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NITRATES

IN

GROUNDWATER

: A REVIEW OF LITERATURE

PREPARED FOR THE

WESTERN CANADA FERTILIZER ASSOCIATION

by

J.L.Henry P.Ag. and W.A. Meneley P.Eng.

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EXECUTIVE SUMMARY

Concern about nitrate contamination of aquifers in other areas has led to questions about the future safety of Western Canadian groundwater supplies. The purpose of this study is to examine the scientific literature on nitrate in the environment and to relate it to possible problems from nitrogen (N) fertilizer use in Western Canada.

Nitrate is not toxic, but nitrite can cause methemoglobin formation which disrupts the oxygen transport system in the blood. In infants and ruminant animals, significant amounts of nitrate can be reduced to nitrite in the upper portion of the digestive tract . The nitrite can then be absorbed into the bloodstream and cause methemoglobinemia.

High nitrate levels in shallow wells in farm yards resulted in infant sickness and death as early as 1945 in Canada and the United States. Thus, the nitrate problem in wells was present before significant use of N fertilizers. The problem wells usually had hundreds of ppm of nitrate-N and were also bacteriologically contaminated. The contamination was from point sources; usually livestock wastes. Based on the early problems of well contamination , and in due consideration of adequate safety factors where health is concerned, the safe level of nitrates has set at 10 ppm nitrate-N in Canada and most other countries. In Britiain , a limit of 22.4 ppm nitrate-N was used for many years with no reported cases of methemoglobinemia.

In the past few decades intensive agricultural systems , involving application of fertilizer N at 150+ kg N/ha annually , or heavy applications of animal or poultry manure have been developed in Britain, Europe and high rainfall or irrigated areas of North America. Where these intensive agricultural systems are situated on surface aquifers a gradual increase in the nitrate content of the aquifers has been noted because of non-point contributions. In areas where the ground does not freeze in winter, most of the leaching of nitrate takes place in the winter months. As the nitrate-N level begins to approach 10 ppm there is concern about the safety of the water supply. There appear to be no documented cases of nitrate related health problems from aquifers with slightly elevated nitrate levels from non-point sources. However, the concern about slightly elevated nitrate levels remains and all possible nitrate sources must be critically examined.

Sources of nitrate include geologic nitrate, nitrate from soil organic matter, nitrate from animal or human wastes, nitrate from legumes or nitrate from fertilizers. All sources can add to the total nitrate load in soil profiles or groundwater . Each situation must be examined to determine the relative contribution of the various sources.

To avoid excess fertilizer derived nitrate in the soil profile or the aquifer beneath it, some principles of fertilizer and irrigation practice are evident . The main principle is to apply N fertilizer at rates which do not greatly exceed crop removal. Soil testing for nitrate, to improve accuracy of recommendations, is an important practice to prevent excess fertilization. A second basic principle is to avoid excess irrigation and to provide crop cover during times when precipitation is likely to exceed evaporation.

In Western Canada, non-point contamination of aquifers with nitrate from N fertilizers is unlikely except in areas where irrigated or intensive rainfed agriculture is practiced on top of surface aquifers . Such conditions occur in Manitoba and in British Columbia. Areas of British Columbia where the ground does not freeze in winter, warrant special attention to avoid groundwater contamination.

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PREFACE

This review of literature forms the first phase of a three phase project. The purpose of the project is to examine the issue of groundwater nitrate from the perspective of the agricultural industry of Western Canada , with a view to avoiding problems that have arisen in other parts of the world. While the major interest is fertilizer and the proper use of fertilizer, this review recognizes the complexities of the N cycle in nature and the fact that nitrate can originate from many sources. This first phase , presented herein, draws on the experience and knowledge about nitrate in the environment as gleaned from the scientific literature. Phase two will document the current status of nitrate in Western Canadian groundwater and the final phase will provide guidelines for the future .

This literature review draws on material that has been published in scientific literature over a period of more than one hundred years. The earlier works used Imperial units while modern references use Metric units. **In this review the units used are those of the original reference.** While this results in different units within one document, it avoids the cumbersome and odd numbers associated with conversion to common units throughout. It is hoped that it will be easier to read.

The exception to using the original units is for nitrate concentration. Lack of clarity with respect to nitrate or nitrate-N has caused confusion in data interpretation in the past. Throughout this review nitrate concentration is expressed as ppm nitrate-N. Where the original paper presented the data as ppm nitrate it has been converted to nitrate-N .

1. Introduction

In areas of high population pressure and intensive agricultural and industrial development, problems have arisen because of contamination of groundwater supplies. One of the contaminants that has received much attention is nitrate. To understand nitrate in the environment it is essential to understand the nitrogen (N) cycle. The processes involved in the N cycle are summarized in Figure 1.1.

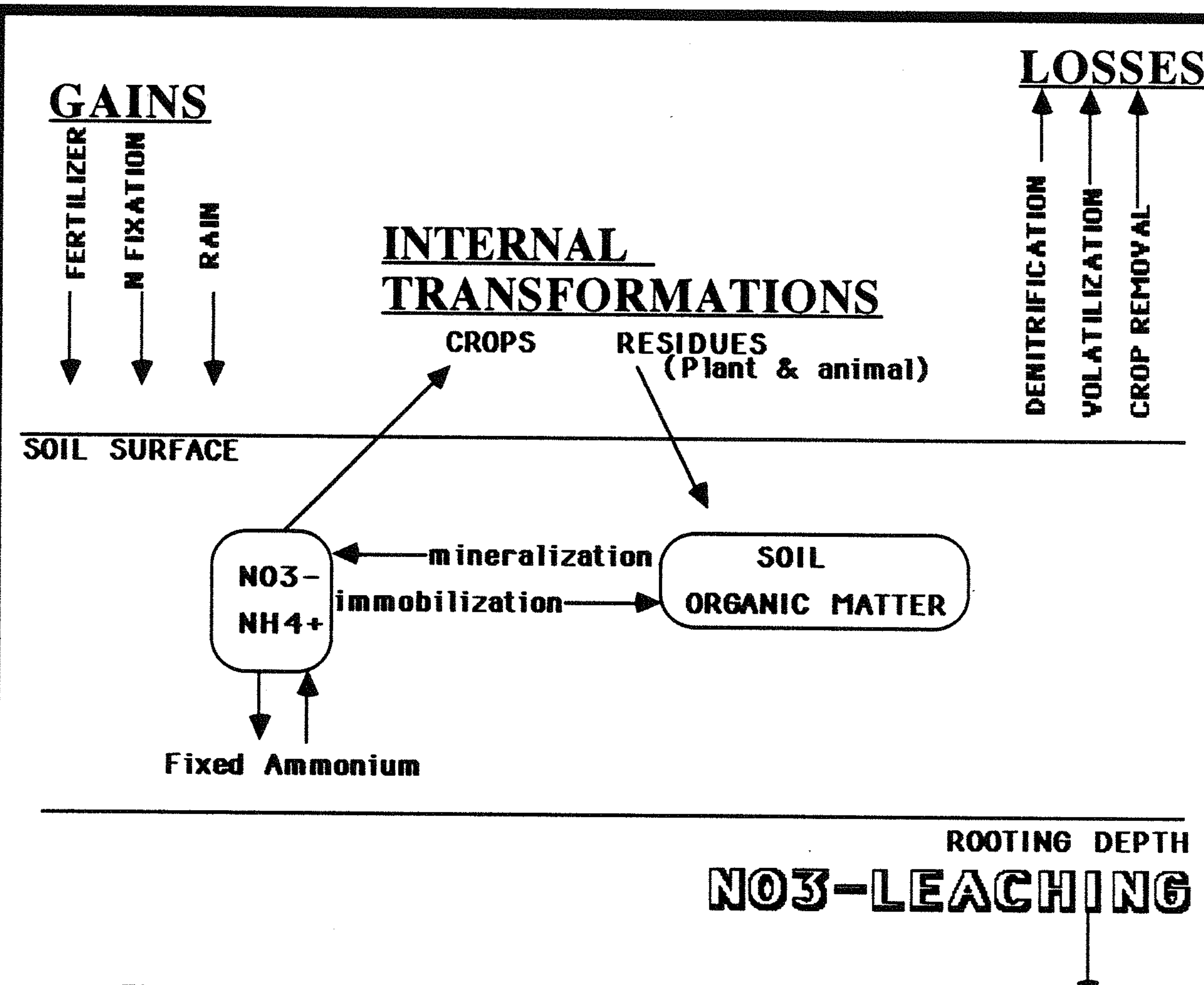

Figure 1.1 Nitrogen in the environment.

