphorus, triazine, and amide pesticides sought and their silica gel fractionation are shown in Table 2. Standard mixtures of all these compounds in the expected concentration ranges were prepared and used to calibrate retention times and detector responses. The presence of a compound was taken to be tentatively confirmed if it occurred within the appropriate chromatographic window. Chromatographic windows were typically 0.07 min. at 80 min. retention time.

Analyses for organophosphorus pesticides were also performed with a Hewlett-Packard 5890A gas chromatograph with a single splitless injector - dual column - dual electron capture detector technique for qualitative confirmation. One column was DB-5 and the other was DB-1701. Column dimensions were 0.25 mm i.d. x 30 m in length, with 0.25 μ m film thickness. Injector and detector temperatures were 250 and 300°C, respectively. The initial column temperature was 120°C, and the program rate was 2°/min to 280°C, with an 8 min. final hold. The hydrogen carrier gas and argon/methane make-up flow rates were 1 - 1.5 and 30 mL/min., respectively. Chromatographic windows were typically 0.04 min. at their widest at 80 min. retention time, which illustrates the superior oven temperature control and reproducibility of our two Hewlett-Packard 5890A gas chromatographs compared to our Varian 3400 gas chromatograph.

(c) PAHs

Analyses of the sample extracts for PAHs were performed with a Hewlett-Packard 5730A gas chromatograph with a splitless injector, DB-5 column and flame ionization detector. Column dimensions were 0.2 mm i.d. x 30 m in length, with 0.25 μ m film thickness. Injector and detector temperatures were 250 and 300°C, respectively. The initial column temperature was 120°C, and the program rate was 2°/min to 280°C, with an 8 min. final hold. The helium carrier gas and make-up, air and hydrogen flow rates were 1 - 1.5, 30, 300 and 30 mL/min., respectively. The identities of the 16 PAHs sought are shown in Table 3. Standard mixtures of all of these compounds in the expected concentration ranges were prepared and used to calibrate retention times and detector responses. The presence of a compound was taken to be tentatively confirmed if it occurred

within the appropriate chromatographic window. Chromatographic windows were typically 0.04 min. at their widest at 80 min. retention time.

(d) Carbamate pesticides

Analyses for carbamate pesticides were performed with a Waters high performance liquid chromatograph (HPLC) and 990+ diode array spectrophotometric detector. After all GC analyses for PCBs and pesticides and HPLC analyses for dyes were performed, the 1 mL isooctane solutions resulting from the five-fraction cleanup were evaporated almost to dryness with a gentle stream of nitrogen at 35 °C and 1 mL acetonitrile was added to the test tube. The acetonitrile was likewise evaporated almost to dryness, and the contents of the test tube were reconstituted with 1 mL of 35% acetonitrile - 65% water preparatory to analysis by HPLC. The third - fifth fractions reconstituted this way were occasionally cloudy, and were therefore filtered using ACRO LC13 disposable filters. Samples of 25 uL volume were injected with a Waters WISP 712 autosampler onto a 15 cm x 4.6 mm i.d. reverse-phase Supelcosil LC-8-DB column preceded by a Supelguard LC-8-DB guard column (Supelco, Oakville). Both guard and analytical columns were thermostatted at 35°C. The identities of the 17 carbamate pesticides for which determinations were made are shown in Table 4. The optimal detector wavelength was 220 nm, and the optimal gradient conditions are also shown in Table 4. Standard mixtures of all of these carbamates were prepared and used to calibrate retention times and detector responses. The presence of a carbamate was taken to be tentatively confirmed if it occurred within the appropriate chromatographic window. Chromatographic windows were typically 0.03 min at their widest at 20 min retention time.

For the present study of silica gel elution behaviour of carbamate pesticides, the diode array spectrophotometric detector was suitable, and was chosen since it is the only available technique for the analysis of Yamaska River samples for dyes. Actual sample analyses for carbamate pesticides will be carried out with a much more sensitive post-column fluorescence detection technique.

RESULTS AND DISCUSSION

For the present study, it was necessary to develop a cleanup procedure that would be used on a large variety of sample media, and that could accommodate an extensive series of dissimilar compounds. The purpose of any cleanup method is to remove any polar impurities and interfering co-extractives. In addition, this method minimizes the instrument analysis time by restricting the number of fractions that must be analyzed for each class of compound, while still providing fractionation information which can aid in the confirmation of pesticide identity.

