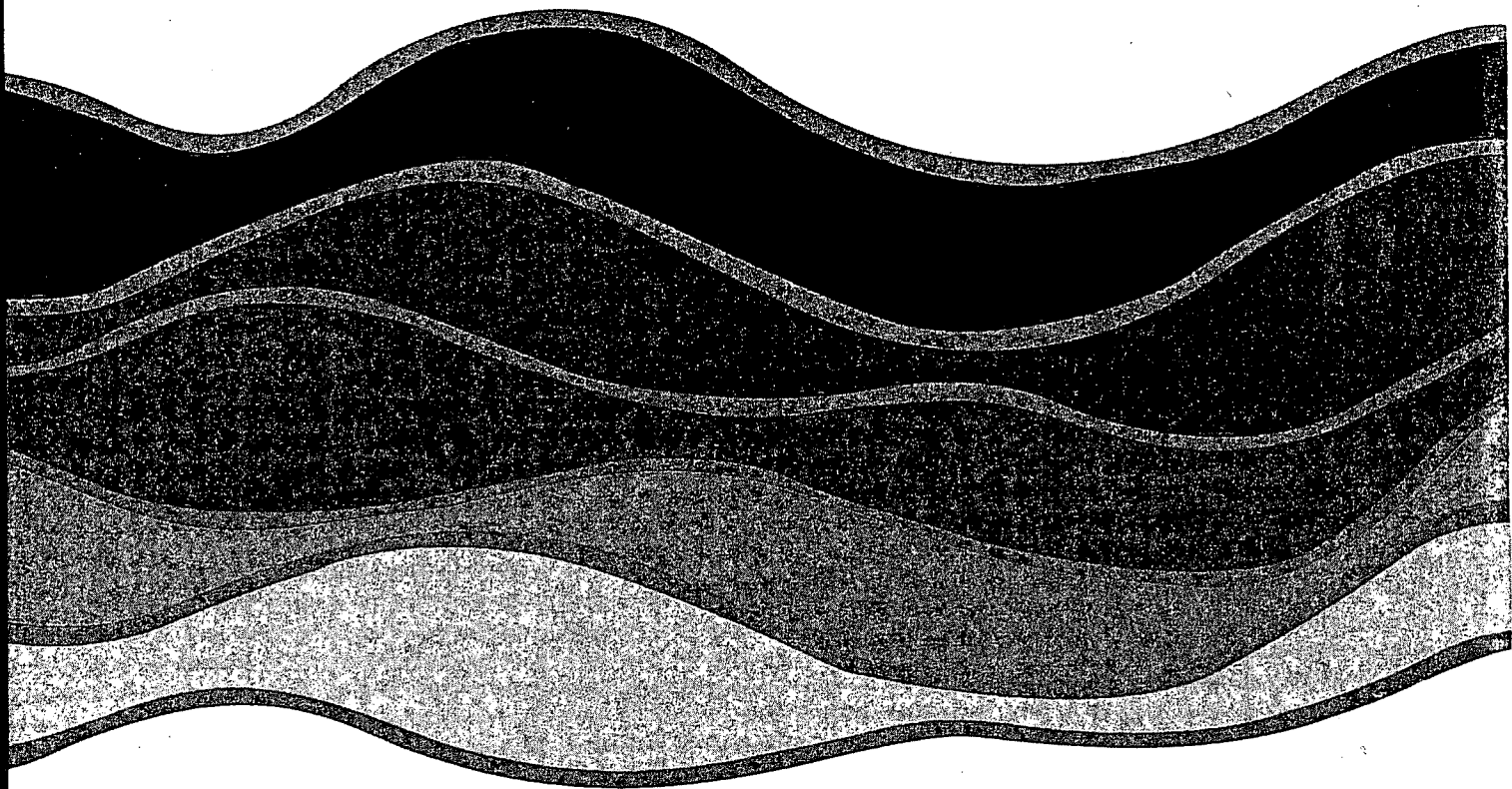
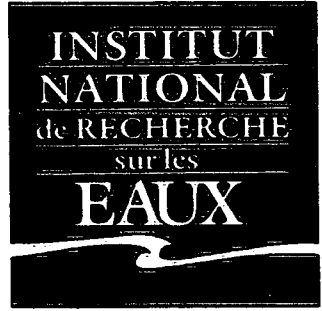


No. 95-149



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IN PRAIRIE SPRINGS**

J.A. Wood and D.H.J. Anthony

NWRI Contribution No. 95-149

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ULTRATRACE DETECTION OF HERBICIDES IN PRAIRIE SPRINGS

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ABSTRACT

Fourteen prairie springs were surveyed from 1991-94 for a suite of 20 herbicides at ultratrace levels of detection (ppt; ng L^{-1}). Herbicides were detected at 6 of the springs surveyed. All of the detections were less than $1 \mu\text{L}^{-1}$. All of the springs originate from shallow surficial aquifers. In most cases, the recharge area is under cultivation with heavy herbicide applications. Tritium isotope data indicates relatively recent recharge of all these aquifers.

A total of 142 spring samples, including replicates, were collected for base/neutral and acid herbicide analysis. The detection frequency was a modest 23% of samples collected. However, this would have been reduced to 3% if 1 litre samples had been collected instead of large volume samples. Detections occurred in 19% of the samples collected in the base/neutral herbicide class and 26% of samples collected in the acid class. The most frequently detected herbicides were atrazine (12% of samples collected), picloram and 2,4-D (7%), 2,4-DP (dichlorprop), 2,4-DB (4%) and simazine (3%). Atrazine, picloram and 2,4-D are among the most commonly detected herbicides in groundwater in North America. Single detections of triallate, diallate, metolachlor, silvex, MCPB and bromoxynil also occurred.

Approximately half of the detections were slightly above the detection limit. The remainder constituted more substantive occurrences, chiefly atrazine, picloram and 2,4-DB. All of the detections were at ultratrace levels (ng L^{-1} ppt). More than 90% of the detections occurred at 3 of the 14 springs surveyed and half of these occurred at one spring, which has shown repeated detections throughout the entire study period. In spite of conditions favourable for herbicide contamination at several of the springs, no herbicides were detected. Some of the herbicides detected (notably atrazine and simazine) were not used on these aquifers. Their presence demonstrates that short to medium range atmospheric transport and fallout can contribute to contamination of groundwater.

Herbicide detections were compared with a variety of guidelines for drinking water,

livestock, irrigation and aquatic life including Canadian, Provincial, World Health Organization and U.S. Environmental Protection Agency guidelines. The concentrations found were several orders of magnitude below known guidelines for health, agriculture or aquatic life. Although herbicides do enter shallow prairie aquifers via infiltration, generally the concentrations are only at ultratrace levels (ppt, ng L⁻¹). At these concentrations the herbicides found do not present a significant risk for human health, agriculture or aquatic life.

The concentrations of herbicides in the aquifers were found to be significantly lower than those in the surface water bodies. This is due to the fact that herbicides are highly soluble in water and are rapidly degraded in the soil and in the water column. The only herbicide found in the aquifers was glyphosate, which is known to be highly stable in the environment.

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RÉSUMÉ

Entre 1991 et 1994, nous avons mesuré la concentration de 20 herbicides au niveau des ultratrace (ppt; ng.L⁻¹) dans 14 sources des Prairies. La présence d'herbicides a été détectée dans 6 de ces sources. Dans tous les cas, la concentration était inférieure à 1 µg.L⁻¹. Toutes les sources sont alimentées par des gisements aquifères superficiels. Dans la plupart des cas, la zone d'alimentation est située dans des terres cultivées et traitées massivement aux herbicides. Les relevés isotopiques au tritium indiquent que ces tous ces gisements se sont rechargés assez récemment.

Au total, 142 échantillons d'eau de source, ce qui comprend les prélèvements répétés, ont été prélevés en vue du dosage d'herbicides basiques, neutres et acides. La fréquence de détection n'a pas dépassé les 23 % du nombre total d'échantillons, ce qui est déjà modeste. Cependant, le pourcentage serait passé à 3 % si nous avions prélevé des échantillons de 1 litre d'eau plutôt que des échantillons de grand volume. Nous avons détecté des herbicides basiques ou neutres dans 19 % des échantillons et des herbicides acides dans 26 %. L'atrazine (12 % des éch.), le picloram et le 2,4-D (7 %), le 2,4-DP (dichlorpop), le 2,4-DB (4 %) et la simazine (3 %) ont été les herbicides le plus souvent détectés. L'atrazine, le picloram et le 2,4-D sont parmi les herbicides le plus communément détectés dans les gisements d'eau souterraine en Amérique du Nord. Nous avons aussi détecté une fois chacun le triallate, le diallate, le métolachlor, le silvex, le MCPB et le bromoxynil.

Environ la moitié des concentrations mesurées dépassait légèrement la limite de détection. Le reste était plus notable et les herbicides détectés alors étaient surtout l'atrazine, le picloram et le 2,4-DB. Dans tous les cas, la concentration mesurée était de l'ordre des ultratrace (ppt; ng.L⁻¹). Plus de 90 % des cas de détection d'herbicides ont été observés dans 3 des 14 sources examinées, la moitié dans une seule, où des herbicides ont été constamment détectés pendant le temps qu'a duré l'étude. Aucun herbicide n'a été détecté à plusieurs des sources malgré des conditions rendant probable leur détection. Certains des herbicides

déTECTÉS (notamment l'atrazine et la simazine) n'étaient pas utilisés au-dessus de ces aquifères. Leur présence est la démonstration d'un transport atmosphérique à moyenne ou longue distance et du fait que les retombées peuvent être sources de contamination de l'eau souterraine.

Les concentrations mesurées ont été comparées à différentes directives applicables à la qualité de l'eau de consommation humaine, de consommation par les animaux d'élevage et d'irrigation ainsi qu'à la qualité de l'eau pour les organismes aquatiques. Ces directives ont été émises par le gouvernement fédéral et ceux des provinces, par l'Organisation mondiale de la santé et l'U.S. Environmental Protection Agency. Les concentrations mesurées sont de plusieurs ordres de grandeur inférieures aux normes sanitaires, agricoles ou relatives aux organismes aquatiques. Même si les herbicides contaminent effectivement les nappes aquifères superficielles des Prairies par infiltration, il demeure que les concentrations mesurées sont de l'ordre des ultratracés (ppt; ng.L⁻¹). À ces concentrations, ces traces d'herbicides ne présentent pas de danger appréciable pour la santé humaine, pour l'agriculture ou pour les organismes aquatiques.

INTRODUCTION

In rural areas of the Canadian Prairies, water for human and livestock consumption is taken primarily from groundwater sources. Frequently, the water for local consumption, such as farm households and livestock, originates from natural springs issuing from small surficial aquifers in shallow sand or gravel deposits. Many of these surficial deposits occur in agricultural lands where local applications of herbicides are heavy and therefore, there is some potential for shallow groundwater contamination. There is concern for the quality of these water sources, as this may present a problem for local consumptive use. To address this concern, a survey was undertaken in 1991-1994 to assess occurrence and levels of herbicide contamination of natural prairie springs used as drinking water sources for humans and livestock.

There are no published studies of herbicide contamination of natural springs in Canada or the United States, although there is voluminous information available on contamination of wells and/or shallow groundwater by herbicides and pesticides (USEPA, 1992; USEPA, 1990; Ritter, 1988; Leonard et al., 1988; Koterba et al., 1993; Smith, 1988; Cavalier et al., 1989; Jayachandran et al., 1994; Agriculture Canada, 1991; Maathuis et al., 1988; Library of Congress, 1983). Contamination can occur by either of two routes. (1) Application of herbicides to the land surface with infiltration and eventual entrainment in the aquifer. (2) Direct contamination wells as a result of handling and washing of equipment near well sites, or surface runoff directly entering wells or infiltration along well casings. The distinction between the two pathways is important because contamination by the latter route can be prevented with appropriate attention given to handling practices. Contamination by the former route is a function of soil and herbicide properties.

An important reason for using natural springs in this study rather than man-made wells, is that any pesticide contamination of these springs which does occur must be the result of application and infiltration and entrainment in the aquifer. There were no wells apparent on any of the aquifers investigated. Wells might act as potential sources of contamination. None of the springs were used to wash spray equipment. All of the springs were relatively inaccessible to vehicular traffic. None of the springs received direct application of herbicide as they were all located in small treed gullies at least 20-30 meters from the nearest agricultural land. All of the springs surveyed in this study drain surficial aquifers which are relatively small and the storage time is of relatively short duration (less than 50 years).

In the Canadian prairies, it is common practice for farmers to clean pesticide application equipment at or near wells, with resultant frequent contamination. Well contamination represents a handling problem and may be quite localized and is not necessarily indicative of widespread contamination of the aquifer. This needs to be considered in hydrogeological assessments of groundwater contamination. In addition, the age of groundwater is not considered in most surveys for pesticides. Wells frequently may penetrate larger and deeper aquifers with much slower rates of replacement - the water predating most herbicide use. Since herbicides have been in use for only about 50 years it is not possible for groundwater older than this to have been contaminated by infiltration following spray application. Any reported herbicide occurrences of older groundwater (older than about 50

years), by inference, must be a result of handling or washing of equipment near wells or, alternatively, surface runoff directly entering the well or well casing. Isotopes such as tritium can be used as a confirmatory tool to exclude this possibility.