The presentation of the N cycle in Figure 1.1 is centered on the soil-plant system. The internal transformations involve uptake of nitrate or ammonium by plants, return of plant or animal residues to the soil organic pool and conversion of organic N to mineral N (mineralization). Immobilization is the conversion of mineral N to organic forms; it occurs most frequently when high C/N crop residues are added to soils. Straw from cereal crops has a high C/N ratio and incorporation of cereal straw into the soil results in immobilization of soil N.

Nitrate-N is readily transported by soil water while ammonium-N can be held on the exchange complex of soils and is therefore not subject to leaching losses. Ammonium can also be fixed by expandable clay minerals.

Additions of N to the soil-plant system can occur as a result of industrial fixation (fertilizers), by symbiotic fixation (legumes) or by non-symbiotic fixation. Lightning can break the strong ,triple N2 chemical bond and result in N additions to the soil-plant system through rain. Contaminants in air could also result in additions of N to the soil system from the atmosphere. However, the N added from rain usually amounts to only a few kg/ha/year and is not significant in the short term.

Losses to the soil -plant system can be by direct removal of harvested crops or animals , or by ammonium or nitrate losses. Ammonium can be lost due to volatilization and such losses will be to the atmosphere.

Nitrate can also be lost to the atmosphere by denitrification ; an anaerobic microbial process favored by excess moisture , warm temperatures, a source of energy and high nitrate levels. Nitrate is negatively charged and not held on the exchange complex. Thus, nitrate is free to move with the soil water and is subject to loss beneath the root zone by leaching. *It is this leaching of nitrate and its posssible accumulation in aquifers that prompted the preparation of this literature review.*

As this document will reveal, very high nitrate levels in well water from point source contamination have been documented for more than 40 years . However, in the last decade , examples of low level nitrate contamination of aquifers have occurred from non-point sources. These examples have been mostly in Britain , Europe or the United States. It is the purpose of this study to examine the conditions and practices where problems have arisen , with a view to avoiding the same problems in Western Canada.

2. Health Aspects of the Nitrate Question

2.1 Methemoglobinemia

Methemoglobinemia is the condition that results when too much hemoglobin in the blood is converted to methemoglobin. Hemoglobin is capable of attracting and releasing oxygen and is thus the oxygen transport system in blood. Methemoglobin forms when nitrites convert the iron of the hemoglobin to the ferric state (Magee 1982). Methemoglobin cannot transport oxygen. When about 10% of blood hemoglobin is converted to methemoglobin, oxygen transport is disrupted to the point that cyanosis occurs (Fraser and Chilvers 1981) . Methemoglobin levels greater than 50% are usually fatal (Magee 1982) . A detailed account of the biochemistry of methemoglobinemia has been prepared (Jaffe 1981).

While numerous articles have been published in the medical journals of recent decades , the fundamental effect of nitrites on methemoglobin formation and it's role in oxygen transport have been known for more than 100 years (Gamgee 1868). Gamgee was probably the first of many to describe the chocolate color of the blood resulting from methemoglobin formation. The understanding of the mechanisms at that time is shown by the following quote from Gamgee's paper of 1868:

" *Nitrites had, by my experiments , been shown to resemble in no way those agents which thrust oxygen out of the blood; on the other hand, it had been proved that the action of nitrites resulted in the locking up of the oxygen of the blood so as to render it irremovable by CO or by a vacuum. A consideration of all the facts which I had observed led me to believe that probably nitrites might actually link themselves to oxidized hemoglobin- a supposition which has been verified in the most ample manner.*"

Nitrate itself is relatively nontoxic (Magee 1982). It is when the nitrate is reduced to nitrite and absorbed into the blood stream that problems occur. The first reported problems with nitrate came from the medical administration of nitrate compounds. An excellent review of some of the medical cases has been published (Green *et al.* 1981). They described the work of Bennecke and Hoffman (1906) who reported the death of a 3-week old infant from methemoglobinemia caused by the use of bismuth subnitrate for obtaining X-ray images. Beck (1909) as reported by Green *et al.* (1981) reviewed cases of bismuth subnitrate poisoning up to that time. Green also described the work of Eusterman and Keith

(1929) who reported methemoglobinemia in a 32 year old man and a 47 year old woman who had been treated with ammonium nitrate as a diuretic.

2.2 Nitrate in Well Water

Excessive nitrate in groundwater has been considered as a health problem since Comly (1945) first described methemoglobinemia in babies associated with high nitrate well water in Iowa. It is interesting to note that the first discovery of the well water as the problem was because of the persistence of a father who did not accept the information from the medical profession and insisted on an analysis of the well water.

The original paper by Comly was quickly followed by similar reported cases from Saskatchewan (Goluboff 1948; Robertson and Riddell 1949), Manitoba and Ontario (Medovy *et al.* 1947), Minnesota (Bosch *et al.* 1950), Kansas (Faucett and Miller 1946), California (Shearer *et al.* 1972), Ohio (Waring 1949), Belgium (Ferrant 1946), Israel (Shuval and Gruner 1972), and Namibia (Super *et al.* 1981).

Analysis of water from Iowa wells <u>in 1939</u> found that 33.5% of dug wells, 21.6% of bored wells and 4.5% of drilled wells contained >10 ppm nitrate-N (Johnson *et al.* 1946).

In 1948 Robertson and Riddell determined the nitrate-N content of water samples from more than 2000 wells from different areas in rural Saskatchewan. They reported that 18% of the wells had 50 or more ppm nitrate. There is some uncertainty about the units in the Robertson and Riddell paper since they state that *10 ppm nitrate* is " a dangerous amount of nitrate ion". However, *10 ppm of nitrate- N* is the critical limit. Regardless of the interpretation of their data, *the 1948 survey clearly established nitrate problems in Saskatchewan farm wells before any significant use of N fertilizers.*

A review of the 1940's literature on nitrate contaminated drinking water was provided by (Walton 1951). Walton reported that 10 ppm of nitrate-N (45 ppm of nitrate) had been suggested as the permissible level but most of the cases of methemoglobinemia were when the nitrate content of the water was in excess of 40 ppm nitrate-N (Walton 1951). *The critical level of 10 ppm of nitrate-N has for the most part remained unchanged and is still accepted as the limit in most jurisdictions today.*

The exception to the 10 ppm nitrate-N rule appears to be Britain. Since 1972, public water supplies have not been used if they contain more than 22.5 ppm nitrate-N but medical authorities are informed when the nitrate level is above 11.3 ppm nitrate-N (Croll and Hayes 1988). No cases of methemoglobinemia have been found in the borderline level of 11.3 to 22.5 ppm nitrate-N (Croll and Hayes 1988). In fact, Croll and

Hayes (1988) report that no cases of methemoglobinemia have occurred in the UK since 1972.

In consideration of the different volume of water intake between infants and adults and between the tropics and Britain , Burden (1961) suggested the following limits on nitrate-N levels of drinking water:

:infant, England =24 ppm ; infant,tropics= 6 ppm

:adult , England =240 ppm ; adult, tropics = 45 ppm.