All PCB congeners and PAHs tested eluted in fraction 1, while those carbamates studied eluted in fractions 3 and 4. Tables 2 and 5 show the patterns of elution of the other pesticide classes.

Of the 16 organochlorines studied, most eluted in fractions 1 or 2, with the exception of beta-endosulfan which appeared in fraction 3. In every case, each compound was found only in one fraction. On the DB5 column, co-elution occurred for o,p'-DDE and alpha-endosulfan. These two were found in fractions

1 and 2 respectively, and could therefore be easily identified. Co-elution also occurred on this column for p,p'-TDE and o,p'-DDT which both appear in fraction 1. The use of a second column of higher polarity (DB1701) allowed both pairs of co-eluting pesticides to be separated and quantified.

The fractionation pattern for organophosphorus, triazine and amide compounds is shown in Table 2. Most triazines eluted in fraction 4, with the exception of metribuzin which elutes in both 3 and 4, and anilazine which elutes only in fraction 3. Three of the amide compounds elute solely in fraction 4, propyzamide only in fraction 3, and allidochlor and alachlor in both 3 and 4. The OP pesticides elute in all four fractions. Three pairs of co-eluting compounds occurred using a single Ultra 2 column with a thermionic specific detector - fonofos/propazine, malathion/fenthion, and chlorpyrifos/parathion. Fonofos and propazine elute in different fractions, which allowed each to be identified. The use of a dual column technique was necessary to resolve the remaining pairs. This was done using DB5 and DB1701 columns with an electron capture detector. Even though the ECD was less sensitive to OPs than the TSD, the use of dual columns with the ECD, provided sufficient separation for qualitative confirmation of closely related compounds.

A summary of the fractionation of all the contaminants studied is provided in Table 6. Analyses of all PCB, PAH, and OC compounds (with the exception of beta-endosulfan) can be accomplished by analyzing only two fractions. Similarly, all triazine, amide, and carbamate data can be obtained through the injection of only two fractions per sample, thus reducing instrument time. Future work could include adjustments to the elution solvents or volumes, in order to reduce the spread of OP compounds, or to provide specific fractionation information for individual contaminant classes.

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Table 1. Chlorinated hydrocarbons sought and elution order on an DB5 column*

| No. | Chemical Abbreviation | Name |
|-----|-----------------------|--------------------------------------|
| 1 | Lindane | gamma-hexachlorocyclohexane |
| 2 | PCB 18 | 2,2',5-trichlorobiphenyl |
| 3 | PCB 15 | 4,4'-dichlorobiphenyl |
| 4 | PCB 54 | 2,2',6,6'-tetrachlorobiphenyl |
| 5 | PCB 31 | 2,4',5-trichlorobiphenyl |
| 6 | Heptachlor | heptachlor |
| 7 | PCB 52 | 2,2',5,5'-tetrachlorobiphenyl |
| 8 | PCB 49 | 2,2',4,5'-tetrachlorobiphenyl |
| 9 | Aldrin | aldrin |
| 10 | PCB 44 | 2,2',3,5'-tetrachlorobiphenyl |
| 11 | PCB 40 | 2,2',3,3'-tetrachlorobiphenyl |
| 12 | PCB 103 | 2,2',4,5',6-pentachlorobiphenyl |
| 13 | Heptachlor epoxide | heptachlor epoxide |
| 14 | PCB 121 | 2,3',4,5',6-pentachlorobiphenyl |
| 15 | PCB 60 | 2,3',4,4'-tetrachlorobiphenyl |
| 16 | o,p'-DDE | o,p'-DDE |
| 17 | PCB 101 | 2,2',4,5,5'-pentachlorobiphenyl |
| 18 | alpha-Endosulfan | alpha-endosulfan |
| 19 | PCB 86 | 2,2',3,4,5-pentachlorobiphenyl |
| 20 | PCB 87 | 2,2',3,4,5'-pentachlorobiphenyl |
| 21 | Dieldrin | dieldrin |
| 22 | p,p'-DDE | p,p'-DDE |
| 23 | PCB 77 | 3,3',4,4'-tetrachlorobiphenyl |
| 24 | PCB 154 | 2,2',4,4',5,6'-hexachlorobiphenyl |
| 25 | o,p'-DDD | o,p'-DDD |
| 26 | Endrin | endrin |
| 27 | PCB 151 | 2,2',3,5,5',6-hexachlorobiphenyl |
| 28 | beta-Endosulfan | beta-endosulfan |
| 29 | PCB 118 | 2,3',4,4',5-pentachlorobiphenyl |
| 30 | PCB 143 | 2,2',3,4,5,6'-hexachlorobiphenyl |
| 31 | p,p'-DDD | p,p'-DDD |
| 32 | PCB 114 | 2,3,4,4',5-pentachlorobiphenyl |
| 33 | o,p'-DDT | o,p'-DDT |
| 34 | PCB 153 | 2,2',4,4',5,5'-hexachlorobiphenyl |
| 35 | PCB 105 | 2,3,3',4,4'-pentachlorobiphenyl |
| 36 | PCB 141 | 2,2',3,4,5,5'-hexachlorobiphenyl |
| 37 | PCB 137 | 2,2',3,4,4',5-hexachlorobiphenyl |
| 38 | p,p'-DDT | p,p'-DDT |
| 39 | PCB 138 | 2,2',3,4,4',5'-hexachlorobiphenyl |
| 40 | PCB 129 | 2,2',3,3',4,5-hexachlorobiphenyl |
| 41 | PCB 159 | 2,3,3',4,5,5'-hexachlorobiphenyl |
| 42 | PCB 182 | 2,2',3,4,4',5,6'-heptachlorobiphenyl |
| 43 | PCB 187 | 2,2',3,4',5,5',6-heptachlorobiphenyl |
| 44 | PCB 183 | 2,2',3,4,4',5',6-heptachlorobiphenyl |