This investigation of springs is unique in two respects. (1) It is the first study in Canada and North America of herbicides in natural springs which originate from very small shallow surficial aquifers. (2) It is the first survey of groundwaters in Canada for herbicides using the enhanced levels of detection (nanograms/litre, parts per trillion) provided by large- sample extraction technology. Previous surveys of groundwater have relied upon 1 litre samples, providing micrograms/litre levels (ppb) of detection.

BACKGROUND

Tritium Dating

Since information concerning the location of springs draining small surficial aquifers is not generally available in the literature, this was obtained by questioning a large number of local sources. An inventory of 27 spring sites was compiled and investigated (Figure 1). All of the springs were sampled for general water chemistry characteristics including conductance, temperature, total dissolved solids, major ions, nutrients (nitrogen and phosphorous), trace metals and tritium.

The primary criterion for screening springs as candidates for herbicide contamination was the age of the groundwater based on tritium activities. Tritium (^3H) activities were obtained by a Canberra Packard 2260XL liquid scintillation counter, at the Alberta Environmental Centre, Environmental Isotopes Section, Vegreville, Alberta. Electrolytic tritium enrichment by a factor of 18 was utilized to enhance detection (Arnold, 1994). Activity levels are reported as tritium activity units (TU), where $1 \text{ TU} = 7.2 \text{ decays/minute/litre} = 0.1183 \text{ Bq L}^{-1} = 3.2 \text{ pCi L}^{-1}$. 1 TU corresponds to a ratio of 10^{18} tritium atoms to 1 atom of stable hydrogen. The detection limit depends upon background radiation levels, which vary, and is approximately 0.5 TU (Arnold 1994). Tritium levels were regarded as "not distinguishable from background radiation levels at 2 standard deviations of the limit of detection" (Arnold, 1994). There was close agreement in reported tritium levels between replicate samples taken from several springs (within 7%).

Tritium levels in northern hemisphere precipitation increased rapidly in the years following the commencement of thermonuclear testing in 1952. Levels reached a peak of over 10,000 TU in Canadian precipitation in 1963 following massive Soviet tests in 1961 and 1962 (IAEA, 1969; Oklahoma Geological Survey Observatory, 1994). Tritium levels declined after the moratorium on atmospheric testing in 1963 although atmospheric tests by France and China continued until 1974 and 1980, respectively (Oklahoma Geological Survey Observatory, 1994). Levels reported in rainwater at Wynard Saskatchewan, in the late 1970's and early 1980's generally ranged between 20 and 60 TU, although levels as low as 7 TU and as high as 173 TU have been recorded (IAEA, 1983, 1986). This station was closed in 1982 and current levels are no longer available.

Two rainwater samples were collected in Regina during this study and the tritium levels were 20.4 TU in August 1991 and 9.7 TU in October 1992 (Figure 2). Given a half-life of 12.3 years, and the estimated natural atmospheric production level of 5-20 TU (Payne, 1972), groundwater recharged prior to 1952 should now have levels less than 0.5-2 TU. The Isotope Hydrology Section of the international Atomic Energy Agency recommended a three-fold classification of tritium ages of groundwater (IAEA, 1973; Davis and Bentley, 1982). Since these guidelines were developed over twenty years ago (1.7 tritium half-lives), estimates of current tritium levels corresponding with these ages in groundwater would be reduced by a factor of 1/1.7. Using this correction factor, current tritium levels of the three classes are estimated as follows: Less than 1.8 TU indicates groundwater older than 1952. Levels of 1.8-11 TU indicates the presence of some fusion bomb tritium and the water probably originates from the period 1952-1961. (3) Levels exceeding 11 TU indicates water younger than 1961.

Tritium activities of the springs surveyed are shown in Figure 2. Thirteen springs had higher tritium levels varying between 14 and 60 TU. These clearly reflect tritium levels associated with current precipitation or precipitation which is younger than 1961. Spring water integrates a mixture of waters with different residence times and travel distances within the aquifer. High tritium levels indicate that most but not necessarily all of the springwater infiltrated since 1961. The residence time of a significant proportion of the water from these springs is probably within a few years at most, and possibly in some cases a few months.

Twelve springs had tritium activities less than 1 T.U., which indicates the water recharged some time prior to 1952 (Figure 2). This is typical of deeper aquifers or aquifers with longer residence times. These were screened out of any further sampling for herbicides. Barring one or two exceptions (e.g. 2,4-D), no herbicides were in use prior to 1952. At Nokomis and Wolseley radiocarbon (^{14}C) activities of the dissolved inorganic carbon ($\delta^{13}\text{C}$ corrected) indicates an apparent age of several thousand years. If ^{14}C is present (eg. Wolseley) this does not necessarily indicate the water is the same age as the dissolved carbon. However, at Nokomis ^{14}C was not detectable. Non-detectable ^{14}C indicates considerable age - probably several thousand years (Van Der Kamp, 1995a). Nokomis is a flowing artesian well and probably originates from the Hatfield aquifer, which is very old. The tritium activity of both sites was below detectable levels indicating that the water is at least older than 1952. Because of its age the water from Nokomis and Wolseley conveniently served as sample blanks for QA/QC purposes.

Tritium activities at Whitewood (7 TU) and Craven (2 TU), were intermediate, suggesting an age category of 1952-1961. Alternatively, since spring water is a mixture of water of different residence times, the activities may reflect mixing of water older than 1952 and younger than 1961. Whitewood was included in the herbicide sampling because at least some of the water is "post-bomb" in age. Craven was screened out as an unlikely candidate for herbicide contamination.

Ion Chemistry

Water samples were collected for major ions and nutrients, including nitrogen and phosphorous. Total dissolved solids (TDS) computed as the sum of the major cation and anion concentrations ($\Sigma \text{Ca} + \text{Mg} + \text{Na} + \text{K} + \text{Cl} + \text{SO}_4 + \text{CO}_3 + \text{HCO}_3$) in mg/L are shown in Table 1. A conductance measurement was also made at each site. These supplemental data assisted in determining the residence time of the water and whether the water originated from a surface aquifer or from a deeper source. Lower conductance and TDS concentrations generally indicate shorter residence times of the water. The springs with elevated bomb tritium had TDS concentrations below 900 mg/L and conductance less than $1400 \mu\text{S cm}^{-1}$. The only exceptions were Outlook South and Outlook North. Higher conductance and TDS concentrations at these sites can be attributed to the fact that they are tile drainage outlets in previously saline soils, with a relatively recent history of flushing (since 1979). With natural springs, prolonged flushing has removed much of the soluble material. At the Outlook sites, although soluble solid levels have declined to a point where cash crops can be grown, evidently some flushing of soluble solids is still occurring.

The remaining springs with older water (less than 1 TU), tended to be brackish. Higher conductance and TDS concentrations indicate deeper aquifers with longer residence times. The highest levels occurred at Nokomis and Oxbow, which are buried wellheads tapping deeper aquifers, rather than natural springs. Exceptions occurred at Radisson, Wolseley and Craven. The lower conductance and TDS concentrations observed at these sites suggests that although these aquifers are probably surficial they probably drain larger areas, and therefore, residence times for the water is much longer.

A trilinear plot of the major ion composition in meq L^{-1} is shown in Figure 3. The springs are classified according to ionic dominance in Table 1. Note that at the pH found in these groundwaters (near neutral), $\text{CO}_3 + \text{HCO}_3 \approx \text{HCO}_3$. Without exception all of the 14 springs characterized by younger "bomb" tritium enriched water are Ca+Mg dominant (greater than 50% Ca+Mg). The majority of these are also $\text{CO}_3 + \text{HCO}_3$ dominant, although three springs are $\text{SO}_4 + \text{Cl}$ dominant. Na+K dominance in the prairies tends to be characteristic of deeper aquifers. Na+K dominance occurred at half of the sites with older "pre-bomb" aged water. The remaining older springs were Ca+Mg dominant, suggesting perhaps that these aquifers are surficial but travel times are longer.

Physical Description

The springs investigated for herbicides originate either as (1) contact springs, in which a highly permeable overburden of sand or gravel overlies glacial till of much lower permeability; or as (2) depression springs occurring at a break in slope or change in surface topography, usually near the head of a small gully. Most of the springs occurred in areas identified by Agriculture Canada as "vulnerable to groundwater contamination" due to shallow depth to the water table (McRae, 1991). Generally these are shallow surficial deposits of sand or gravel, which are glacio-fluvial, glacio-lacustrine or eolian in origin, remaining from Pleistocene glaciation. In most cases, the aquifer boundaries can be easily delimited on surficial geology maps as gravel, sand or high permeability

deposits. Flow at all of the springs was continuous throughout the year, although, in some cases, flow rates showed some tendency to decline slightly toward late summer indicating shorter residence times (van der Kamp 1995a). Detailed site descriptions and georeference information for all of the spring sites investigated is presented in the Appendix at the back of this report.

In most cases the springs are tapped as a drinking water supply, and the source is usually protected by a short length of metal or PVC pipe. In a few cases, the springs were not tapped (eg. Broderick East, Broderick West, Antelope Lake, Dundurn) and issue directly from the ground. At each spring, a visual survey was made of the area to ensure that there are no well sites within the surficial boundaries of the aquifer. Where possible, information was also compiled on the herbicides applied each year.

Two of the 15 sites investigated for herbicides were not natural springs (Outlook North and Outlook South, Figure 1). These are tile drain outlets from irrigated fields at an experimental research plot. These two sites were selected because there is detailed information on the amount of water and herbicide added each year. Tiles are located at 3 meters depth in several acres of land, the drainage network simulating a shallow aquifer. Water samples were collected at the drainage outlets.

METHODS

Sample Collection and Handling

Water samples for herbicide extraction and analysis were collected in October of 1991, October 1992, and August, 1993 at the 14 locations indicated in Table 1. Additional sampling at 4 sites (Outlook North, Outlook South, Antelope Lake and Carnduff) was carried out in November, 1993 and March, June and October, 1994. Sample extracts were analyzed at Environment Canada's National Laboratory for Environmental Testing (NLET), in Burlington, Ontario. A total of 142 spring samples were collected to October 1994 and analyzed for herbicides, including 28 replicates for QA/QC purposes. Replicate samples were analyzed by Envirotest, in Edmonton, in 1991-92 using similar methods. This was discontinued in 1993-94 in favour of sending replicates separately to NLET, as a cost saving measure.

The study initially included sampling for a suite of 19 organochlorine insecticides, chlorobenzenes and total polychlorinated biphenyls (PCB's) (Table 2). This was targeted primarily at endrin, toxaphene and chlordane which were used in the prairies well into the 1980's, as well as lindane and methoxychlor which are still in use. Since there were no detections in this category of analytes sampling was discontinued after 1991.

The primary focus of the study was on the base/neutral and acid herbicide classes (Table 3). A list of the analytes is provided in Table 3. The list includes seven of the top ten most commonly used herbicides in Saskatchewan (Constable and Bhardia, 1990; Agriculture Canada, 1993). The acid and base/neutral distinction is based partly on analytical convenience for reporting purposes rather than on the actual chemistry.

The base/neutral herbicides are extracted at ambient pH. This class includes a wide diversity in functional chemistry, which shares the property only of being neutral or slightly basic. The term neutral does not necessarily imply a sufficient degree of hydrophobicity for effective recovery by solvent extraction. Neutral compounds may possess a significant polarity making recovery by solvent extraction less effective. (Foster et al, 1991, Agemian and Chau, 1977; Anthony and Wood, 1993). This group includes herbicides in the triazine, thiocarbamate, arylocarbamate, and dinitroaniline phenoxypropionic ester classes.

The acid herbicide class is diverse in its properties sharing the primary characteristic of possessing one or more phenoxyalkanoate functional groups capable of being derivatized for sensitive determination by esterification with electron capture detector-sensitive substituents (Anthony and Wood, 1993). This group includes compounds in the phenoxyacetic, benzoic, phenoxybutyric and phenoxypropionic acid class, as well as nitrile, and pyridine compounds.

Springwater samples were collected from each site in 4.23 L bottles - 4 bottles each site. Separate water samples were obtained for the acid and the base/neutral herbicide analyses. At some locations, sample collection was by direct filling at the spring. At other sites this was not possible and the water was pumped via solvent cleaned teflon tubing. A small amount of solvent, 4 mL dichloromethane per 4 L bottle (less than saturation), was dissolved in each sample at the time of collection as a preservative. This enhances considerably the recovery of the acid herbicides. Water samples were transported to the laboratory, where they were stored at 4°C in the dark until extraction, usually within 24 hours of collection.

Sample Extraction

To our knowledge, this is the only study of herbicide contamination of springs or shallow ground water ever carried out using large-sample extraction technology. The study, therefore, is unique in several respects, including the technology used and the low limits of detection. Detection limits for the various analytes investigated in this study are shown in Table 3.