In Canada the current limit of nitrate in drinking water is 10 ppm nitrate-N (Guidelines for Canadian Drinking Water Quality, 4th Edition,1989 , Prepared by Federal-Provincial Subcommittee on Drinking Water of the Federal-Provincial Advisory Committee on Environmental and Occupational Health. Pub. by authority of Minister of National Health and Welfare).

WHY ONLY INFANTS ?

In most of the above literature the problem of methemoglobinemia was restricted to infants. In the original reference (Comly 1945) , it was reported that blood samples from the parents of the sick infants contained no abnormal level of methemoglobin despite the fact that they consumed the same well water as the infant.

In very young infants a pH greater than 4 is present in the gastric juices in the upper gastrointestinal tract . This allows the reduction of nitrate to nitrite and it's subsequent absorption into the blood stream where the methemoglobin forms (Cornblath and Hartmann 1948).

The common factor in well water problems reviewed above was that the wells were in rural areas, they were usually shallow, hand dug and almost always placed so that contamination from animal or human waste was easily visualized. *Thus, nitrate problems in water from rural wells was well established before the N fertilizer industry was a significant factor in North American agriculture.*

2.3 Nitrate in Food

Nitrate itself in food has not been a problem even though the content may be much higher than that in contaminated well water (Green *et al.* 1981). Problems can arise however when green leafy vegetables like spinach are high in nitrate and storage conditions allow the reduction of the nitrates to nitrite (Phillips 1968). Under these conditions the N can be introduced into the diet directly as nitrites and methemoglobinemia could result regardless of age. However , Phillips (1968) suggested that spinach be ommitted from the diet of infants less than three months , because with infants the reduction of nitrates to nitrites could occur in the digestive tract.

2.4 Nitrate in Livestock Feed and Water

Nitrate poisoning of animals from water is not common but it has occured in Saskatchewan (Campbell *et al.* 1954). Those researchers reported the death of 5 cattle at Maple Creek from well water containing 626 ppm of nitrate-N. They subsequently conducted experiments with sheep which showed a high degree of variability among animals in the rate of conversion of nitrate to nitrite. Thus, it has been difficult to derive firm guidelines for nitrate content of water used for livestock consumption.

A much more common occurrence is the nitrate poisoning of animals, particularly ruminants, resulting from consumption of feed high in nitrate . The earliest account of nitrate poisoning is usually credited to a case of cattle death in Kansas after consumption of corn stalks containing 18.8% potassium nitrate which is equivalent to 2.6% nitrate-N (Mayo 1895). At that very high concentration the crystals of potassium nitrate could be detected by visual inspection and by taste and the corn stalks would burn like a fuse. The corn had been grown on a plot of land that had been used as a hog yard for many years.

Oat hay or straw has been found to contain levels of nitrate that can be a problem in animal health. In January 1941 a loss of 13 head of cattle occurred on a ranch at Sceptre, Sask. The oat straw being fed contained 3.5% potassium nitrate (Davidson *et al.* 1941) . Campbell *et al.* (1954) listed four references dealing with high nitrate problems in oat hay or straw. There are reports of abortions related to sublethal nitrate doses associated with feedstuffs containing elevated levels of nitrate (Davison *et al.* 1964) .

The accumulation of nitrates in oat straw was studied at Swift Current and high soil N supply along with sudden drought conditions lead to high nitrate levels (Doughty and Warder 1942). Where drought was present throughout the growing season nitrate did not accumulate to the same extent . Doughty *et al.* (1954) compared nitrate contents of oats on adjacent stubble and summerfallow fields and found that the nitrate content of oats was always higher on summerfallow.

Silo gases such as nitrogen dioxide can be a serious health hazard and can occur even when the nitrate content of the silage is not high. In Minnesota , 42% of silos investigated were found to have hazardous levels of nitrogen dioxide (Scaletti *et al.* 1960) .

An excellent review of all aspects of nitrate accumulation in plants and nitrate poisoning in animals has been provided by Wright and Davison (1964) .

2.5 Nitrate and Gastric Cancer

There is a considerable and controversial medical literature surrounding various N compounds found in food (nitrates, nitrites, nitrosamines and other N-nitroso compounds) and their possible role in human cancer. A complete review of that literature is beyond the scope of this document, but summary statements will be provided. Fraser and Chilvers (1981) stated " at present there is too little scientific evidence to justify firm conclusions about the safety of any concentration of nitrate with regard to carcinogenic risk". As well, Magee (1982) stated " there is some very controversial evidence that nitrites are carcinogenic in rats , but this is certainly not established".

3. Geologic (Natural) Nitrate Sources

3.1 Natural (Mineable) Nitrate Deposits

In certain environments, nitrate compounds can accumulate as a natural phenomenon. Indeed, the mining of natural sodium nitrate deposits was the beginning of the fertilizer industry in the early and mid 1800s. Between 1810 and 1812 several nitrate refineries were built in the Terapaca region of Chile. In these refineries, pulverized caliche was boiled in water dissolving the nitrate which then settled out as the liquid cooled (O'Brien 1982). By the 1830s chemical fertilizer use in European agriculture had increased to the point where Chilean nitrate was a useful return cargo for ships sailing to Europe. The comprehensive work of O'Brien (1982) has described the Chilean nitrate industry in some detail .

The origin of the Chilean nitrate deposits has been examined (Mueller 1968). He demonstrated that all of the workable nitrate deposits were situated in areas with less than 10 mm annual precipitation and high evaporation potential. He described the concentration process for nitrate as a gradual concentration and precipitation of nitrate and other salts by capillary action and evaporation.

During the First World War nitrate was used extensively in the munitions industry. When supplies of nitrate from Chile were endangered, the United States Geological Survey was instructed to investigate occurrences of natural nitrate in the continental United States. Investigations in many states were conducted over almost two decades. This work was collated and published as a United States Geologic Survey Bulletin (Mansfield and Boardman 1932). In that work, the existence of natural deposits of saltpeter (potassium or sodium nitrate) was documented in a number of regions including relatively humid states such as Pennsylvania, Tennessee and Alabama. However, occurrences were more numerous in the arid and semi-arid parts of the country and California was considered to have the greatest potential for usable supplies of natural nitrate. In this comprehensive document Mansfield and Boardman identified the occurrence of nitrate deposits in Alabama, Arizona, Arkansas, California, Colorado, Idaho, Indiana, Kentucky, Missouri, Montana, Nevada, New Mexico, North Carolina, Ohio, Oregon, Pennsylvania, Tennessee, Texas, Utah, Virginia, Washington, West Virginia and Wyoming. They described the nitrate deposits as being either cave deposits, caliche deposits or playa deposits. The cave deposits were surface or near surface accumulations formed as coatings on rock walls or fillings of crevices. Caliche deposits were confined to arid regions and form blankets a few inches thick and about a foot below the surface. Playa deposits consist of nitrate concentrations in the clay just under the dry surface of playa lakes.

3.2 Nitrate and Nitrate Precursors (Ammonium) in Rocks.

One of the earliest accounts of N compounds of rocks came from workers at the famous Rothamsted experimental station in England (Hall and Miller 1908). They reported small but significant quantities of both nitrate and ammonium in rock materials at depths from 10 to more than 1200 feet.

In the state of Georgia in 1952 significant soluble N compounds were found in water samples in unpolluted mountain streams at elevations well above human habitation (Ingols and Navarre 1952). They attributed these N compounds in the water as having come from leaching of soluble N compounds from granite during weathering .

In Wisconsin, analysis of 210 limestone samples from quarries revealed 10 samples with greater than 10 ppm nitrate-N and 65 samples containing from 2.6 to 10 ppm nitrate-N (Chalk and Keeney 1971).

The presence of fixed ammonium in rocks provides a possible precursor to nitrate in the environment. Early accounts of fixed ammonium in rocks and in soils were by Stevenson and coworkers (Stevenson 1959; Stevenson *et al.* 1958). They obtained samples from the states of Illinois, New Hampshire and Vermont and found approximately 300 to 400 ppm of fixed ammonium-N in shale samples and approximately 5 to 25 ppm of fixed ammonium-N in granite rocks (Stevenson 1959).