cont'd next page

Table 1 cont'd

| No. | Chemical Abbreviation | Name |
|-----|-----------------------|--|
| 45 | PCB 128 | 2,2',3,3',4,4'-hexachlorobiphenyl |
| 46 | PCB 185 | 2,2',3,4,5,5',6-heptachlorobiphenyl |
| 47 | PCB 202 | 2,2',3,3',5,5',6,6'-octachlorobiphenyl |
| 48 | PCB 171 | 2,2',3,3',4,4',6'-heptachlorobiphenyl |
| 49 | PCB 156 | 2,3,3',4,4',5-hexachlorobiphenyl |
| 50 | PCB 173 | 2,2',3,3',4,5,6-heptachlorobiphenyl |
| 51 | PCB 200 | 2,2',3,3',4,5',6,6'-octachlorobiphenyl |
| 52 | Methoxychlor | methoxychlor |
| 53 | PCB 180 | 2,2',3,4,4',5,5'-heptachlorobiphenyl |
| 54 | PCB 191 | 2,3,3',4,4',5',6-heptachlorobiphenyl |
| 55 | Mirex | mirex |
| 56 | PCB 170 | 2,2',3,3',4,4',5-heptachlorobiphenyl |
| 57 | PCB 201 | 2,2',3,3',4',5,5',6-octachlorobiphenyl |
| 58 | PCB 203 | 2,2',3,4,4',5,5',6-octachlorobiphenyl |
| 59 | PCB 196 | 2,2',3,3',4,4',5',6-octachlorobiphenyl |
| 60 | PCB 189 | 2,3,3',4,4',5,5'-heptachlorobiphenyl |
| 61 | PCB 208 | 2,2',3,3',4,5,5',6,6'-nonachlorobiphenyl |
| 62 | PCB 195 | 2,2',3,3',4,4',5,6-octachlorobiphenyl |
| 63 | PCB 207 | 2,2',3,3',4,4',5,6,6'-nonachlorobiphenyl |
| 64 | PCB 194 | 2,2',3,3',4,4',5,5'-octachlorobiphenyl |
| 65 | PCB 205 | 2,3,3',4,4',5,5',6-octachlorobiphenyl |
| 66 | PCB 206 | 2,2',3,3',4,4',5,5',6-nonachlorobiphenyl |
| 67 | PCB 209 | decachlorobiphenyl |

*The IUPAC numbering scheme for the PCB congeners is given in Ballschmiter and Zell (1980).