Solvent extraction of the groundwater was done by a Goulden large-sample extractor (GLSE-95) developed by the National Water Research Institute, Environment Canada (Goulden and Anthony 1985; Anthony and Nagami 1993). The apparatus is designed to provide continuous liquid-liquid extraction for ultratrace detection capability to ng L⁻¹ (ppt) levels and lower, for various classes of semi-volatile organic contaminants (Anthony and Wood, 1993; Anthony, 1994; Wood and Anthony, 1995). The apparatus was modified from the original design to accommodate a second main extractor body, so that effluent from the first extractor flows directly into the second extractor to allow for a two stage (tandem) extraction (Figure 4). This enhances considerably the recoveries of the acid herbicides.

Prior to each extraction, groundwater from four bottles (4.23 L each) is composited into a single 20 L pyrex carboy, thereby constituting a single water sample of 16.9 litres from each site. The

base/neutral herbicides are extracted from the first sample at ambient pH. The pH is measured and recorded at the time of extraction. For the acid extraction the second spring sample is acidified to pH 1.8 (+/-0.1) with concentrated H_2SO_4 . The required acid addition is determined by titration of a 500 mL aliquot of springwater. Acidified water samples are continuously stirred during the extraction. The pH of the extracted effluent is measured to ensure the sample is at the desired value.

Water samples are pumped from the carboy to the extractor at a precisely metered rate of 0.50 Litres min^{-1} . Initially, the sample was filtered through a "binder-free", 500 C baked, $0.7\mu m$ nominal pore diameter, triple solvent-rinsed, glass fibre filter in a stainless steel filter holder. However, filtration was discontinued after 1991, as there was no significant residue found from any of the springs. The refrigerated sample is warmed to $22^\circ C$ by a fused silica heater located in a glass heating chamber (Figure 4). Methanol solution of surrogates or standard additions for recovery assessment is metered into the sample at the inlet port to the glass mixing chamber, to minimize volatility and sorption losses. The mixing chamber is initially charged with 300 mL of dichloromethane. The water/solvent matrix is emulsified by a 4 bladed turbine type propeller, driven by a constant torque stirrer. Larger solvent drops settle out in the first and second settling chambers. Small solvent droplets are collected in the effluent scrubber column packed with teflon "Raschig" rings located in the upper part of the second settling chamber. Dichloromethane is added at a precise rate at the top of the scrubber column to make up for the rate at which it is lost by dissolution in water (1.3% by volume). The water sample then passes through a second extractor body identical to the first and then a 1 Litre glass separator trap which captures any fine droplets escaping the second extractor body (ideally none). After the extraction is completed, solvent from both extractor bodies and the trap (approximately 600 mL) is collected in 1 Litre amber glass jars and stored at $4^\circ C$ in the dark until analysis.

All liquids used in the extraction process (including water, dichloromethane, and methanol) come in contact only with precleaned glass, teflon, stainless steel (pump-head and ports) and ceramic surfaces (pump piston). These surfaces are thoroughly rinsed with distilled water, acetone and dichloromethane prior to each extraction. The solvents used, dichloromethane, acetone and methanol are Burdick and Jackson "high purity pesticide grade". The 4-L groundwater sample bottles and the 1 L extract storage jars are Eagle-Picher amber glass with teflon liners. These are triple rinsed in acetone and dichloromethane prior to use. The sample bottles, the extract storage bottles, the solvents and the distilled rinse water were subjected to QC analysis on several occasions and no herbicide residues were ever detected.

Throughout the study large sample blanks were routinely extracted. Ten "blank" samples were obtained from the springs at Nokomis and Wolseley. No analytes were detected. The significant age to these waters precludes any possibility of herbicide occurrences. Distilled water blanks were also extracted routinely using the laboratory water supply which is filtered for organics removal. Again there were no detections. This was done to ensure that there was no pesticide residue carry-over in the glassware from successive extractions or residues in the laboratory water supply which was used for rinsing.

Analytical Methods

For the base/neutral herbicides the dichloromethane extract is first dried using anhydrous sodium sulphate and then solvent-exchanged into iso-octane and reduced to 3 mL by rotary evaporation under vacuum. Clean-up of the iso-octane extract is done by elution on a packed chromatographic florisil column (10% deactivated). The extract is fractionated by elution of the column using dichloromethane/hexane (15:85) and methanol/dichloromethane (2:98) solutions. This separates the extract into a trifluralin and triallate fraction and a barban, endaven, dichlofop-methyl, atrazine, and metolachlor fraction. The two concentrates resulting from fractionation are then twice rinsed with iso-octane and reduced to 1 mL under nitrogen. Analysis of the final iso-octane concentrates is done by gas chromatography on HP-5890 dual DB-1 and DB-5 capillary columns (30 m, 0.25 mm ID, 25 μ m film thickness), equipped with dual electron capture detectors and a split/splitless injection system. The column head pressure is 15 psi with hydrogen as the carrier gas, at a flow rate of 2.5 mL min⁻¹. The detector make-up gas is 5% methane in argon at a flow rate of 30 mL min⁻¹. This procedure is used to detect all of the neutral herbicide analytes except atrazine and metalochlor. Chromatographic separation is temperature-programmed starting at an initial column temperature of 80°C, holding for 2 minutes, then ramped to 260°C at 6°C min⁻¹ with a final hold for 8 minutes. Atrazine and metolachlor are determined using a HP-5890 split injection, single column (DB-17) gas chromatograph equipped with a nitrogen/phosphorous detector. The chromatograph is temperature-programmed from an initial temperature of 80°C, with a 2 minute hold, to 140°C at 20°C min⁻¹ for the first ramp, and 140°C to 260°C at 4°C min⁻¹ with a final hold of 8 minutes at 260°C. The detector gases are hydrogen and air at a flow rate of 3.8 mL min⁻¹ and 120 mL min⁻¹, respectively. Helium is used as the carrier gas at 2 mL min⁻¹ flow, with column head pressure of 15 psi.

The acid herbicide extracts are concentrated by rotary evaporation with solvent-exchange into acetone. The residue is then derivatized by reacting with 4.0 mL of 5% (w/v) pentafluorobenzyl bromide in acetone and 30 μ L of 30% potassium carbonate K₂CO₃ in water to form the corresponding pentafluorobenzyl esters. The extract containing the herbicide esters is roto-evaporated and then dried with anhydrous sodium sulphate and cleaned on a 5% deactivated silica gel column. The concentrate is fractionated by sequential elutions of the column with 5% methanol in toluene and 75% toluene in hexane. This separates the concentrate into a fraction containing the pentafluorobenzyl ester of picloram and a second fraction containing pentafluorobenzyl esters of all the other acid herbicides (see Table 3). The final iso-octane concentrates are analyzed by a HP-5890 gas chromatograph with dual DB-1 and DB-5 capillary columns (30 m, 0.25 mm ID, 25 μ m film thickness), equipped with dual electron capture detectors and a split/splitless injection system. Hydrogen is used as the carrier gas at a column head pressure of 15 psi, with 5% methane in argon as the make-up gas. The apparatus is temperature-programmed from an initial temperature of 80°C, holding for 2 minutes, ramping to 200°C at 15°C min⁻¹, followed by a second ramp from 200°C to 260°C at 5°C min⁻¹ with a ten minute hold at 260°C.

A Hewlett-Packard 5871 GC-mass selective quadrupole, 70eV, mass analyzer and a negative ion chemical ionization VG TRIBRID high resolution mass spectrometer were used for confirmation of the neutral and acidic category herbicides. Confirmation was obtained when herbicide detections were

of sufficient magnitude to permit use of these instruments. In some cases, several samples with very low analyte detections on the gas chromatograph were composited to bring the analyte concentration up to a sufficient level for mass spectrometer identification.

Analysis of the dichloromethane extracts was carried out at Environment Canada's National Laboratory for Environmental Testing (NLET) in Burlington, Ontario. Replicate samples were analyzed (1991-92) by Envirotest Laboratories, Edmonton Alberta by gas chromatograph equipped with mass selective detector. Envirotests detection limits were somewhat higher than the values given in Table 3.

RESULTS

Herbicide Detections

Analyte detections in springs and summary statistics are shown in Table 4. Detections occurred in 23% of the 114 spring samples analyzed from 14 locations (not including replicates). All of the detections were less than $1 \mu\text{L}^{-1}$. In the base/neutral category, there were 11 detections, or 19% of 59 samples analyzed (excluding replicates). All of these occurred at 2 sites. In the acidic category, there were 15 detections, or 26% of 58 samples analyzed. These occurred at 6 locations. The detection frequency of individual analytes ranged between 2% and 12% in the base/neutral class of analytes, and 2% and 7% in the acid class (Table 4). Eight of the detections (30%) were confirmed by either mass selective detector or high resolution mass spectrometer - indicated by § on Table 4. The remainder were too low in concentration for these techniques to be applied. Many of the detections were only slightly above the detection limit. Examples include 2,4-D at Dundurn and Beaver Creek and triallate at Carnduff, and 2,4-DB and 2,4-DP at Outlook North.

Multiple herbicide detections occurred at 3 springs (Carnduff, 11 detections, Antelope Lake, 6 detections and Outlook North, 4 detections). The detections at Carnduff were observed throughout the study (1991-94) whereas, at the latter two sites, all but two of the detections occurred in 1991. At Carnduff, the detections included a spectrum of both base/neutral and acid herbicides. At Antelope Lake most of the analytes detected were base/neutral herbicides. At Outlook North only acid herbicides were detected.

Ten of the detections were occurred in 1991 while the remaining 16 were spread out over the remainder of the study period, 1992-94. A possible explanation for the higher detection frequency in 1991 is that this was a relatively wet year. The mean annual precipitation at the meteorological stations nearest to the springs in Table 4 was 542 mm in 1991, compared to 348 mm in 1992 and 455 mm in 1993. During wet years, the recharge of these aquifers is increased and pesticide inputs are accordingly higher. Precipitation events containing pesticide residues may show up quickly in the spring if there is significant infiltration of the water and recharge near the spring. The travel time of this water to the spring would be relatively short, within a few weeks or months.

A total of 28 replicate samples (25% of the total) were analyzed in the base/neutral and the acidic herbicide classes, 14 in each class (Table 4). Detections in replicate samples occurred on four

occasions at Carnduff in the base/neutral herbicide class, and on one occasion each at Outlook North and at Carnduff in the acid herbicide class. Detections were not always confirmed by a corresponding detection in a replicate sample (column R_N, Table 4). In most instances, this occurred when the reported concentration was slightly above the NLET detection limit and the replicate sample was analyzed by Envirotest. The apparent discrepancy can be attributed to methodological differences between the two laboratories. Envirotest used a mass selective detector coupled with a gas chromatograph for all of their analyses. Their detection limit was accordingly higher than the values given in Table 3. Hence, a marginal detection reported by NLET would not be detected by Envirotest.

Several sites, including Broderick East, Delmas and Outlook South appeared to be likely candidates for herbicide contamination because herbicides are heavily used on these aquifers. However, in spite of this, no analytes were detected at these springs. The conditions at Outlook South are very similar, to Outlook North. Several acid herbicides were detected, at the latter site but not the former although the two sites are only 1-2 kilometers apart. A possible explanation is that most of the herbicides detected at Outlook North were only slightly above the detection limit. Minor differences between the two sites may have been enough to reduce herbicide concentrations below the detection limit at Outlook South.

In contrast to the above, some detections occurred at sites which appeared to be unlikely candidates for herbicide contamination. At Beaver Creek Camp and Dundurn, in particular, the surface of these aquifers is primarily woodlots and the nearest herbicide applications are some distance beyond the apparent boundaries of these aquifers. The detections at these sites (2,4-D) may have originated from atmospheric fallout on these aquifers following spray drift from applications in neighbouring areas.

Further evidence for atmospheric transport and fallout as a source of aquifer contamination is given by the atrazine and simazine detections at Antelope Lake and the repeated atrazine detections at Carnduff. Since these herbicides are not used anywhere in the vicinity of these aquifers, atmospheric fallout as aerosols, dry deposition, or as precipitation from neighbouring areas, or perhaps even further away, is the most likely source of contamination. Atrazine is used in small amounts in Saskatchewan, primarily for suppression of grasses. Although it is used as a corn herbicide and on certain varieties of canola (triazine tolerant rapeseed) these applications are relatively rare in Saskatchewan. There are numerous reports in the literature of atrazine occurrences both in North America and Europe, far from the source of application (Eisenreich and Strachan, 1992; Muir 1991; Buser, 1990). Hill (1995) reported the ubiquitous nature of low levels of atrazine in shallow groundwater wells in southern Alberta in areas where it is not used. Studies of a large number of wells in the United States also found atrazine to be the most frequently detected herbicide primarily because of its persistence in the environment and mobility in soil (Ritter, 1990; USEPA, 1992).