Sedimentary rocks by their very nature are more likely to contain significant nitrate or nitrate precursors than are igneous rocks. An early account of very high surface nitrate content referred to as salt slicks was associated with Cretaceous shales in Utah (Stewart and Peterson 1917). In their study of "nitre spots" they described areas of barren land as being associated with the presence of high concentrations of soluble salts, including nitrates. The "nitre spots" were always characterized by a brown color due to the organic material associated with the deposit. They found the "nitre spots" in virgin as well as cultivated soils.

The San Joaquin Valley of California is an area of very intensive agriculture and high fertilizer use. Nitrate problems in groundwater have led to numerous studies to determine the sources of nitrate. The geological contribution of nitrate to the San Joaquin Valley has been substantial and has been carefully documented (Sullivan *et al.* 1979 and Strathouse *et al.* 1980). On the western side of the San Joaquin Valley the geologic formations include shale and mud flows high in nitrate whereas the east side of the valley contains a greater percentage of granite formations and much less nitrate (Sullivan *et al.* 1979). An equation has been developed to predict the nitrate-N of soils based on the geologic formations and sediment conditions (Sullivan *et al.* 1979) .

It was also found that within the San Joaquin valley there were important differences in the types of sedimentary rock (Strathouse *et al.* 1980). In one basin they found shales or fine-grained mud rocks which contained considerable organic debris which provided a source of N. In other basins the sedimentary rocks were chiefly coarse sandstones and sandy shales which did not contain appreciable quantities of organic matter or clay minerals. The workers concluded that the extremely high N concentrations in sediments derived from the Cantua Creek Basin leading in to the San Joaquin Valley had contributed geologic N directly to the alluvial soils on the western San Joaquin Valley (Strathouse *et al.* 1980).

A detailed literature summary of geologic N was provided by Sullivan *et al.* (1979) . The following summary statement is taken directly from that work. "*Sedimentary rocks contain a significantly higher quantity of N than igneous rocks. However, igneous rocks comprise most of the lithosphere (95%), thus contain most of the N , but are only exposed at 25% of the earth's surface. Sedimentary rocks, on the other hand, comprise only 5% of the lithosphere's volume but are exposed over 75% of the earth's surface. As a result, sedimentary rocks are more readily available, upon weathering and erosion, to contribute N into water and depositional environments.*" (An original reference has been deleted from the above quotation.)

More recently, elevated nitrate levels located at depths between 5 and 20 metres below ground surface have been found in the eastern Mojave Desert of California (Marrett *et al.* 1990). The nitrate concentrations were in the range of 20 to 60 ppm nitrate-N in a saturation extract but at one site were in excess of 200 ppm nitrate-N . They concluded that the localized concentrations of soil nitrate were Pleistocene relics.

Investigations surrounding coal mine spoils have resulted in new information which indicates that the nitrate may have its origin in ammonium compounds present in Cretaceous and Paleocene shales. In North Dakota and eastern Montana it has been reported that ,beginning at a depth of 10 metres , approximately 200 kg/ha of exchangeable ammonium-N were present for each metre of depth in the soft shale of Paleocene age (Power *et al.* 1974). It was also found that when these shale samples were incubated the exchangeable ammonium was rapidly nitrified. They concluded that the nitrate in lignite beds used as domestic water supplies had its origin in the exchangeable ammonium. These lignite beds contain water with 20 to 100 ppm of nitrate-N.

In northwestern Colorado about 1000 ppm of total N was found in shale, vegetated mine spoil and associated soil (Reeder and Berg 1977). However, in contrast to the work of Power *et al.* (1974) the Colorado workers did not find evidence of net N mineralization in shale samples and only small quantities of nitrate-N accumulated upon incubation of fresh mine spoil. However, significant mineralization was found in vegetated mine spoil and soil (Reeder and Berg 1977). It should be noted that the shale and fresh mine spoil samples were moderately saline.

Enclaves of high nitrate have been found in weathered till in southern Alberta (Hendry *et al.* 1984). Depth profiles of N showed bulges of nitrate and very low ammonium in the weathered till but no nitrate and high (about 30 ppm) ammonium-N in the unweathered till. They concluded that the enclaves of high nitrate found in the weathered till resulted from nitrification of the exchangeable ammonium present in the unweathered till.

3.3 Subsoil Nitrates in Virgin Soil Conditions

A region of loess containing nitrate has been reported in central and southern Nebraska (Boyce *et al.* 1976). They found a bulge of nitrate at depths of 10 to 15 metres with concentrations up to 40 to 50 ppm of nitrate -N. These bulges of nitrate were found under upland conditions but were missing under rough broken land such as canyons and steeply rolling sites. Sampling adjacent native range and irrigated corn for nitrate-N and moisture confirmed the leaching of the nitrate to greater depths under irrigation. They attributed the lack of nitrate under the rough broken areas to leaching from the water that collects in such areas. They suggested nitrification from organic matter or release and subsequent nitrification of fixed ammonium as possible sources for the geologic N.

In Runnels County, Texas, the average nitrate-N concentration of 230 groundwater samples was 56 ppm . These contaminated waters were not restricted to aquifers beneath areas of concentrated animal wastes but were also found in pastures and cultivated fields (Kreitler and Jones 1975). This contaminated water occured in a dryland area with little N fertilizer use. They concluded that dryland farming since 1900 resulted in oxidation of organic N to nitrate. During the period from 1900 to 1950 , nitrate was leached below the root zone but not to the water table. After the drought in the early 1950s, extensive terracing to improve soil moisture retention raised the water table to approximately six metres and leached the nitrate into the groundwater. Tritium dates suggested that the groundwater was less than 20 years old (Kreitler and Jones 1975).

3.4 Geologic Sources for Nitrate in Western Canada

The Western Plains have been subjected to several episodes of continental glaciation which have resulted in the deposition of glacial till, glaciolacustrine sediments and glaciofluvial sediments which form the parent materials for the present day soils. These parent materials contain N , primarily as ammonium which replaces potassium in silicate minerals and rarely as soluble ammonium salts (Faure 1986). The average concentration of N in terrestrial rocks is summarized in Table 3.4.1. It is evident that coal , shale and sandstone will be the dominant geologic sources of N in the Western plains in those areas where the parent materials are composed predominantly of Cretaceous and Tertiary sandstone, shale and coal sequences or glacial deposits derived by glacial erosion of those sources. This is consistent with the findings of Hendry *et al.* (1984) in southern Alberta.

Table 3.4.1 Average concentration of N in terrestrial rocks and minerals . (Modified from (Wlotzka 1972))

Rocks and Minerals	N ,ppm	Rocks and Minerals	N ,ppm
Muscovite	68	Andesite	87
Biotite	55	Basalt	30
K-Feldspar	23	Shale	602
Plagioclase	22	Greywacke	180
Horneblende	18	Sandstone	120
Quartz	13	Carbonate rocks	73
Pyroxene	11	Chert	210
Phonolites and trachytes	36	Modern Marine Sediments	1771
Gabbro &Diorite	11	Coal	2000-30,000
Ulramafic rock	14	Petroleum	100-20,000
Rhyolites and Obsidian	28	Natural Gas	Variable,up to 90% by volume
Granites and granodiorite	21		

With each episode of continental glaciation, rock materials from the north were transported by the glacier in a southerly direction. The constituent makeup of each sequence of glacial deposits reflects an inversion of the lithologic sequence present in the source area. Thus, the first continental glacier which advanced across Western Canada carried the weathered residual soils from the Canadian Shield and the uppermost Cretaceous and Tertiary sedimentary rocks from the Western Canada sedimentary basin and deposited them over the glacially eroded bedrock surface. Typically no " weathered zone" is evident at the bedrock surface in southern Saskatchewan and the regolith which is present at the contact between the PreCambrain rocks and the overlying rocks is absent for the most part in northern Saskatchewan. These weathered and presumably nitrate rich materials were incorporated and deposited as the lowermost glacial deposits in the southern part of Western Canada. Similarily, extensive development of soils occurred during each of the major interglacial intervals (Christiansen 1970; Klassen 1989) and these were eroded and incorporated into the glacial deposits of subsequent glaciations.