Table 2. Organophosphate, triazine, and amide pesticide fractionation on 5% water deactivated silica gel*.

| Chemical | Fraction | | | | |
|------------------|----------|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 |
| dichlorvos | | | X | X | |
| allidochlor | | | X | X | |
| mevinphos | | | | X | |
| acephate | | | | X | |
| trichlorfon | | | | X | |
| demeton | | X | | | |
| ethoprophos | | | | X | |
| naled | | | X | | |
| desethylsimazine | | | | X | |
| desethylatrazine | | | | X | |
| phorate | | X | | | |
| sulfotepp | | X | | | |
| dimethoate | | | | X | |
| simazine | | | | X | |
| atrazine | | | | X | |
| fonofos | | X | X | | |
| propazine | | | | X | |
| terbufos | | X | | | |
| propyzamide | | | X | | |
| disulfoton | | X | | | |
| diazinon | | | X | X | |
| metribuzin | | | X | X | |
| alachlor | | | X | X | |
| fenchlorphos | X | X | | | |
| prometryn | | | | X | |
| metolachlor | | | | X | |
| malathion | | X | X | | |
| fenthion | | X | X | | |
| chlorpyrifos | X | X | X | | |
| parathion | X | X | X | | |
| aspon | | X | X | | |
| cyanazine | | | | X | |
| diphenamide | | | | X | |
| anilazine | | | X | | |
| methidathion | | | X | | |
| crotoxyphos | | | | X | |
| napropamide | | | | X | |
| fensulfothion | | | | X | |
| ethion | | X | | | |
| phosmet | | | X | X | |
| azinphos-methyl | | X | X | X | |
| phosalone | | | X | | |
| coumaphos | | | X | | |

*Chemicals are listed in order of elution from an Ultra-2 column.

Table 3. PAHs sought, and elution order on a DB-5 column.

| |
|---------------------|
| indane |
| indene |
| naphthalene |
| 1-methylnaphthalene |
| acenaphthalene |
| acenaphthene |
| fluorene |
| phenanthrene |
| anthracene |
| 2-methylnaphthalene |
| 9-methylanthracene |
| fluoranthene |
| pyrene |
| benzo(a)anthracene |
| benzo(a)pyrene |
| 2-methylnaphthalene |

Table 4. Carbamate pesticides sought.*

aldicarb sulfoxide
aldicarb sulfone
methomyl
phenmedipham
desmedipham
thiram
aldicarb
thiophanate-methyl
propoxur
carbofuran
benomyl
carbaryl
pirimicarb
chlorpropham
EPTC
cycloate
butylate

*Compounds are listed in order of elution from a Supelcosil LC-8-DB HPLC column under the following conditions, with flow 1 mL/min and linear gradients throughout:

| time, min | % acetonitrile | % water |
|-----------|----------------|---------|
| 0 | 35 | 65 |
| 4 | 48 | 52 |
| 7 | 51 | 49 |
| 9 | 55 | 45 |
| 13 | 100 | 0 |
| 20 | 100 | 0 |
| 25 | 35 | 65 |

Table 5. Fractionation of organochlorine pesticides on 5% water deactivated silica gel*.

| Chemical | Fraction | | | | |
|--------------------|----------|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 |
| lindane | | X | | | |
| heptachlor | X | | | | |
| aldrin | X | | | | |
| heptachlor epoxide | | X | | | |
| o,p'-DDE | X | | | | |
| alpha-endosulfan | | X | | | |
| dieldrin | | X | | | |
| p,p'-DDE | X | | | | |
| o,p'-TDE | X | | | | |
| endrin | | X | | | |
| beta-endosulfan | | | X | | |
| p,p'-TDE | X | | | | |
| o,p'-DDT | X | | | | |
| p,p'-DDT | X | | | | |
| methoxychlor | | X | | | |
| mirex | X | | | | |

*Compounds are listed in order of elution from a DB5 column.

Table 6. Fractionation of various contaminant classes on 5% water deactivated silica gel*.

| Chemical | Fraction | | | | |
|----------------------|----------|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 |
| ORGANOCHLORINES (16) | X | X | X | | |
| PCB (52 CONGENERS) | X | | | | |
| PAH (16) | X | | | | |
| TRIAZINES (9) | | | X | X | |
| AMIDES (6) | | | X | X | |
| CARBAMATES (16) | | | X | X | |
| ORGANOPHOSPORUS (28) | X | X | X | X | |

FIGURE CAPTION

Figure 1. Location of Yamaska River basin.