Significance of Detections

Analyte detections are compared with Canadian Water Quality Guidelines for drinking water, livestock watering, irrigation and aquatic life, as well as World Health organization guidelines for

drinking water and U.S. Environmental Protection Agency lifetime health advisories and other guidelines for groundwater and irrigation (CCREM, 1987; WHO, 1993; USEPA 1989; OME 1989; OME, 1984; NACA, 1985). The Saskatchewan Municipal drinking water guideline for pesticide residues is zero (SEPA, 1991). Apart from the Saskatchewan zero tolerance guideline, there was not a single exceedance of any of the above guidelines. The maximum detectable residues in springwaters ranged from 2 to 5 orders of magnitude lower than the most sensitive guideline (Table 5). The only exceptions were the larger picloram detections at Carnduff. However, these were still less than any known guideline, including the Ontario guideline for irrigation. In summary, none of the herbicide occurrences appear to be a concern with respect to current guidelines for health or agriculture or aquatic life.

To place the level of analyte detections in these shallow prairie aquifers in perspective, springwater appears to be relatively "clean" in comparison with surface water. The concentrations detected and the frequency of detection is low compared to the concentrations commonly detected in most prairie surface waters. A recent summary of selected acid and base/neutral herbicide detections from 5000 samples of prairie surface waters shows detection frequencies of 40% for 2,4-D, 9% for 2,4,5-T, 5% for atrazine and MCPA, 1-5% for 2,4-DP, 2,4-DB, picloram and triallate and 0.3-1% for the remaining base/neutral and acid herbicide analytes listed in Table 3 (Integrated Environments, 1991). Although these detection frequencies are not particularly high they were obtained using 1 litre water samples. Detection limits were one to two orders of magnitude or more higher, than the detection limits applicable to this study (Table 3). At the 1 litre level of detection, the overall detection frequency in our springs would have been reduced from 23% to 3%. The only analytes which would have been detected in our springs are the single 2,4-DB and three picloram detections (all at Carnduff). Base/neutral detections would decrease from 19% to 0% and acid detections from 26% to 7%.

Comparison To Other Studies

Our study of springs shows similarities in the herbicides detected and frequency of detection compared to other groundwater surveys for herbicides in the United States and Canada. Ritter (1990), in a review of the literature on groundwater contamination by pesticides in the U.S., found atrazine and alachlor to be the most frequently detected herbicides followed by other s-triazine herbicides, metolachlor and trifluralin. In a national survey of 68,000 wells throughout the United States the most frequently detected herbicides were atrazine (6.8%), picloram (2.5%), 2,4-D (2.3%), dicamba (2.3%), simazine (2.2%), cyanazine (2.1%), alachlor (2.0%), trifluralin (1.0%) and metolachlor (1.0%), (USEPA, 1992). The most frequently detected herbicides atrazine, picloram and 2,4-D are also the three most frequently detected herbicides in our study of springs. The detection frequencies of these herbicides in our springs are roughly twice those in the U.S. well survey, presumably because of our low detection limits. A few analytes, such as diallate and MCPB were detected in our springs which were not detected in the U.S. well study despite a sample size of several hundred wells.

With respect to guidelines, other studies in the Canadian prairies by Miller et al. (1992) and Hill et al. (1994) have also found most herbicide concentrations in shallow groundwater wells are well below Canadian Water Quality Guidelines, similar to our springs. They applied herbicides including dichlofop-methyl, bromoxynil, MCPA, triallate and 2,4-D to a number of plots above shallow groundwater in southern Alberta. They found overall detection frequencies of 28% of water table samples collected from wells, and 37% of samples from tile drain effluent. Mass balance estimates indicate that approximately 0.0003%-0.002% of herbicide applied is recovered in drain effluent. Despite modest detection frequencies, the levels detected were generally well below Canadian Water Quality Guidelines. Most of the detections (79%) were less than 5000 ng L⁻¹, and generally in the range of a few tens to hundreds of ng L⁻¹. However, the concentrations detected were several orders of magnitude greater than the levels detected in our springs. Similar findings were also obtained in another study in Saskatchewan by (Maathuis et al., 1988). The detection limits in both these studies was about two orders of magnitude higher than the limits applicable to this study. If the detection levels in these studies had been similar to our study of springs, it is likely that their detection frequencies would have been considerably higher. The higher magnitude and frequency of their detections compared to our springs can be attributed to the fact that their samples were taken from the water table. However, water table samples are not necessarily good indicators of overall aquifer contamination. There is also the possibility of water table contamination by direct entry into wells. In cases where direct entry can be ruled out, water table samples are indicators of vadose zone contamination. Significant attenuation of herbicides can occur through adsorptive, microbial and other losses as the water moves deeper into the aquifer. The concentrations found in our springs suggest that these losses are rapid and that aquifer contamination is relatively minor.

Although many surveys of herbicide contamination of wells have found modest contamination of the water table, agreement on this point is not universal. For example, the modest detection frequencies of the above mentioned well studies in the United States and Alberta are in stark contrast to the findings of another survey by Agriculture Canada (1991). This survey of shallow groundwater wells was carried out in areas of Alberta and Manitoba identified as highly vulnerable to pesticide penetration (Agriculture Canada, 1991). Analysis included many of the herbicides listed in Table 3 at the $\mu\text{g L}^{-1}$ (ppb) level of detection. In Alberta three detections were found in 177 wells sampled and in Manitoba, there was only one detection from 186 wells sampled.

Other Considerations

Studies such as Miller et al. (1992) demonstrate that herbicide detection frequencies are consistent with the predicted mobility of the herbicide. Most of the herbicides detected in our survey have "moderate" to "high" leaching potential. However, there were a few exceptions. We used an index of leaching potential defined by Gustafson (1989). This index was used by Agriculture Canada in their national assessment of areas vulnerable to groundwater contamination by pesticides (McRae, 1991). The index is based on the partition coefficient between soil organic carbon and water, K_{oc} , and the half-life of the pesticide in soil, $T_{1/2}$ (Gustafson, 1989). The groundwater ubiquity value (GUS) describes a hyperbolic transition zone of $\log T_{1/2}$ versus $\log K_{oc}$, separating "leachers" from

"non-leachers" by: $GUS = \log_{10}(T_{1/2 \text{ soil}})(4 - \log_{10}(K_{oc}))$

Gustafson (1989) noted that most "leachers" tend to have values exceeding 2.8 while most-"non-leachers" are less than 1.8. The intermediate transition zone, 1.8-2.8, describes pesticides with "moderate" potential to leach. GUS values for a large number of pesticides can be found in McRae (1991). GUS values for the analytes detected in our springs versus the detection frequency are described in Table 6. The correspondence between high GUS values and high detection frequency was strongest with atrazine and picloram. The relationship was not as strong with 2,4-D as it has GUS values indicating a "moderate" leaching potential, although it was one of the more frequently detected herbicides in our springs. In some instances there was a poor correspondence with the GUS values. For example 2,4-DB has a "low" leaching potential, although there were multiple detections in our springs (Table 6).

Although the index is potentially useful as a rough guide to predict pesticide occurrences, probably the greatest success is with herbicides at the extreme ends of the distribution, i.e. extreme "leachers" and extreme "non-leachers". However, with herbicides in the more intermediate ranges, GUS scores are, at best, difficult to predict. There is a fairly wide margin of error in predicting both the half-life and the partition coefficient under local conditions. Both parameters show an extremely broad range of variability for many herbicides depending upon a large number of local factors (Montgomery, 1993). GUS values cannot be estimated with much reliability with the majority of herbicides.

Some surveys have shown a relationship between herbicide detections in groundwater and elevated nitrate concentrations (Ritter, 1990; Koterba et al., 1993). Elevated nitrate (NO_3^-) concentrations in groundwater are indicative of surficial inputs to the aquifer and/or high dissolved oxygen. Dissolved nitrite (NO_2^-) + nitrate (NO_3^-) expressed as $mg L^{-1}$ nitrogen is indicated in Table 1. Although herbicide detections occurred at two springs with modest concentrations of dissolved $NO_2^- + NO_3^-$ (eg. Carnduff, Outlook North), herbicide detections also occurred at several locations where $NO_2^- + NO_3^-$ concentrations were near or below detection limit ($0.01 mg L^{-1}$) (eg. Antelope Lake, Beaver Creek Camp and Dundurn). Our data does not suggest that there is any relationship between nitrate levels and detection frequency in our springs. However, the small size of our database limits meaningful analysis.

Standards Recovery Assessment

Recovery ranges of surrogate and standard additions as well as median and mean recoveries for the various analytes assessed are shown in Table 7. For the OC/PCB's, apart from Heptachlor, the surrogates used are the standard protocols established by Environment Canada for this category of analytes. There are no protocols established by Environment Canada with respect to appropriate surrogates or standards for evaluating field handling or extraction efficiency of neutral herbicides. Acid herbicide standards are currently in development stage but not in use. Deuterated 2,4-D and atrazine were considered as standard additions. However, this option was not pursued because costs are

prohibitively expensive. For this study two types of standard additions were involved:

(1) Each groundwater sample was "spiked" at the time of extraction with a standard addition of an appropriate neutral or acid herbicide. Endaven (benzoylprop ethyl) was used for the base/neutral class (1992-94). For the acid herbicides, picloram was used in 1991, and 2,3,6-TBA in 1991-92. The latter was replaced by 2,4,5-T in 1993-94 because of poor recoveries with 2,3,6-TBA. The recoveries with 2,4,5-T were much improved. Endaven and 2,3,6-TBA were selected because they are not used in the prairies and 2,4,5-T has not been in use since the 1970's. Therefore, it is reasonable to assume that these compounds would not be present in Saskatchewan springwaters. Picloram use in Saskatchewan is low. However, this turned out to be a poor choice as a spike because it was one of the more frequently detected analytes and several detections did occur at Carnduff in 1993 and 1994. It was discontinued after 1991 in favour of 2,3,6-TBA and 2,4,5-T.

(2) A large number of distilled water samples 16.9 L were "spiked" in the laboratory with several of the acid and neutral herbicides given in Table 7. These were added to each sample at appropriate concentrations, usually about 5-10 times the detection limit. In some cases higher concentrations were used. The analytes used varied from year to year as new ones were added to the list for trial (Table 7).

Recoveries of the OC/PCB surrogates was within reasonable ranges, at least from the National Laboratory for Environmental Testing (NLET). Envirotest had some difficulty with this category of analytes. Recoveries of the base/neutral herbicides by NLET was generally very good, in the range of about 60% to 130%, with a median near 100%. The only analyte in this category in which NLET had some difficulty was dichlofop-methyl. None of the spikes were detected by NLET in 1991, although good recoveries were obtained in 1993. The recoveries from Envirotest in the base/neutral category were poor. This may be due to concentrations of the standard additions being too low for their mass selective detector.

Recovery of the acid herbicides presented a number of difficulties. In general, recoveries were much lower than the base/neutral herbicides. The highest recoveries were MCPA, 2,4-D and 2,4,5-T which were in the 30-50% range. Dicamba was not recovered at all, even at large concentrations 50 times the detection limit. There was only a single recovery of bromoxynil. Recoveries of 2,3,6-TBA and picloram were very low, in most cases less than 5%. Recoveries of MCPA, 2,4-D, and 2,4,5-T increased between 1991 and 1993 as improvements were made to the solvent extraction technique, such as provision for tandem (series) extraction, as well as changes to the procedures for handling samples and standards. The range of recoveries shown in Table 7 reflects these changes. It is notable that in spite of the relatively low recoveries of the acid herbicides, especially picloram, most of the really large detections in the springs were acid herbicides, in particular picloram and 2,4-DB (Table 4).

The low recoveries of the acid herbicide standards raises the possibility that actual concentrations of these compounds in the groundwater may have been considerably higher than the levels detected (eg. the picloram detections at Carnduff, Table 4). Also, there is the possibility that some herbicides such

as dicamba might be present in springwater but went undetected. However, these seem unlikely explanations for the following reasons.

The low recoveries of the acid standards are most likely a result of loss during storage prior to use, as a result of adsorption to glass container walls or decomposition, rather than loss after extraction or during field handling. Analysis of the standard solution stock after storage for several weeks showed the concentration of the analytes had declined to levels comparable to the recoveries in Table 7. The low recoveries, therefore, appear to be an artefact of the storage medium of the standards and are not indicative of the actual recoveries in spring samples. Standard solutions of herbicides in methanol were stored in glass bottles at 4°C (in the dark), often for several weeks prior to use. For some analytes such as 2,4-D, adsorption to glassware is a known problem for long term storage (Kan, et al. 1982). It should not present a problem after extraction since the herbicide readily desorbs from glassware in the presence of dichloromethane. Potential adsorption problems have since been rectified by storing spikes in teflon bottles in a frozen state at low temperatures (-80°C) prior to use.

CONCLUDING REMARKS AND RECOMMENDATIONS

This study has shown that herbicides are present in some prairie springs used as drinking water sources for humans and livestock. However, the concentrations are very low. At the concentrations found, herbicide occurrences do not present a significant risk for human health, agriculture or aquatic life. There were no exceedances of Canadian Water Quality Guidelines, World Health Organization Guidelines, or United States Environmental Protection Agency Guidelines for drinking water, livestock use, irrigation, or aquatic life.

Although there are numerous studies of contamination of well water by herbicides, the possibility of contamination by direct entry from the surface (well contamination) cannot be ruled out in many instances. Studying springs rather than wells eliminates this possibility. The herbicides found in springs represent aquifer contamination as opposed to well contamination. The water table samples collected in most well surveys are more representative of vadose zone contamination rather than contamination of the whole aquifer. Springs represent integrated aquifer discharge from various depths and over a wide area, and herbicide concentrations reflect this effect. Given these considerations, future studies of herbicide contamination of shallow groundwater might better be conducted on springs rather than wells.