The source of glaciolacustrine and glaciofluvial materials associated with each episode of glaciation was from the ice sheet with a significant and perhaps dominant contribution of materials by meltwater transport from the mountain glaciers in the Rockies. Thus, glaciolacustrine sediments, particularly those associated with the later glaciations of Western Canada are probably low in N.

Both the distribution of late Cretaceous and Tertiary coal-bearing and organic sediments (Corkery 1987; Green 1972; Whitaker and Pearson 1972) and the process of continental glaciation will tend to concentrate geologic sources of N in the extreme southern plains of Manitoba, Saskatchewan and Alberta. From the information available it appears that the major source of geologic N will be Cretaceous and Tertiary non-marine sand and silt, particularly where these strata are rich in organic material and lignite coal.

The Dawson Creek district in British Columbia and the Peace River district in Alberta are mantled with glacial deposits which were derived principally from fine grained Lower Cretaceous marine sedimentary rocks and Upper Cretaceous silty to sandy non-marine sedimentary rocks. These rocks are similar to the non-marine silty to sandy rocks of southern Alberta and specific investigations will be required to determine whether significant geologic N may be present in those areas.

The potential geologic sources of nitrate in British Columbia are less readily generalized because the geology is much more complex and the sources of surficial materials are constrained by the mountainous topography (Claque 1989). Each of the major valleys in which agriculture is practised must be considered as a separate entity. Claque, (1989) summarized the bedrock and Quaternary geology of the Canadian Cordillera and the controls on Quaternary deposition and erosion. Alluvial valleys such as the Okanogan Valley and the lower Fraser Valley are filled with locally derived glaciofluvial and glaciolacustrine sediments which contain relatively low concentrations of N from the granitic, metamorphic and volcanic terrains from which they were derived. The climate, soil and rock permeability , and the high relative relief will all contribute to determining the significance of geologic sources of N in British Columbia.

4. Nitrate in Soil

4.1 Nitrate from Soil Organic Matter

The soil organic matter comprises the main storehouse of N in the soil-plant system. A soil with 5% organic matter will contain about 5,000 lbs/acre of N to a depth of 6 inches. The factors affecting mineralization of this large N reserve to the mobile nitrate form, and the amount of this mineralization have been the subject of investigations since the beginnings of scientific agriculture.

The classical drain gauge experiments at Rothamsted provided some of the first information on nitrate quantities that might be produced directly from the soil organic matter (Lawes *et al.* 1881a). A detailed account of the Rothamsted drain gauge experiments will be provided in Section 5. More recently Addiscott (1988b) utilized the information from the Rothamsted drain gauge experiments to determine the potential nitrate that might be derived from soil organic matter and be potentially available for leaching to the ground water. He reported that the soil organic matter derived nitrate-N was 45 kg/ha during the first 7 years of the experiments and that the half life of the organic matter providing the nitrate was 41 years. Based on his analysis of the Rothamsted work, Addiscott concluded that the N source for leaching was N that was remobilized by soil organisms in warm, moist soil during autumn. The major leaching loss took place in the cool, wet winter months. He also pointed out that even *in the 1870s the water draining from the gauges of unfertilized, bare fallow plots had a nitrate concentration exceeding the limit for potable water under the current European community regulations.* Addiscott (1988b) also commented that a policy of "set aside" in which land was left as bare fallow would be disastrous environmentally.

An early study of nitrate production under fallow was conducted in Montana (Buckman 1910). He showed that cultivated fallow could accumulate up to 70 ppm of nitrate-N in the first foot of soil and in one growing season.

Early work in Alberta established the high nitrification potential under fallow for the rich prairie soil at the University of Alberta in Edmonton (Wyatt *et al.* 1926). Even at that early date it was pointed out that some of the nitrates had been leached below the depth of sampling (40 in) especially under fallow conditions but they also showed that nitrates under crops showed very little fluctuation in the lower soil depths. In subsequent Alberta work the large nitrification potential when sod crops were ploughed up was determined (Newton *et al.* 1939). This study demonstrated that the nitrate content of the soil under wheat following alfalfa was increased for a period of three or four years after the alfalfa was ploughed up. Furthermore, fallow plots were always higher in moisture than crop plots at the end of each season and higher in nitrates in the latter half of each season.

At the University of Saskatchewan a study of the nitrate content of soil on experimental plots was conducted from 1928 through 1932 (Larson and Mitchell 1939). That data clearly showed the accumulation of nitrates under summerfallow, with the main accumulation taking place in June and July. They reported some leaching of N during periods of heavy precipitation but concluded that loss of N by leaching would be of little importance in the medium to heavy textured soils of the Saskatoon area.

Investigations in southwest Saskatchewan , conducted by the Swift Current Research Station , provided a valuable source of information on nitrate-N leaching in Brown soils. Data collected in the early 1950s showed amounts of nitrate-N up to 400 lbs/acre at a depth from 4 to 10 ft below surface for clay loam and clay soils (Doughty *et al.* 1954). They sampled adjacent virgin and cultivated fields and reported no significant nitrates below 4 ft under virgin conditions but large quantities under cultivated fields. The subsoil nitrate was typically present as a "bulge" beneath the crop rooting zone.

A follow-up study at Swift Current helped to further clarify the effects of wheat summerfallow rotations on subsoil nitrates (Campbell *et al.* 1975). After 35 years nitrate was still accumulating below the root zone in Sceptre clay but the nitrate bulge had disappeared from the Wood Mountain loam and the nitrate was uniformly distributed through the subsoil. This study confirmed that soil nitrate concentrations under virgin grassland conditions were very low.

In a subsequent study at Swift Current it was estimated that in the wet 1982 growing season at least 123 kg N/ha were leached from the top 2.4 metres of a fallowed soil (Campbell *et al.* 1984). Extrapolation based on long-term precipitation data suggested that about 20% of the N initially present in the topsoil of a Wood Mountain loam had been lost by leaching since it was broken for agriculture. *In that same study they determined that the application of fertilizer N and P at moderate rates actually reduced nitrate leaching* (Campbell *et al.* 1984). As part of the same long-term crop rotation study the Swift Current workers determined that nitrate-N production in fallow land in the period from spring thaw to freeze up was in excess of 100 kg N/ha (Campbell *et al.* 1983).

The effects of tillage system on N conservation or leaching was the subject of an interesting study recently in Nebraska (Lamb *et al.* 1985). The study was initiated in 1970 with a mixed native prairie sod and three separate tillage treatments were imposed on a winter wheat-fallow rotation. They found that the plough tillage system resulted in leaching of

100 kg/ha more nitrate-N than with no till or stubble mulch tillage systems. Since the experiments were established on virgin sod, they were able to determine the effects in the first few years of cultivation when large mineralization and large nitrate-N leaching potential was present.

The rapid loss of organic matter in the first few years after cultivation of native sod has also been documented in warm climates. In Israel, Reinhorn and Avnimelech (1974) found a very rapid release of N in the first few years after cultivation of soils not cultivated in the known past. The amount of N released in the first few years amounted to several thousand kg /ha of N .

In summary, N released from soil organic matter is a significant source of nitrate for possible leaching . The presence of bare fallow conditions can significantly increase the amount and the rate of nitrate -N lost below the root zone and potentially add to groundwater nitrate supplies.