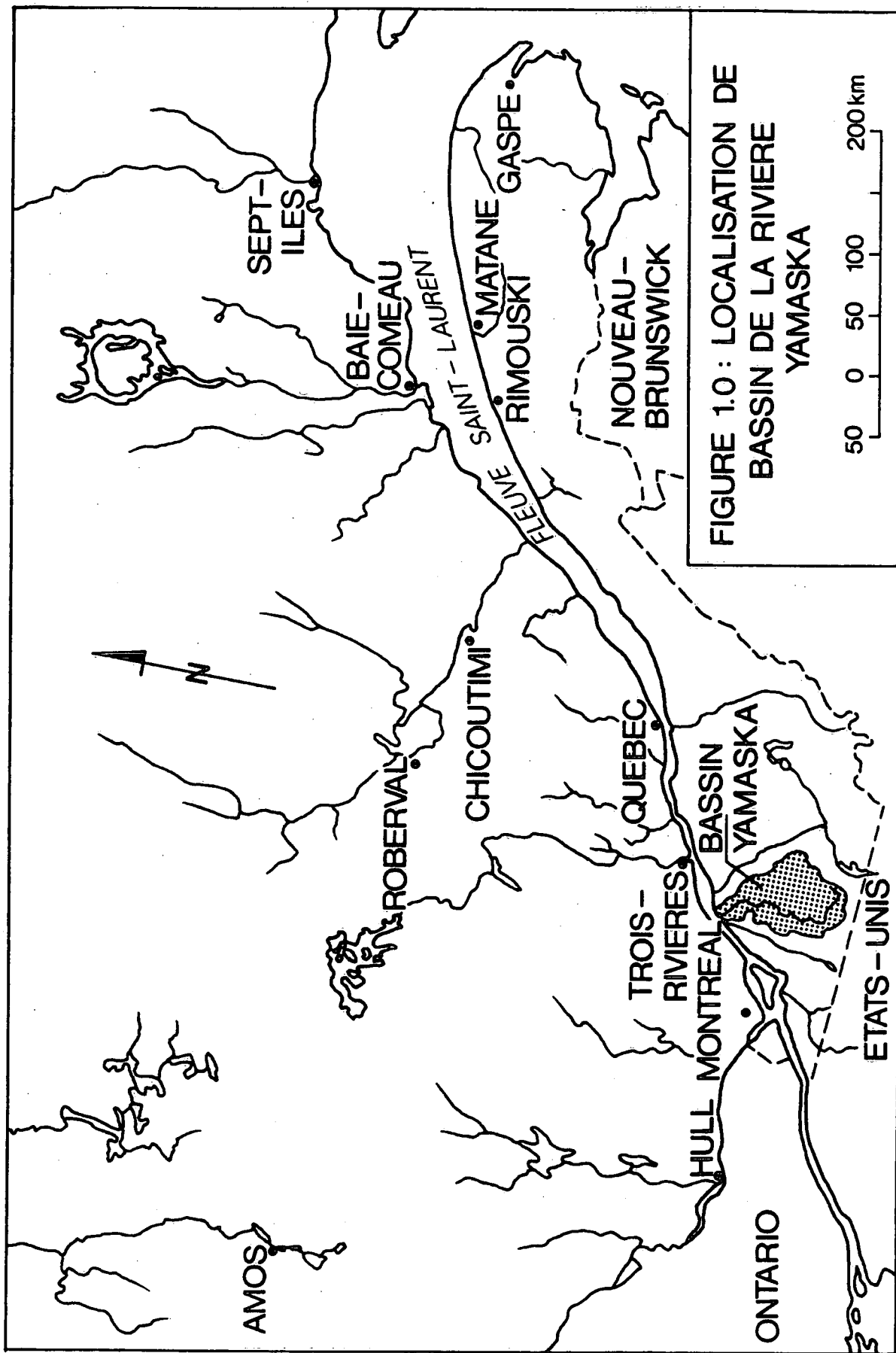


FIGURE 1.0 : LOCALISATION DE
BASSIN DE LA RIVIERE
YAMASKA