The detection frequency of herbicides in this study was a modest 23% of samples collected, which is comparable to the detection frequencies found in many surveys of groundwater wells for herbicides. However, the detection limits in this study were one to two orders of magnitude lower than any previous studies of groundwater, owing to the large sample technology used. If conventional 1 litre samples had been used, the detection frequency would have been only 3% of samples collected. Therefore, the main conclusion of this study is that herbicide contamination of shallow prairie aquifers is a relatively infrequent event. Contamination appears to be much less frequent than indicated by most well surveys and the concentrations of herbicides found in springs tends to be very low. Provided

technological developments keep pushing the detection limits lower, we will continue to discover herbicides in groundwaters at ever lower levels. Although detections at low levels are of interest they are not a major health concern.

This study provides a "snapshot" of herbicide contamination of prairie springs. In addition, it represents the most detailed compilation of information on springwater quality ever assembled. With the documentation provided, the assessment could be repeated in approximately 5-10 years to determine if any trends are apparent with respect to contamination by commonly used herbicides, or as new herbicides are brought into use.

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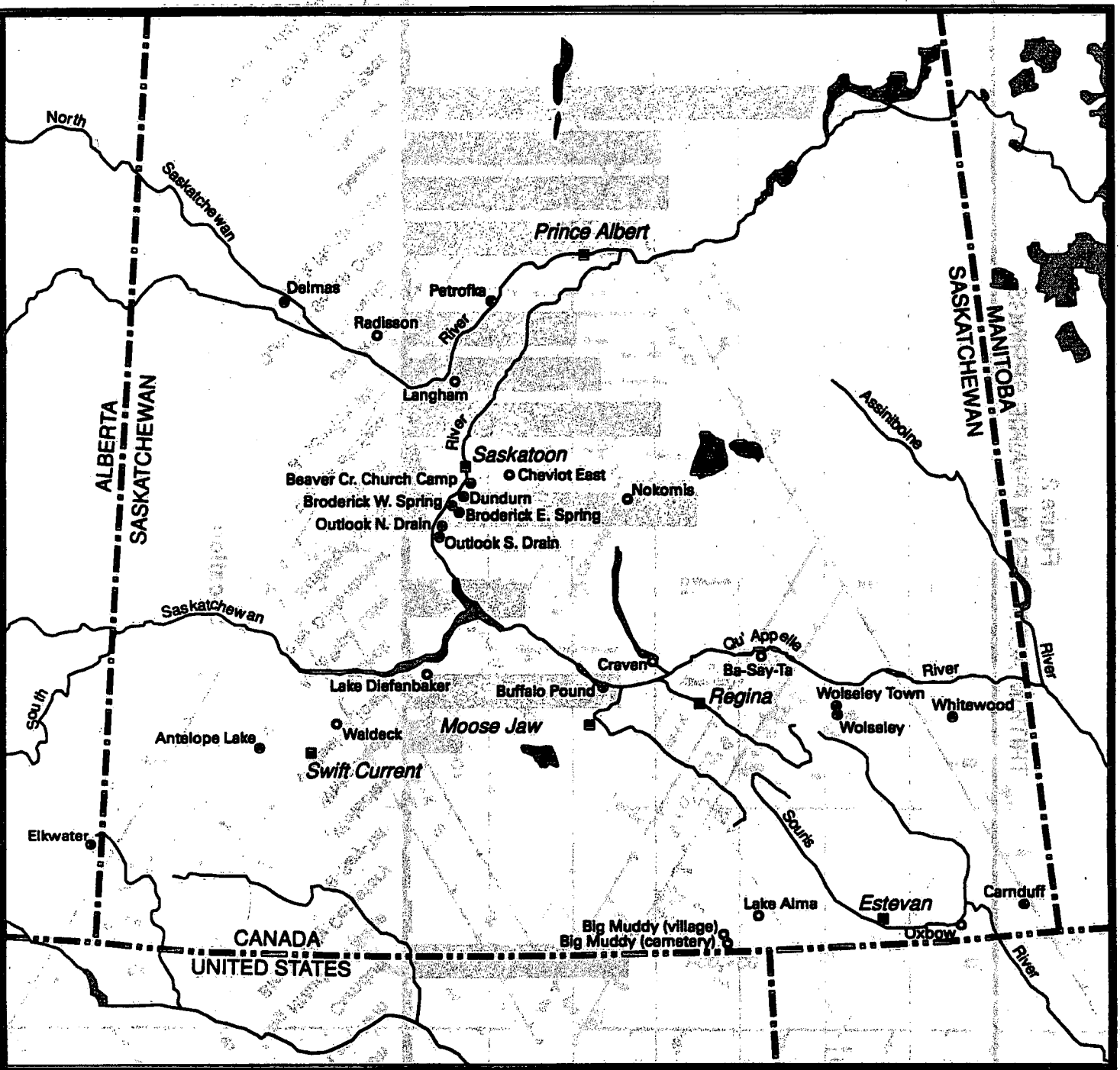
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Figure 1
 SAMPLING LOCATIONS, PRAIRIE SPRINGS



- Springs sampled for pesticides
- Other springs investigated for tritium levels

Figure 2
TRITIUM ACTIVITIES IN PRAIRIE SPRINGS

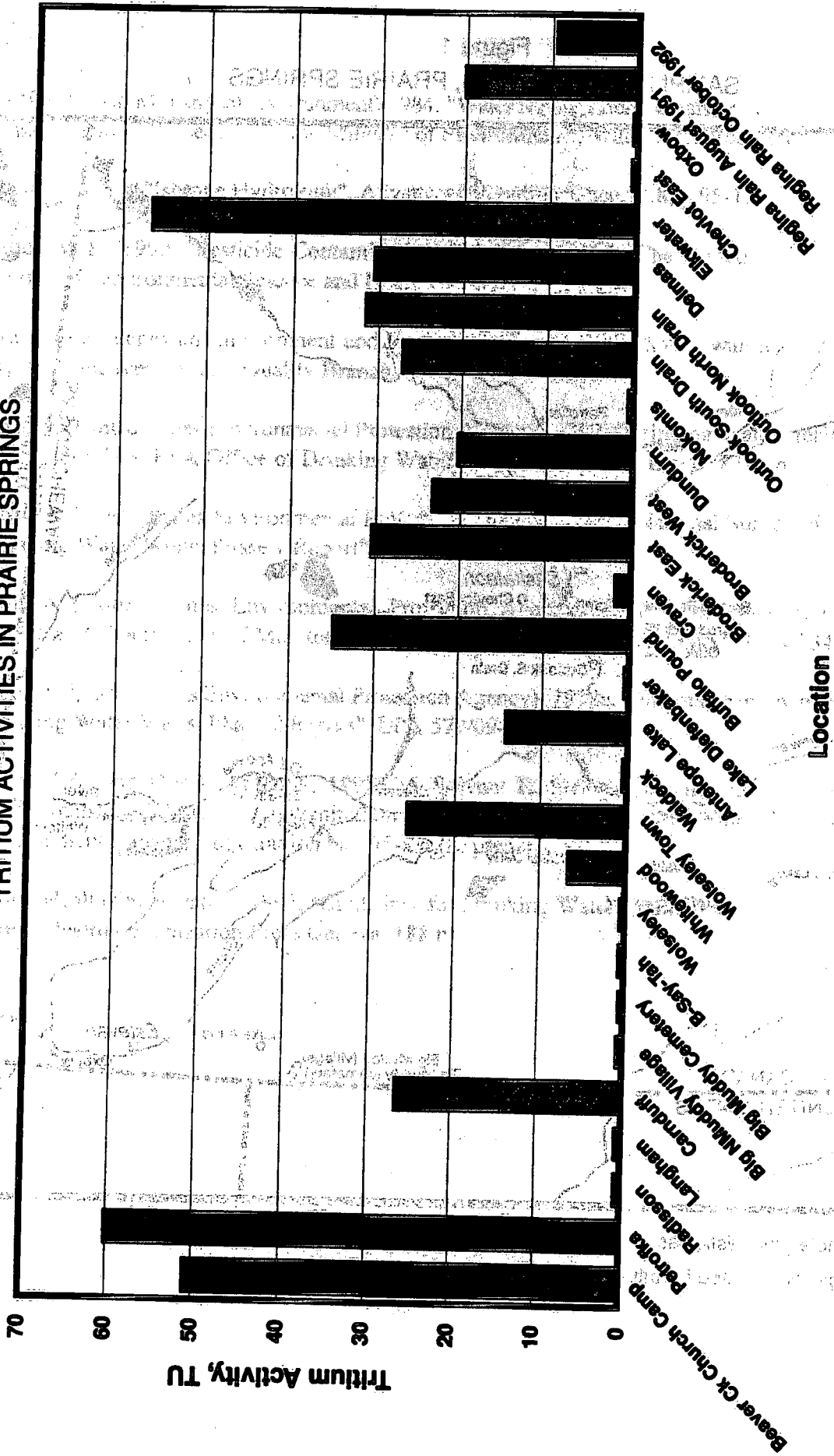
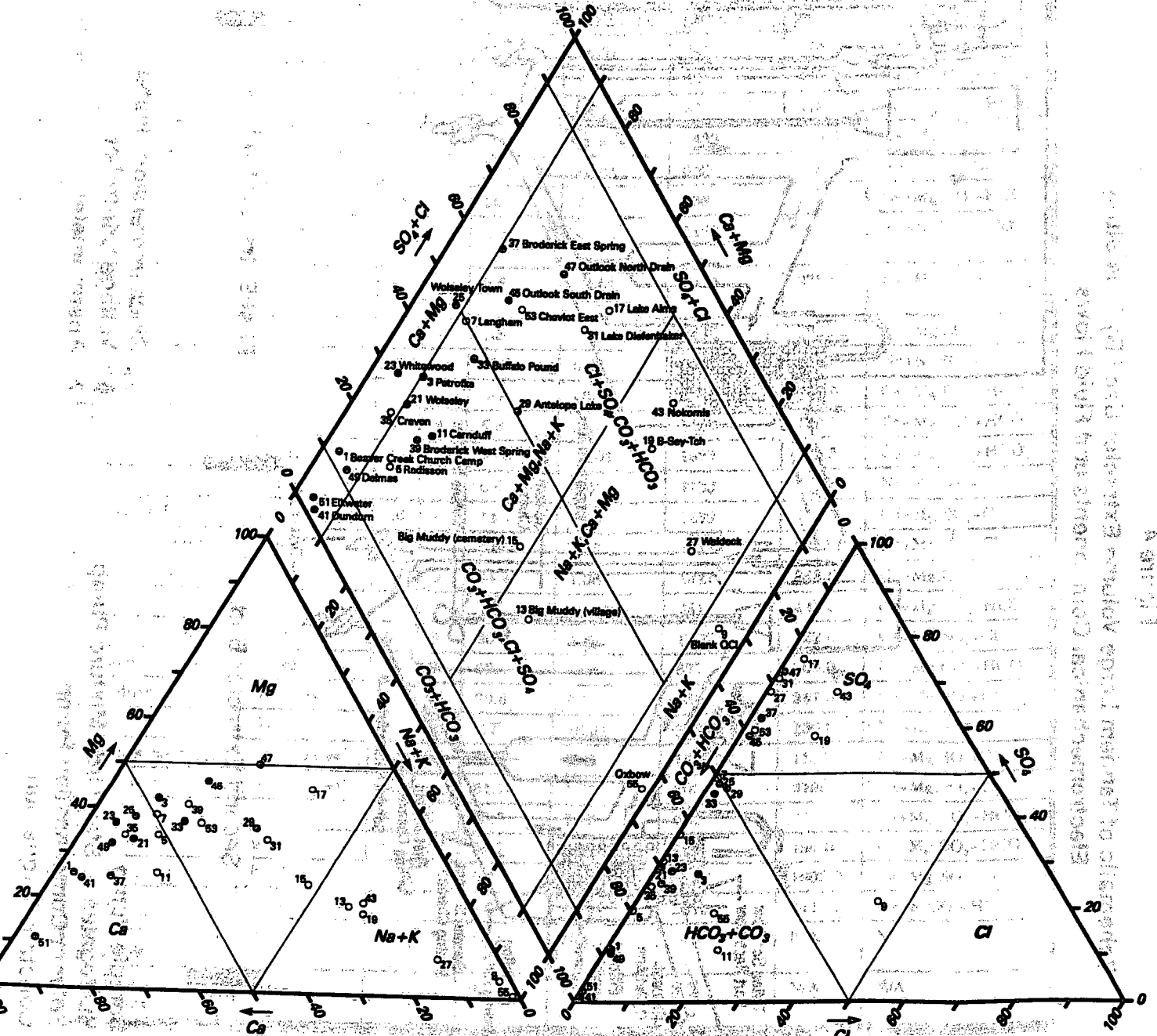