4.2 Perennial Forage Crops

The native grassland that formed the basis of Chernozemic soils of the Canadian prairies was an N conserving system. The fibrous root sytem of the native prairie plants acted as a "sponge" to effectively and almost immediately absorb any nitrate produced by mineralization. Thus, under the natural grass condition nitrate is seldom present. This has been documented in Saskatchewan by Doughty *et al.* (1954), Campbell *et al.* (1975) and Henry (1975). Only a few ppm of nitrate-N was found under native range conditions to a depth of 2.8 metres in South Dakota (White and Moore 1972). Permanent grass swards have such a high absorption capacity for nitrate-N that even annual fertilization at relatively high rates can be absorbed. On a Fargo clay soil in North Dakota N applications up to 298 kg N/ha were applied to a brome grass sod annually for 15 years. At annual rates up to 74 kg N/ha little or no residual nitrate-N was found in the profile. At rates from 149 to 298 kg N/ha residual N was present but it was all contained within the upper metre of soil (Larson *et al.* 1971).

Thus, in the Palliser Triangle region of the Western Canadian prairies leaching of N below perennial grass sod crops would not be expected, even at the highest current recommended annual rates of application.

In other parts of the world grass leys are managed in a much more intensive manner. In England, a three year investigation was conducted into nitrate leaching from field plots and monolith lysimeters. The lysimeters employed N-15 labelled fertilizers (Barraclough *et al.* 1984). The results of the field and lysimeter data are summarized in Table 4.2.1.

Table 4.2.1 Leaching losses from a permanent grass sward in U.K.		
N Fert. Rate kg/ha/yr	3 Year Cumulative Nitrate-N Leaching as a % of Fertilizer N Applied	
	Field[1]	Lysimeter[2]
250	1.5	0.14
500	5.4	3.1
900	16.7	18.1

[1] (Barraclough *et al.* 1983)
[2] (Barraclough *et al.* 1984)

The data in Table 4.2.1 show the relatively small leaching component for rates of N application up to as much as 500 kg N/ha. The field and lysimeter results were almost identical. At rates greatly in excess of crop uptake , a significant leaching component was present.

Also in England , Dowdell and Webster (1980) found that 2 to 5% of fertilizer N applied to perennial rye grass swards was lost to leaching in the winter after application. In Finland , Jaakkola (1984) found much less nitrate leaching from a grass ley than from barley plots.

Further evidence of the nitrate absorbing capacity of grass crops was provided for a vertisol soil in Australia (Standley *et al.* 1990). That study demonstrated that perennial Rhodes grass was capable of absorbing residual N from previous cropping.

The very intensive grassland systems in use in the Netherlands can result in leaching loss of N. It was found that for cut grass crops, on both sandy and clay soils ,the amount of mineral N in the soil profile at the end of the growing season increased when rates of N fertilizer application exceeded 350 kg/ha/year (Steenvoorden *et al.* 1986). The highest nitrate concentrations were usually observed below grazed grasslands.

The question of grazed versus cut swards was investigated intensively in both New Zealand and the U.K. (Ball and Ryden 1984). It was reported that for cut swards with annual inputs of 200 to 400 kg N/ha about 55 to 80% of the N is recovered in the harvested herbage. However, in the U.K. annual leaching of 150 to 190 kg N/ha has been observed for grazed swards receiving 420 kg N/ha/year. *The grazing situation results in much more* *concentrated applications of N in the droppings of animals and subsequent inefficient recirculation of these nutrients.*

Except for intensively managed, and particularly grazed, grass leys, perennial grass stands will allow very little N movement below the root zone. However, when grass stands are plowed up to return to annual cropping, large leaching losses of nitrate are possible. Working with 3 to 7 year leys in England Cameron and Wild (1984) found that a total of 100 kg N/ha was leached over 2 winters following plowing. Late fall mineralization of N appeared to be a major contributing factor to these losses.

LEGUMES

In England, Low (1973) compared the nitrate moving beneath grass, white clover or uncropped lysimeters which received no N fertilizers. The experiments ran for 4.5 years. The nitrate-N in the drain water from pure grass sward was < 1 ppm ; from actively growing white clover it was 29 ppm ; and from bare soil it was 42 ppm. After the clover was removed, nitrate-N in the drain water averaged 34 ppm for a year .

In Idaho, Robbins and Carter (1980) found that 44 kg nitrate-N /ha/yr moved below the root zone of an alfalfa crop at concentrations from 3-15 ppm. In the growing season after the alfalfa was broken up and planted to beans , 85-96 kg/ha of nitrate-N moved below the root zone.

While alfalfa can fix large quantities of N and can be a source of nitrate to contaminate groundwater , it is also capable of absorbing large quantities of excess soil nitrate. In Illinois, it was found that alfalfa would be of help in absorbing excess N applied to previous crops (Schertz and Miller 1972). The N had been applied at rates up to 600 kg N/ha and large residual levels were present in the soil profile.

4.3 Animal Manures

Modern methods of animal production can result in significant concentration of nutrients and create the potential to concentrate nitrate in the soil which could eventually end up in the groundwater.

Work in Alberta has shown that manure applied at 70 tonnes/ha annually for 40 years did not cause an undesirable buildup of N, P or soluble salts in the soil (Sommerfeldt *et al.* 1973). In that same study, it was reported that the nitrate-N content of surface soil adjacent to feedlots was greater than away from the feedlots but the differences were generally small at depths beyond 1.5 metres. Their overall conclusion from the feedlot study was that levels of N (and P) were increased in the solum but that there was little evidence of extensive downward movement of the nutrients except under one feedlot that was located in a slight depression.

In Eastern Canada liquid dairy cattle manure was applied at rates up to almost 900 kg/ha/yr of N equivalent, on the sandy clay loam soil of the Central Experimental Farm at Ottawa. The experiment was carried on for five years. At the maximum manure rate about 250-300 kg/ha of mineral N (nitrate + ammonium + nitrite) was found in the 0-120 cm depth (Culley *et al.* 1981).

In California, the relative quantity of nitrate-N found below the root zone and available for potential leaching to the groundwater was in the order of livestock corrals, pastures used as manure disposal areas and cropland. They considered the unsaturated zone above the water table to the best indicator of the likely eventual contribution of nitrate to the water table. Livestock densities had only recently increased to high levels and there may not have been time for nitrate movement to the water table. (Adriano *et al.* 1971).

The role of denitrification in mitigating negative effects of nitrate compounds derived from livestock manures has also been the subject of investigation. In Vermont, it was found that more nitrate was lost by leaching when N was applied as ammonium nitrate than when applied as dairy manure (Kimble *et al.* 1972). Although soils amended with ammonium nitrate contained more nitrate in the profile, it was less susceptible to denitrification. The denitrification potential from livestock manure is related to the presence of organisms capable of denitrification and an energy source for the microorganisms.

In an intensively farmed Colorado valley containing many concentrated livestock feeding operations, more than 1000 kg/ha of nitrate-N was found to a depth of 6.7 metres beneath feedlots (Stewart *et al.* 1967). While the average value was high the amount of nitrate found under feedlots was extremely variable. Some feedlots contained corrals with extremely high levels of nitrate at shallow depths ,while others had none. Much higher bacteria counts were present under corrals , suggesting that a significant denitrification potential existed. It was concluded that much of the nitrate found under feedlots would probably never reach the water table.

4.4 Nitrogen Fertilizer and Moisture Effects

4.4.1 The Corn States

Over the past several decades corn production in the "corn states" of the United States has made liberal use of N fertilizer. This has resulted in numerous scientific publications concerning the residual nitrate-N present within or just beneath the rooting zone of corn. A cross-section of the many United States experiments with corn include studies in Wisconsin (Olsen *et al.* 1970), Missouri (Linville and Smith 1971), Iowa (Jolley and Pierre 1977), Virginia (Hahne *et al.* 1977), Minnesota (MacGregor *et al.* 1973) and Pennsylvania (Roth and Fox 1990).

In a three year experiment at Wisconsin , accumulation of nitrate was found at about the 60-120 cm depth when 336 kg N/ha was topdressed each year (Olsen *et al.* 1970). It was concluded that a major step to reduce the amount of nitrate passing through the soil profile,and eventually to the water table, would include limiting the rate of N fertilizer to approximately that required by the crop.

In Missouri, a twenty year experiment was conducted on a silt loam soil in which 134 kg N/ha was applied annually as ammonium nitrate to corn. At the conclusion of the experiment , there was approximately 200 kg N/ha as residual nitrate-N in the top 2.44 metres of the soil profile. However, at 2.74 and 3.05 metres the nitrate-N concentration was essentially the same as the control indicating no leaching beneath that depth (Linville and Smith 1971). In shorter term experiments (6 and 7 year) conducted on four soil types the residual N was small and there was no evidence of deep leaching for rates of 112 and 134 kg N/ha. However, when 168 or 224 kg N/ha was applied there were very large bulges of N at approximately 1.2-2.4 metres depth. The N content for these high rates was still above that of the control at a depth of 4 metres, suggesting deep leaching (Linville and Smith 1971). The Missouri study also found that fine textured soils were less susceptible to leaching losses than medium textured soils. They also concluded that N fertilizer rates should not exceed crop removal.

In Iowa, experiments of 17 and 15 years duration , located on two silty clay loam soils, showed significant accumulations of nitrate at the 1-2 metre depth but no evidence of leaching to greater depths (Jolley and Pierre 1977). The N rates used in these experiments were up to 134 kg N/ha on one soil and up to 168 kg N/ha on the second soil.

In Virginia, experiments conducted on fine sandy loam to clay loam soils for five years showed appreciable amounts of nitrate accumulation when the optimum N rates had been exceeded (Hahne *et al.* 1977) . The optimum N rate was 140 kg N/ha at one location and 168 kg N/ha at another location. They found that proper irrigation could actually reduce nitrate lost through leaching by stimulating increased corn production to enhance use of N so it was not available for leaching.

Studies on clay loam soils in Minnesota with N rates up to 268 kg N/ha indicated little nitrate remained below the drain tile depth after ten growing seasons (MacGregor *et al.* 1973). However, on untiled soil, considerable nitrate was present at depths of 6-7 metres after 11 growing seasons . After 15 years , appreciable nitrate occurred to at least the 10 metre depth. It was determined that the downward movement of nitrate was about 1.8 mm/day.

In Pennsylvania, N fertilizer applications at the economic optimum rates resulted in nitrate-N accumulations to the 100-120 cm depth that ranged from 41-138 kg N/ha (Roth and Fox 1990). In these same experiments, increased nitrate-N accumulation was found when manure had been applied in addition to the N fertilizer. The researchers suggested that residual soil nitrate accumulation should be considered in arriving at N fertilizer recommendations for corn.

An extensive study of soil and subsoil nitrate was conducted in Nebraska in the early 1970s (Seim *et al.* 1972). In irrigated medium to fine textured upland soils only small accumulations of mineral N were observed above the water table and most of this N was located in the upper part of the soil profile within the rooting range of crops. However, on irrigated sandy lands they found 700 lbs/acre of additional mineral N spread throughout the profile above the water table, in comparison to adjacent pasture lands which had received no fertilizer N. It was concluded that on irrigated sandy lands planted to corn and fertilized with N , some nitrate had passed through the soil profile to the water table. In the same study adjacent situations of known high nitrate content contained much higher levels of subsoil nitrate under pasture than under irrigated corn (Seim *et al.* 1972) . The source of N in this situation was the geologic N referred to earlier (see Section 3).

In Nebraska, a two year experiment with corn and N rates up to 336 kg N/ha included irrigation management and N time and method of application as variables (Smika and Watts 1978). They concluded that on fine sandy soils fertilizer N time and method of application and water management were key to controlling the nitrate movement below the root zone of an irrigated corn crop. When the N was applied as a single broadcast application very little nitrate remained in the soil at the end of the growing season. However, when the N was applied during the growing season through the sprinkler irrigation system the nitrate that remained at the end of the growing season was determined by the total amount of N applied and the water application rate. In an earlier study with irrigated corn in Nebraska, there was little indication of appreciable or rapid movement of nitrates below the corn rooting zone in deep loess soils , except for soils fertilized with N in excess of 200 kg N/ha (Herron *et al.* 1968).

In Colorado, 273 irrigated farm fields were found to contain an average of 173 kg /ha of nitrate-N to a depth of 90 cm (Ludwick *et al.* 1976). They also conducted a 4 year corn experiment which illustrated that nitrate could accumulate in a soil profile even when fertilizer N was applied at rates below that required for maximum production. However, for rates less 134 kg N/ha the nitrate in the soil profile was not above that of the check treatment.

SUMMARY STATEMENT OF CORN EXPERIMENTS

Most of the very extensive work with corn in the United States emphasizes the fact that to avoid excessive nitrate in the soil profile and the possibility of leaching of this excessive nitrate to the groundwater, the amount of N fertilizer applied should be approximately in balance with the amount of N being removed from the soil by the corn crop. There are also numerous accounts suggesting that measurement of residual nitrate in the profile would be a useful guideline to follow in deriving N fertilizer recommendations for corn. This point will be expanded upon in a subsequent section.

4.4.2 California Studies

The potential risk associated with the intensive agriculture practiced in the irrigated valleys of California has resulted in several studies concerning soil nitrate concentrations. It should be recalled that California was one of the areas in which significant quantities of geologic N have been found (see Section 3).

A number of studies were conducted in intensive California agriculture in which soil samples were obtained to the water table or to the 15 metre depth and N balances were determined. These studies include the work of (Adriano *et al.* 1972a; Adriano *et al.* 1972b; Lund *et al.* 1974; Pratt *et al.* 1972) and this work was susequently summarized in a technical bulletin by Pratt (1972). These studies have shown that the nitrate concentration of water in the unsaturated zone in open porous soils with N inputs of about 150 kg N/ha/year can be reasonably estimated . The estimate is made by considering the excess N in the soil calculated as N input minus crop removal and by the drainage volume. When N applications were much higher than 150 kg N/ha/year to porous soils or at lower rates in soils with textural discontinuities denitrification had to be assumed to allow a reasonable N balance calculation. The California workers calculated the transit time for water to move 30 metres in the unsaturated zone to vary from 12-49 years (Pratt *et al.* 1972)

4.4.3 Australia

An interesting study in Australia addressed the question of leaching of soluble nutrients like nitrates under different scenarios of irrigation or rainfall (McLay *et al.* 1991). They found that more rapid leaching would be expected if irrigation or heavy rainfall were received immediately after application of a soluble fertilizer material. Continuous rainfall or irrigation was likely to result in higher nutrient losses from surface applied materials than an equivalent amount applied intermittently. These varying transport mechanisms were related to preferential flow of water through natural soil micropores.

4.4.4 U.K., Europe and Scandanavia

Numerous studies have addressed the question of residual nitrate and nitrate loss in the soil profile in humid climates with intensive agriculture systems. Measurement of leaching losses of nitrate by drain flow measurements in the United Kingdom suggested that N fertilizer applications up to the recommended rates resulted in little influence of the amount applied on the amount leached (Vinten *et al.* 1991). They also found that incorporation of legume green manure in autumn increased the leaching of nitrate-N by 10-15 kg N/ha during the winter.

A comprehensive lysimeter study was conducted in the United Kingdom utilizing N-15 labelled N fertilizer to trace the fate of fertilizer applications and determine the role of fertilizer in nitrate leaching (Dowdell *et al.* 1984). This study involved N fertilizer additions at 0, 80 and 120 kg N/ha/yr. Within this range of applications nitrate-N concentrations in the drainage water beneath the lysimeters ranged from 12-27 ppm and the nitrate concentration did not differ significantly between N fertilizer treatments. The mean annual losses over the four year experiment from the lysimeters ranged from 65-83 kg N/ha. Over the four years of the experiment less than 7% of the N-15 labelled fertilizer was accounted for in the drainage water and this represented only 2-3% of the total N lost by leaching.