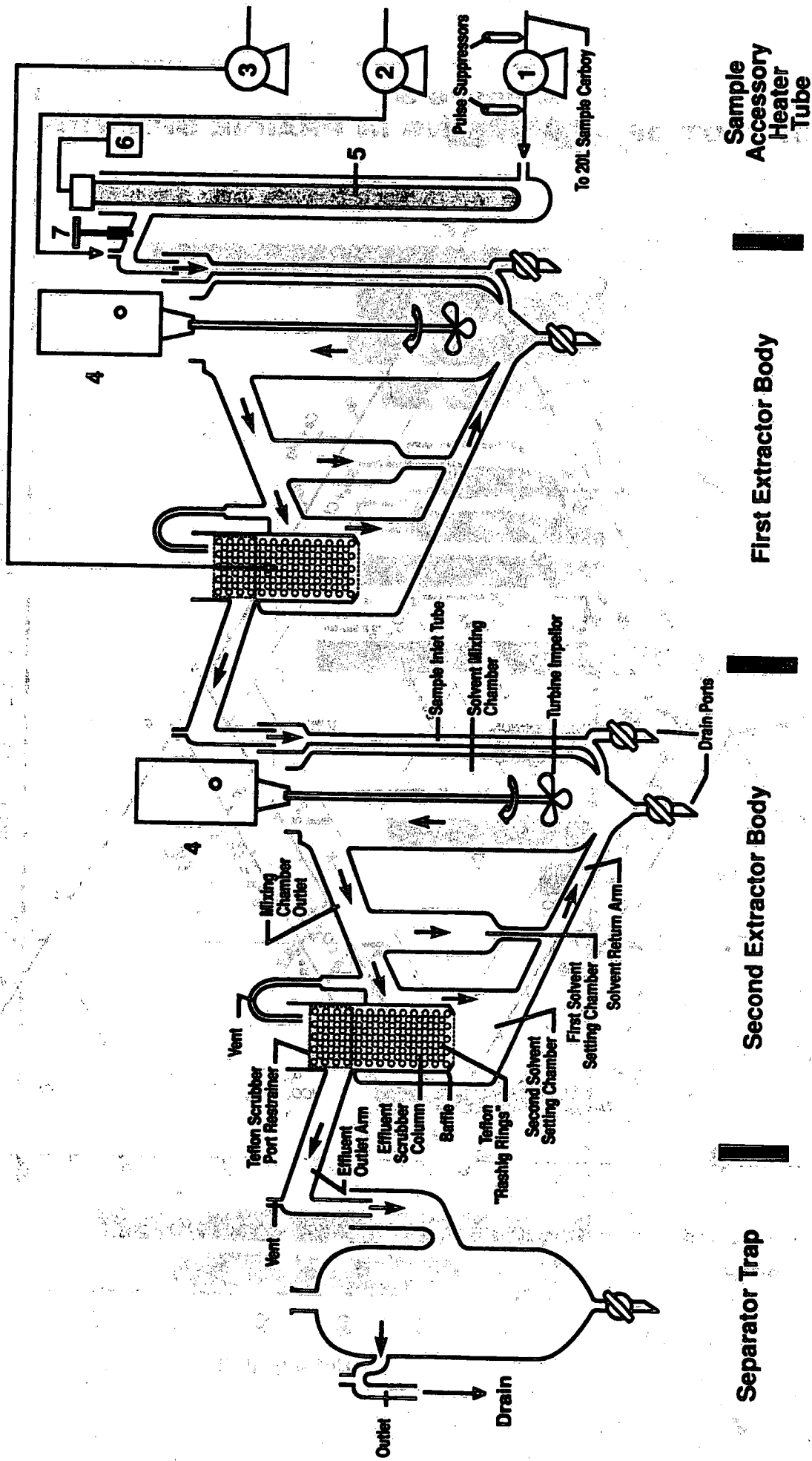
Figure 3
PIPER PLOT OF MAJOR IONS IN PRAIRIE SPRINGS



- Spring selected for pesticide sampling and analysis
- Spring sampled

ESCALANTE PLATEAU COUNTY PUBLIC HEALTH DEPARTMENT
 ANALYTICAL CHEMISTRY DIVISION
 11-1984

Figure 4
Schematic of Tandem Large Volume Extractor Used By This Study:
Electromechanical Components and Fluid Flows



- 1 : Sample Pump
- 2 : Surrogates or Standards Mixture Pump
- 3 : Solvent Compensation Pump
- 4 : Constant Torque Stirrer
- 5 : Silica Immersion Heater
- 6 : Voltage Controller
- 7 : Thermometer

Sample
 Accessory
 Heater
 Tube

First Extractor Body

Second Extractor Body

Separator Trap

TABLE 1: SUMMARY OF WATER CHEMISTRY OF 27 PRAIRIE SPRINGS SITES INVESTIGATED

SITE NAME	Herbicide Analysis	N	R	Tritium	dissolved NO ₃ -NO ₂ as N	Conductance	TDS [†]	Ionic Dominance [‡]
	Years			TU	mg L ⁻¹	µS cm ⁻¹	mg L ⁻¹	Greater than 50%
Beaver Ck Camp	92,93,94*	6	0	51.1	<0.01	448	248.5	Ca+Mg,CO ₃ +HCO ₃
Petrofska	91,92,93	6	4	60.2	7.56	801	467.5	Ca+Mg,CO ₃ +HCO ₃
Radisson	None	-	-	0.8	0.01	687	413.0	Ca+Mg,CO ₃ +HCO ₃
Langham	None	-	-	0.8	0.36	1439	949.0	Ca+Mg,CO ₃ +HCO ₃
Blank QC	N/A	-	-	N/A	<0.01	0.83	1.0	Na+K,SO ₄ +Cl
Carnduff	91,92,93,94*	16	9	26.7†	7.70	738	433.5	Ca+Mg,CO ₃ +HCO ₃
Big Muddy Village	None	-	-	0.8	<0.01	1462	910.0	Na+K,CO ₃ +HCO ₃
Big Muddy Cemetery	None	-	-	0.6	<0.01	1539	976.0	Ca+Mg,CO ₃ +HCO ₃
L. Alma	None	-	-	NS	0.04	2435	1828.5	Ca+Mg,SO ₄ +Cl
B-Say-Tah	None	-	-	0.7†	0.01	3099	2049.5	Na+K,SO ₄ +Cl
Wolseley	91,94	4	2	0.7	<0.01	852	535.0	Ca+Mg,CO ₃ +HCO ₃
Whitewood	92,93	4	0	6.8	0.15	1182	729.5	Ca+Mg,CO ₃ +HCO ₃
Wolseley Town	92,93	4	0	25.8	<0.01	1089	705.5	Ca+Mg,CO ₃ +HCO ₃
Waldeck	None	-	-	0.6	0.22	3423	2239.0	Na+K,SO ₄ +Cl
Antelope L.	91,92,93,94*	16	4	14.4	0.14	1239	730.5	Ca+Mg,SO ₄ +Cl
L. Diefenbaker	None	-	-	0.6	0.32	3079	2323.5	Ca+Mg,SO ₄ +Cl
Buffalo Pound	92,93	4	0	34.9	1.06	1327	848.5	Ca+Mg,CO ₃ +HCO ₃
Craven	None	-	-	1.9	<0.01	761	452.0	Ca+Mg,CO ₃ +HCO ₃
Broderick East	91,92,93	6	0	30.6	1.30	1107	722.0	Ca+Mg,SO ₄ +Cl
Broderick West	91,92,93	6	0	23.5	0.03	877	509.0	Ca+Mg,CO ₃ +HCO ₃
Dundurn	92,93,94*	6	0	20.6	0.01	483	247.0	Ca+Mg,SO ₄ +Cl
Nokomis	94	2	0	0.7†	<0.01	3630	2360.5	Na+K,SO ₄ +Cl
Outlook South	91,92,93,94*	14	5	27.3†	0.89	1619	1111.0	Ca+Mg,SO ₄ +Cl
Outlook North	91,92,93,94*	16	4	31.7†	1.27	3024	2195.5	Ca+Mg,SO ₄ +Cl
Delmas	91,92,93	6	0	30.7	7.52	425	248.0	Ca+Mg,CO ₃ +HCO ₃
Elkwater, ALTA	92,93	4	0	56.7	0.08	324	185.0	Ca+Mg,CO ₃ +HCO ₃
Cheviot East	None	-	-	0.7	<0.01	2221	1602.0	Ca+Mg,SO ₄ +Cl
Oxbow	None	-	-	0.6	<0.01	2413	2413.0	Na+K,CO ₃ +HCO ₃
Rainwater Aug 1991	N/A	-	-	20.4	N/A	N/A	N/A	N/A
Rainwater Oct 1992	N/A	-	-	9.7	N/A	N/A	N/A	N/A

N Total number of base/neutral and acid herbicide samples analyzed excluding replicates to October 1994.

R Total number of replicate samples analyzed, including base/neutral and acid herbicides to October 1994.

* Springs sampled quarterly for herbicides in 1994.

† Median of replicate tritium samples.

‡ All TDS values are the mean of 2 or more replicate samples.

§ Dominant cations (Ca+Mg or Na+K), Dominant anions (HCO₃ or SO₄+Cl). For these groundwaters HCO₃=CO₃+HCO₃.

TABLE 2: DETECTION LIMITS FOR ORGANOCHLORINES, CHLOROBENZENES AND PCB'S

Analyte	Detection Limit This Study	Sample Time	Number of Samples 1991
OC/PCB	ng L⁻¹	Years	
HCB (Hexachlorobenzene)	0.07	1991	12
p,p'-DDT	0.28	1991	12
o,p'-DDT	0.26	1991	12
p,p'-DDD (p,p'-TDE)	0.22	1991	12
p,p'-DDE	0.20	1991	12
p,p'-Methoxychlor	1.10	1991	12
Heptachlor	0.11	1991	12
Heptachlor Epoxide	0.06	1991	12
Alpha-Endosulfan	0.05	1991	12
Beta-Endosulfan	0.09	1991	12
Alpha-Chlordane	0.07	1991	12
Gamma-Chlordane	0.04	1991	12
Lindane (Gamma-Hexachlorocyclohexane)	0.40	1991	12
Alpha-Hexachlorocyclohexane (α-BHC)	1.30	1991	12
Mirex	0.11	1991	12
Aldrin	0.07	1991	12
Endrin	0.14	1991	12
Dieldrin	0.18	1991	12
Total PCB's (Arochlor)	3.30	1991	12

OC/PCB	Detection Limit	Sample Time	Number of Samples
HCB (Hexachlorobenzene)	0.07	1991	12
p,p'-DDT	0.28	1991	12
o,p'-DDT	0.26	1991	12
p,p'-DDD (p,p'-TDE)	0.22	1991	12
p,p'-DDE	0.20	1991	12
p,p'-Methoxychlor	1.10	1991	12
Heptachlor	0.11	1991	12
Heptachlor Epoxide	0.06	1991	12
Alpha-Endosulfan	0.05	1991	12
Beta-Endosulfan	0.09	1991	12
Alpha-Chlordane	0.07	1991	12
Gamma-Chlordane	0.04	1991	12
Lindane (Gamma-Hexachlorocyclohexane)	0.40	1991	12
Alpha-Hexachlorocyclohexane (α-BHC)	1.30	1991	12
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Endrin	0.14	1991	12
Dieldrin	0.18	1991	12
Total PCB's (Arochlor)	3.30	1991	12

TABLE 3. DETECTION LIMITS FOR THIS STUDY, 16.9 LITRES SAMPLE VOLUME, COMPARED TO 1 LITRE SAMPLE, ng L⁻¹

ANALYTE	CHEMICAL NAME	Detection Limit, 16.9 L Sample [†]	Detection Limit, 1 L Sample	Maximum Springwater Detection	Minimum Springwater Detection	
BASE/NEUTRAL HERBICIDES	Trifluralin	0.4	5.0	-	-	
	Diallate	6.5	100.0	8.9	8.9	
	Triallate	0.7	10.0	0.7	0.7	
	Atrazine	3.0	50.0	11.0	3.0	
	Simazine	3.0	50.0	0.6	0.6	
	Carbyne (Barban)	7.6	100.0	-	-	
	Dichlofop-Methyl (Hoegrass)	3.4	50.0	-	-	
	Benzoylprop Ethyl (Endaven)	2.1	25.0	-	-	
	Metolachlor	5.0	100.0	23.7	23.7	
	ACID HERBICIDES	3,6-dichloro-2-methoxybenzoic acid	0.3	30.0	-	-
		(4-chloro-2-methylphenoxy)acetic acid	0.3	30.0	-	-
		4-(4-chloro- <i>o</i> -tolylloxy)butyric acid	0.4	50.0	2.0	2.0
		2,3,6-trichlorobenzoic acid	0.4	30.0	-	-
		(2,4-dichlorophenoxy)acetic acid	0.4	30.0	1.0	0.47
4-(2,4-dichlorophenoxy)butyric acid		0.4	50.0	210.0	0.6	
(RS)-2-(2,4-dichlorophenoxy)propionic acid		0.3	30.0	1.0	0.6	
(4,5-trichlorophenoxy)propionic acid		0.3	30.0	0.5	0.5	
(2,4,5-trichlorophenoxy)acetic acid		0.4	50.0	-	-	
4-amino-3,5,6-trichloropicolinic acid		0.5	50.0	225.0	19.0	
3,5-dibromo-4-hydroxybenzotrile		0.3	30.0	-	-	

[†] Detection limits normalized for a 16.9 Litre sample

TABLE 4. SUMMARY OF ANALYTE DETECTIONS (ng L⁻¹) IN PRAIRIE SPRINGS 1991-94

ANALYTE	LOCATION						DATA SUMMARY					
	Outlook North	Carnduff	Antelope Lake	Beaver Ck Camp	Dundurn	Broderick West	N _b	N _r	F _b %	R _c	R _n	Years Detected
EASE/NEUTRALS												
Diallate			8.9 ^{†§§}				1	59	2	0	2	92
Triallate	0.7						1	59	2	0	2	91
Atrazine		11.0, 10.0 ^{†§} , 11.0 ^{†§} , 3.9 ^{†§} , 3.0 ^{†§} , 3.0 ^{†§} , 3.3 ^{†§} , 3.6 ^{†§} , 4.4 ^{†§} , 3.0 ^{†§}	11.9				7	59	12	4	1	91, 92, 93, 94
Simazine			0.6 ^{†§}				1	57	3	-	-	94
Metolachlor			23.7				1	59	2	-	-	91
N _{nit}	8	8	8	3	3	3						
F _{nit} %	0	88	50	0	0	0						
ACIDS												
MCPB	2.0						1	58	2	0	1	91
2,4-D			1.0	0.47 ^{†§} , 0.7 ^{†§}	0.48 ^{†§}		4	58	7	-	-	91, 92
2,4-DB	0.6, 18.0 ^{†§}	210.0 ^{†§}					2	58	4	1	1	91
2,4-DP	0.6		1.0				2	58	4	0	1	91
Silvex	0.5						1	58	2	0	1	91
Picloram		19.0 ^{†§} , 50.0 ^{†§} , 65.0 ^{†§} , 104.0 ^{†§} , 225.0 ^{†§}					4	58	7	1	1	92, 93, 94
Bromoxynil							1	58	2	0	1	91
N _{AM}	8	8	8	3	3	3						
F _{AM} %	50	63	25	66	83	83						

COLUMNS

N_b Number of spring samples not including replicates in which analyte was detected.
 N_r Total number of samples analyzed for herbicide to October 1994, excluding replicates.
 F_b Frequency of detection of analyte %.
 R_c Number of detections confirmed by a detection in a replicate sample. (- no replicate sample collected from site of detection).
 R_n Number of detections in which there was no detection in a replicate sample. (- no replicate sample collected from site of detection).

ROWS

N_{NIT} Total number of samples analyzed at spring site in base/neutral analyte class, excluding replicates.
 N_{AE} Total number of samples analyzed at spring site in acidic analyte class, excluding replicates.
 F_{NIT} Frequency of detection at spring in base/neutral analyte class.
 F_{AE} Frequency of detection at spring in acidic analyte class.

OTHER INFORMATION

† Detection in replicate sample analyzed by Envirotest laboratories.
 ‡ Detection in replicate water sample analyzed by NLET (1993, 1994 only).
 § Detection confirmed by GC-mass selective detector or high resolution mass spectrometer.

TABLE 5. GUIDELINES FOR WATER QUALITY COMPARED TO HERBICIDE DETECTIONS IN SPRINGS, μL^{-1}

ANALYTE	CWQG Drinking Water	WHO Drinking Water	CWQG Livestock Watering	CWQG Irrigation	CWQG Aquatic Life	USEPA Drinking Water	Other	Maximum Detectable μL^{-1}	Minimum Detection μL^{-1}
BASE/NEUTRAL HERBICIDES									
Trifluralin	45	20	45	-	0.1	2	-	-	-
Diallate	-	-	-	-	-	-	-	0.0089	0.0089
Triallate	230	-	230	-	0.24	-	-	0.0007	0.0007
Atrazine	60	2	60	10	2	3	10EPA	0.0119	0.003
Simazine	10	2	10	0.5	10	4	-	0.0006	0.0006
Barban	-	-	-	-	-	-	-	-	-
Dichlofop-Methyl	9	-	0.18	9	6.1	-	-	-	-
Benzoylprop-Ethyl	-	-	-	-	-	-	-	-	-
Metolachlor	50	10	50	28	8	100	-	0.0287	0.0237
ACID HERBICIDES									
Dicamba	120	-	122	0.006	10	200	200ONT	-	-
MCPA	-	2	-	-	-	10	-	-	-
MCPB	-	-	-	-	-	-	-	0.002	0.002
2,3,6-TBA	-	-	-	-	-	-	-	-	-
2,4-D	100	30	100	100	4	-	4 ONT	0.001	0.00047
2,4-DB	-	90	-	-	-	-	-	0.21	0.0006
2,4-DP	-	100	-	-	-	-	-	0.001	0.0006
Silvex	10	9	-	-	-	-	-	0.0005	0.0005
2,4,5-T	-	9	-	-	-	70	-	-	-
Picloram	190	7	-	190	29	500	250 NACA, 0.5ONT	0.225	0.019
Bromoxynil	5	-	11	0.35	5	-	25 NACA	0.0003	0.0003

CWQG Canadian Water Quality Guideline

WHO World Health Organization Guideline

USEPA U.S. EPA lifetime guideline for continuous exposure in drinking water.

EPA U.S. EPA guideline for irrigation

ONT Ontario guideline for aquatic life.

ONT Ontario guideline for irrigation water.

NACA U.S. National Agricultural Chemicals Association guideline for groundwater.

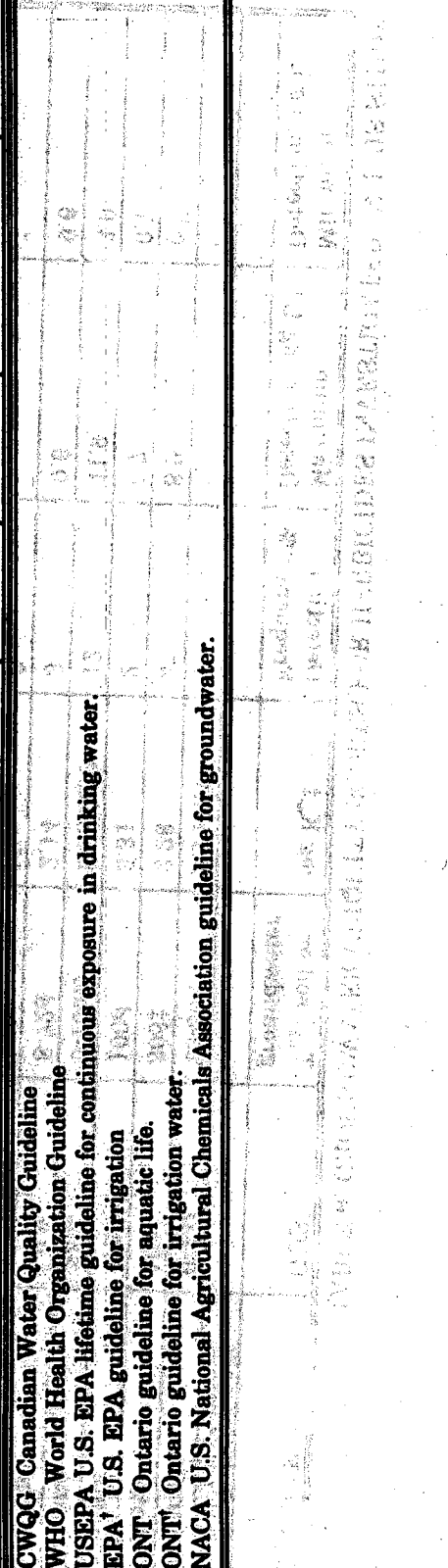


TABLE 6. GROUNDWATER UBIQUITY SCORES FOR HERBICIDES INVESTIGATED IN THIS STUDY

ANALYTE	GUS [*]	T _{1/2} [†] soil or groundwater	log K _{oc} [‡]	Detection Frequency %	Maximum Detection, ng L ⁻¹	Minimum Detection, ng L ⁻¹
BASE/NEUTRALS						
Trifluralin	0-1.0	20-30d	2.94-4.49	0	-	-
Diallate	N/A	30d†	2.28	2	8.9	8.9
Triallate	1.0-1.8	100d	3.31	2	0.7	0.7
Atrazine	>2.8	6-15mo	2.33-2.80	12	11.9	3.0
Simazine	>2.8	8-72d	2.14	3	0.6	0.6
Barban	N/A	N/A	N/A	0	-	-
Dichlofop-Methyl	<0	10-30d†	4.89	0	-	-
Endaven	N/A	N/A	N/A	0	-	-
Metolachlor	>2.8	15-100d†	2.08-2.49	2	23.7	23.7
ACIDS						
Dicamba	1.8-2.8	>160d	0.30	0	-	-
MCPA	>2.8	15-25d	2.03-2.07	0	-	-
MCPB	>2.8	<1d	N/A	2	2.0	2.0
2,3,6-TBA	N/A	N/A	1.50	0	-	-
2,4-D	1.8-2.8	>170d	1.68-2.73	7	1.0	4.7
2,4-DB	1.0-1.8	N/A	N/A	4	210.0	0.6
2,4-DP	N/A	N/A	N/A	4	1.0	0.6
Silvex	N/A	2.5d	N/A	2	0.5	0.5
2,4,5-T	N/A	27d	1.72, 2.27	0	-	-
Picloram	>2.8	>15mo	1.41	7	104.0	19.0
Bromoxynil	0-1	10d†	2.48	0	0.3	0.3

d Days

mo Months

NA Not available

* McRae (1991).

† Muir (1991).

‡ Montgomery (1993).

TABLE 7: RECOVERIES OF ANALYTES USED AS STANDARD ADDITIONS.

STANDARDS	Years Used	Number of samples analyzed		Median Recovery %		Mean Recovery %		Recovery Range (Max-Min) %	
		NLET	Envirotest	NLET	Envirotest	NLET	Envirotest	NLET	Envirotest
BASE/NEUTRALS									
Endaven	92,93	54	7	98	NA	102	NA	86-128	NA
Triallate	91,92,93	14	3	81	76	84	97	58-127	0-214
Trifluralin	92,93	12	2	101	0	99	0	64-128	0-0
Dichlofop-Methyl	91,93	9	1	96	0	68	0	0-119	0-0
Atrazine	93	6	0	98	NA	102	NA	86-128	NA
ACIDS									
2,3,6-TBA	91,92	35	12	3	0	4	5	0-15	0-34
Picloram	91	13	5	3	0	3	1	0-6	0-6
2,4,5-T	93	29	0	42	NA	49	NA	14-90	NA
2,4-D	91,92,93	14	3	35	37	31	31	4-59	0-55
Bromoxynil	91	2	1	0	73	0	73	0-0	73-73
MCPA	91,92,93	13	3	42	49	48	50	21-76	0-101
Dicamba	93	5	0	0	NA	0	NA	0-0	NA
OC/PCB									
Heptachlor	91	10	0	84	NA	87	NA	80-100	NA
1,3,5-Tribromobenzene	91	9	3	123	132	113	132	68-144	125-139
1,2,4,5-Tetrabromobenzene	91	9	3	114	54	117	275	100-162	44-727
deltas-HCH	91	9	3	122	44	123	48	112-138	41-59

NA - Not applicable. Analyte excluded from Envirotests analytical schema.

APPENDIX

Location and Description of Springs

Spring	NTS Map, Lat., Long (to nearest 5")	Directions/Site Description/Approximate Flow Rate/Surficial Geology (Map ID)
Carnduff	NTS (1:50,000) 62F4; 49°10'40"N, 101°42'25"W	6 km east of Carnduff on left side of Hwy 18. Spring issues from a metal pipe by a solitary clump of trees 20 m from highway. Public drinking water by Carnduff residents and also livestock. Flow 5 L min ⁻¹ . Contact Carnduff town office. Surficial Geol: Glacio-fluvial floodplain. (62E,F).
Antelope Lake	NTS (1:50,000) 72K8; 50°16'30"N, 108°25'00"W	Spring feeds large wetland on west side of Antelope Lake Regional Park. Follow park road to entrance kiosk, follow south fork 100 meters. Spring issues from several locations at base of arc-shaped bluff inside trees adjacent to road. Flow hundreds L min ⁻¹ . Contact Antelope L. Regional Park. Surficial Geol: Glacio-lacustrine kames and kettles. (72K).
Outlook North	NTS (1:50,000) 72O11; 51°32'35"N, 107°03'25"W	Irrigation tile drain Dutch Potato Farm. Metal pipe outlet located in small gully 1.5 km on farm north perimeter access laneway off grid road. Metal pipe. Flow 20 L min ⁻¹ . Contact John Konst Box 1092 Outlook SK 867-8939. Surficial Geol: Glacio-lacustrine delta. (72O).
Outlook South	NTS (1:50,000) 72O11; 51°33'40"N, 107°03'25"W	Irrigation tile drain Dutch Potato Farm. Follow main farm access laneway for 1.5 km. At cattle gate turn south for 0.5 km. Tile drain metal pipe outlet located in small gully next to bushes and scrub. Flow 20 L min ⁻¹ . Contact John Konst Box 1092 Outlook SK 867-8939. Surficial Geol: Glacio-fluvial deposits and eolian dunes. (72O).
Broderick East	NTS (1:50,000) 72O10; 51°40'05"N, 106°55'55"W	Turn north on grid road from Hwy 15 at Broderick. Turn west at road end and then north at first junction (300 m) next to cemetery. Follow road to the access laneway. At end of laneway head west across field. Spring issues from several locations at base of arc-shaped bluff and feeds large wetland in treed area at north end of field near South Sask R. Flow hundreds L min ⁻¹ . Contact Randy & Margaret Dahl 867-8081 or Georgina Dahl Box 8 Broderick SK. Surficial Geol: Interbedded eolian veneer and glacio-lacustrine plain. (72O).
Broderick West	NTS (1:50,000) 72O10; 51°39'55"N, 106°56'40"W	Follow access laneway at Dahl farmhouse west parallel to irrigation canal. Turn north at road end and follow access laneway for 2 km which skirts field perimeter. Spring issues from small 30 cm diameter pool at base of tree. Pool is located just inside treed area about 10 m from grass perimeter of cultivated field. Flow 2 L min ⁻¹ . Contact Margaret and Randy Dahl 867-8081. Surficial Geol: Interbedded eolian veneer and glacio-lacustrine plain. (72O).
Buffalo Pound	NTS (1:50,000) 72I11; 50°33'30"N, 105°17'55"W	Spring located at Nicol Flats Historical Farmhouse on south end of Buffalo Pound. PVC pipe with cistern. About 100 m west of farmhouse on boardwalk. Public drinking water. Flow 40 L min ⁻¹ . Contact Sask Historical Parks Office. Surficial geology: Alluvial plain but recharge area is probably neighbouring Glacio-fluvial plain. (72I).
Dundurn	NTS (1:50,000) 72O15; 51°49'45"N, 106°39'35"W	Head 3.5 km east of Hwy 215 on Dundurn access road. Turn north at Camp Strathcona intersection. Spring located in treed wetland area next to road in the camp. Flow hundreds L min ⁻¹ . Contact Dundurn Base Commander. Surficial Geol: Eolian sand dunes. (72O).

APPENDIX (cont'd)
Location and Description of Springs

Spring	NTS MAP, Lat. Long (to nearest 5')	Directions/Site Description/Approximate Flow Rate/Surficial Geology (Map ID)
Beaver Creek Church Camp	NTS (1:50,000) 72O15; 51°58'20"N, 106°42'05"W	Follow access laneway at Salvation Army Camp about 1 km from Hwy 215 to deep gully about 300 m from Camp trailer. Spring located in small wetland about 100 m down the gully. Flow 10 L min ⁻¹ . Contact Salvation Army Major Frazer Regina 757-1631. Surficial Geol: Eolian sand dunes. (72O)
Delmas	NTS (1:50,000) 73C15; 52°56'50"N, 108°37'05"W	Turn North on first grid road 1 km after Delmas on Hwy 16. Spring located in deep gully 100m from farmhouse at end of road. Metal pipe at head of wetland area. Farmhouse drinking water. Flow 10 L min ⁻¹ . Contact Dick Metro Gabruck Box 1174 North Battleford 446-0758. Surficial Geology: Glacio-lacustrine delta. (73C)
Elkwater	NTS (1:50,000) 72E9; 49°38'20"N, 109°18'00"W	Follow Cypress Hill Prov park campground access road south. At intersection at top of bluff turn east on gravel road 0.5 km. Follow hiking trail approximately 0.5 km. Mitchell spring on left side of trail in forest. Protected by metal pipe with cistern and fence. Public drinking water. Flow 10 L min ⁻¹ . Contact Prov Park HQ, ALTA. Geol: Cypress Hills Fm., quartzite and chert gravel interbedded with sand silt and clay, locally a conglomerate with carbonate cement. (Geol Map of Saskatchewan, 1972).
Whitewood	NTS (1:250,000) 62L; 50°29'00"N, 102°15'30"W	Spring on Hwy 9 at base of Qu'Appelle River bluff exactly 16.7 km north of turnoff from Hwy 1 at Whitewood. Metal pipe with cistern 100 m from Hwy. Marked by road sign. Public drinking water. Flow 10 L min ⁻¹ . Surficial Geol: Morainal plain. Aquifer most probably a glacio-fluvial or lacustrine deposit beneath moraine. (62L,K)
Petrofka	NTS (1:50,000) 73B10; 52°39'40"N, 106°51'25"W	Hwy 12 turn east to Provincial Park Campsite at top of hill on east side of road after North Saskatchewan R. bridge. Metal pipe with cistern in campsite. Designated by sign. Public drinking water Contact Regional Park. Flow 20 L min ⁻¹ . Surficial Geol: Interbedded glacio-fluvial kames and eskers, glacio-lacustrine and morainal deposits. (73B).
Wolseley Town	NTS (1:50,000) 62L6; 50°25'15"N, 103°17'00"W	Springwater access at Wolseley road side stop next to information booth. Contact Wolseley Town Office 698-2477. Public drinking water. Flow hundreds L min ⁻¹ . Surficial Geol: Glacio-lacustrine plain and morainal drumlins. (62L,K)
Wolseley	NTS (1:50000) 62L6; 50°21'30"N, 103°17'15"W	From service station Hwy 1 at Wolseley turn north on first grid road 0.5 km after service station. Spring is located on east side of road exactly 6.65 km from Hwy 1, about 0.5 km from farmhouse. Spring issues from rubber pipe with concrete base beside road. Wet area in field adjacent to road designates location. Public drinking water and livestock. Contact Wolseley town office 698-2477. Flow 10 L min ⁻¹ . Surficial Geol: Glacio-lacustrine plain. Spring at S.E. perimeter of plain. (62L,K).

APPENDIX (cont'd)
Location and Description of Springs

Spring	NTS MAP; Lat. Long (to nearest 5')	Directions/Site Description/Approximate Flow Rate/Surficial Geology (Map ID)
Nokomis	NTS (1:50000) 72P11; 51°30'00"N, 105°10'10"W	Head west on Hwy 15 from Nokomis. Turn north on 4th Grid road for 3.5 km. At intersection turn east on grid road for 2 km and then north for 2.1 km. Cased well head in field with 4 wooden posts marking location. Used for livestock. Contact Lee Hawkes Box 163 Watrous Sk 946-2218. Flow hundreds L min ⁻¹ . Geology: Hatfield Valley aquifer. Bedrock Valley aquifer consisting of thick alluvial deposits on bedrock. Well several hundred meters deep. Recharge zone is not local. (72P). (Geol Map of Saskatchewan, 1972).
L. Diefenbaker	NTS (1:50000) 72J11; 50°40'35"N, 107°08'35"W	Turn off Hwy 1 at Herbert. Head north on grid road to Goultdown. Follow main grid road to Taggart Creek. Follow road 1.7 km after crossing Taggart Creek. Head east on access laneway past farmhouse. At end of laneway follow cart track past abandoned bldgs for 1.0 km to double fence. Follow valley south on foot. Spring is located halfway up second gully on east side and is marked by a wooden post. Used for livestock. Distinct H ₂ S odour. Contact D. Donald, Environment Canada, Regina 780-6723. Flow 5 L min ⁻¹ . Surficial Geol: Glacio-lacustrine plain and morainal plain. (72J).
Waldeck	NTS (1:50000) 72J5; 50°21'00"N, 107°37'40"W	Follow Hwy 1 to access laneway 3.4 km west of Waldeck on south side of Hwy. Turn east onto cart track beside irrigation canal for 1 km. Spring is located in shrub area at base of small bluff beside canal. Visible from Hwy 1. Used for watering livestock. Distinctive H ₂ S odour. Contact D. Donald, Environment Canada, Regina 780-6723. Flow 20 L min ⁻¹ . Surficial Geol: Interbedded morainal and thin eolian deposits. (72J).
B-Say-Tah	NTS (1:50000) 62L13; 50°47'45"N, 103°52'45"W	Hwy 10 turn north on Echo Valley Prov Park road. Head east on gravel road on south shore for exactly 0.7 km to road sign "Barlett Place" followed by telephone pole. Path next to telephone pole leads to spring in small wetland located in dense brush along Echo lake shoreline. Metal pipe. Extensive travertine deposits. Contact Don Waite, Environment Canada, Regina, 780-6438. Flow hundreds L min ⁻¹ . Surficial Geol: Alluvial plain and glacio-fluvial plain. (62L,K).
Oxbow	NTS (1:50000) 62E1; 49°04'30"N, 102°17'50"W	Head south on Hwy 9 to bridge crossing Souris River. Spring is located about 20 m from bridge on west side of Hwy and south shore of Souris R. Contact Harvey Wood Box 41 Alameda SK 486-4437. Flow 5 L min ⁻¹ . Surficial Geol: Alluvial plain in moraine but recharge zone is probably in glacio-fluvial plain. (62E,F).
Cheviot East	NTS (1:50000) 62L13; 52°02'15"N, 106°16'25"W	Turnoff Hwy 14 at Floral heading east for 12.6 km. Head south for 1.5 km on access laneway on east side of Cheviot lake to fence. Head east on cart track for 1.2 km. Spring located in wetland/pond on south side of cart track. Cased well hole inside pond. Pipe barely visible above water surface. Used for livestock watering. Contact Garnet Forrieter RR 6 Saskatoon. Flow hundreds L min ⁻¹ . Geol: Deep well. Recharge zone is probably not local. May be bedrock aquifer, minor tributary of Battleford and Tyner Valley Aquifers. (73B).

APPENDIX (cont'd)
Location and Description of Springs

Spring	NTS MAP, Lat, Long (to nearest 5")	Directions (Topo Map)/Site Description/Approximate Flow Rate/ Surficial Geology (Map ID)
Langham	NTS (1:50000) 73B6 and 73B7; 52°22'25"N, 107°00'15"W	Heading north on Hwy 5 turn north on grid road toward Langham Regional Park (map 73B7). At intersection head west for 1.6 km on access laneway and then south for 0.85 km to sign "Keep Out". Head west on cart track through field. Follow cart track which passes between abandoned farm bldgs (Map 73B6). Follow pasture which passes between the two forested areas. Trail to spring at indentation in forest on west side. Spring is about 50 m from edge of forest. Spring is marked by extensive travertine deposits. Flow 10 L min ⁻¹ . Contact Garth Van Der Kamp, National Hydrology Research Institute, Saskatoon 975-5721. Surficial Geol: Morainal deposit but recharge zone is probably neighbouring glacio-lacustrine delta and plain. (73B).
Big Muddy Cemetery	NTS (1:50000) 72H2; 49°01'40"N, 104°52'40"W	Heading south on Hwy 6 turn west on grid road for Big Muddy Valley. Access laneway south side of road opposite Burgess Ranch. Spring at base of cliff on east side of road below cemetery. Metal pipe. Used for watering livestock. Contact Burgess Ranch, Big Muddy Valley, SK. Flow 10 L min ⁻¹ . Surficial Geol: Interbedded bedrock (Ravenscrag Fm, interbedded sand silt clay and lignite) and morainal deposits. (72H) (Geol Map of Saskatchewan, 1972)
Big Muddy Village	NTS (1:50000) 72H2; 49°01'15"N, 104°52'25"W	Follow access laneway 1.4 km from turnoff at grid road to abandoned village of Big Muddy. Cross culvert and follow hiking trail up to trough past historical monument. Spring emits from small stone grotto in bushes 300 m from road. Used as private drinking water source. Contact Burgess Ranch, Big Muddy Valley, SK. Flow 20 L min ⁻¹ . Surficial Geol: Interbedded bedrock (Ravenscrag Fm, interbedded sand silt clay and lignite) and morainal deposits. (72H). (Geol Map of Saskatchewan, 1972).
Craven	NTS (1:50000) 72I10; 50°43'35"N, 105°52'10"W	Head 4 km north of Craven on Hwy 20. Walk across south wildlife refuge causeway in Valeport marsh to west shore of Last Mountain L. Head west on cart track on south side of gully up the slope past abandoned bldgs. Spring located at base of small bluff inside treed area near top of gully. Contact D. Donald Environment Canada, Regina 780-6723. Flow 20 L min ⁻¹ . Surficial Geol: Morainal deposit but recharge is probably neighbouring interbedded glacio-fluvial plain and thin morainal deposit. (72I).
Radisson	NTS (1:50000) 73B11; 52°30'50"N, 107°26'25"W	Heading west on Hwy 5 turn north for 2 km on grid road west side of Radisson Lake. Spring is on east side of road beside abandoned well shed about 50 m from road. Used as drinking water source. Contact G. Van Der Kamp National Hydrology Research Institute Saskatoon 975-5721. Flow 50 L min ⁻¹ . Surficial Geology: Glacio-lacustrine plain. (73B).

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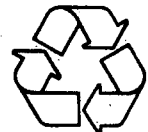


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