In the same lysimeter study in the U.K. 25% of the N-15 labelled fertilizer was found remaining in the roots and soil four years after application. Total recovery of applied labelled N was 81-87% and the remainder was assumed to be lost by denitrification (Dowdell and Webster 1984).

Work in Sweden found only moderate loss of fertilizer N due to leaching when 100 kg N/ha/year was applied but at the 200 kg N/ha/year rate leaching loss of 91 kg N/ha/year was recorded in a wet year (Bergstroem and Brink 1986). They emphasized the importance of applying N fertilizer in balance with crop needs and maintaining a growing crop in order to reduce leaching.

Studies of field sites on nine different farms in Denmark showed that the type of crop and history of application of farmyard manure was important in determining the nitrate concentration of the soil solution at the 80-90 cm soil depth (Nielsen and Jensen 1990). Only about 1% of the total variation in nitrate concentation in the soil solution was explained by the level of fertilizer N application . The three levels of N included in the study were described as 0, 0.5 and 1N. The 1N was the normal application rate considered optimum by the farmer and his advisor for the given site. Unfortunately, they did not indicate the actual rates applied but obviously their rates were well within agronomic feasibility.

In a recent simulation modeling study of N fertilizer recommendations in the Netherlands it is stated that economically optimum N fertilizer applications to arable crops were unlikely to accumulate soil mineral N except in the case of potatoes (Neeteson 1990).

CONCLUDING STATEMENT REGARDING FERTILIZERS

In summarizing a broad range of experimental work conducted over a wide variety of soil and climatic conditions in North America and Europe some principles of operation appear. The main principle is to maintain N fertilizer application rates in keeping with N removal by the crops in question. The second basic principle for reducing N leaching, regardless of fertilizer additions, is to avoid over irrigation and to maintain a crop cover during times when precipitation is likely to exceed evapotranspiration.

4.5 Septic Tanks

In areas not served by sewer systems, septic tanks and field drain systems are the method of disposal of human waste. The field drains normally consist of sand or gravel packs around a perforated pipe. The drain field must be separated from the water table by at least three feet (Walker *et al.* 1973a). The purpose of the unsaturated zone is to provide the biological "filter" to remove microorganisms before they reach the water table. Microorganisms can be transported long distances in the water table and can contaminate groundwater supplies.

The N in septic tanks is primarily in the ammonium form. Studies of septic tank effluent in Wisconsin discovered the formation of crusts at the interface of the gravel pack and the unsaturated soil (Walker *et al.* 1973a). These crusts reduced the flow and maintained anaerobic conditions within the saturated gravel pack. Therefore, in the gravel pack the N remained in the ammonium form. When the effluent moved into the unsaturated soil beneath the drain, nitrification commenced within two centimetres of the crust and essentially all of the ammonium was nitrified. In a separate case study where the seepage bed was beneath the water table, nitrification did not ocur but the ammonium was absorbed by the soil (Walker *et al.* 1973a).

Subsequent groundwater studies in Wisconsin found that in deep sandy soils, disposal of septic tank effluent added significant quantities of nitrate to the ground water (Walker *et al.* 1973b). Approximately 33 kg/ha of nitrate-N would be added to the ground water for each family of four. The ammonium was nitrified and with sandy soil and aerobic conditions, denitrification was not active. The Wisconsin study concluded that for deep sandy soils, dilution was the only mechanism to reduce the nitrate content of groundwater (Walker *et al.* 1973b).

In a soil with a fluctuating water table in Virginia, ammonium in septic tank effluent was nitrified and subsequently denitrified when a water table rise inundated the original nitrification zone (Reneau 1977; Reneau 1979).

In 1985, Yates (1985) summarized cases in Colorado,Delaware,New York and North Carolina where elevated nitrate levels were related to septic tank effluent. Yates (1985) quoted the U.S. E.P.A. guideline of one septic tank system per sixteen acres.

In summary, septic tank effluent is most likely to add to ground water nitrate problems where sandy soils rest on unconfined surface aquifers. This is the same scenario in which fertilizers or animal manures can be nonpoint sources of nitrate to groundwater. Limiting the density of septic tanks is seen as the main way to deal with the problem of nitrate contamination from septic tank effluent.

4.6 Urban Lawns and Turf

Turf grass on home lawns, golf courses, sports fields, parks and commercial areas often receives large doses of N fertilizer with little control of the amount applied and with significant possibilities for overwatering. The combination of excessive rates and overwatering provide a definite risk of adding nitrate to the groundwater.

A study of a simulated urban lawn situation in Sidney ,Nebraska showed well defined nitrate pulses beneath the turf rooting zone when ammonium nitrate was applied at rates from 100 to 240 kg N/ha (Exner *et al.* 1991). In the Nebraska study area the irrigation water contained enough nitrate to satisfy the N needs of the turf.

A Texas study demonstrated that slow release fertilizers such as ureaformaldehyde resulted in much lower leaching losses of nitrate than was the case with ammonium nitrate fertilizer (Brown *et al.* 1982). They concluded that regular moderate applications of slow release N fertilizers was the management option to provide sufficient N with minimal risk of leaching losses.

In Rhode Island,scheduling irrigation was shown to reduce leaching losses of fertilized treatments to a level equal to the control treatment (Morton *et al.* 1988). In the Rhode Island study overwatering by homeowners was seen as a major cause of potential nitrate additions to groundwater.

Work in Nassau county, Long Island showed that N fertilizers applied to various types of turfgrass was a source that could not be overlooked in attempts to reduce nonpoint source inputs of nitrate to aquifers (Porter 1980). In Nassau county the largest area of turfgrass was in home lawns.

4.7 The Nitrate Soil Test

The use of residual nitrate in the soil profile to improve N fertilizer recommendations has been the subject of considerable interest for decades and is currently receiving much attention. One of the earliest reports of the use of the nitrate soil test to predict N uptake by crops was in Montana (Burke 1925). In 1959 work in Iowa showed that 90% of the variations in N yield of oats on corn stubble could be accounted for by the soil content of nitrate-N to the 21 inch depth (White and Pesek 1959). Work in Wisconsin with tobacco and sweet corn also demonstrated the importance of soil nitrate levels in making N fertilizer recommendations(Peterson and Attoe 1965) . However, in the past, the major corn states made little use of the nitrate test because of concern about denitrification or leaching losses between the time of sampling and crop uptake of N.

The first major use of the nitrate test came after extensive work with barley in Manitoba (Soper and Huang 1963; Soper *et al.* 1971). *Since the mid 1960s soil testing laboratories in all three Canadian Prairie provinces have used the nitrate soil test as the primary tool for making N fertilizer recommendations.*

Research in Texas demonstrated that even under sub-tropical conditions soil profile nitrate was a very useful indicator of the N supply to grain sorghum and cotton (Hipp and Gerard 1971) and corn (Onken *et al.* 1985). In Washington State, sweet corn response to N fertilization could be predicted from soil nitrate levels (Roberts *et al.* 1980). More recently, work in Wisconsin has shown that soil profile nitrate significantly influenced corn response to applied N (Bundy and Malone 1988).

Despite the widespread evidence supporting the use of the nitrate soil test to improve N fertilizer recommendations , it has not been extensively used in the main corn states of the United States. However, more recently, the spring soil nitrate test has received renewed research attention (Binford *et al.* 1990; Davis and Blackmer 1990; Elhout and Blackmer 1990; Roth and Fox 1990) and mobile soil nitrate testing clinics have been established in Michigan (Vitosh *et al.* 1990) and rapid turnaround nitrate tests have been established in Ontario (Kachanoski 1991).

It is clear that the use of some form of the nitrate soil test to refine N fertilizer recommendations is an important step in improving N fertilizer use efficiency and reducing losses of N to leaching.

5. Nitrate in Drainage Water

5.1 The Classic Rothamsted Drainage Experiments

DRAIN GAUGES- UNMANURED AND UNCROPPED

At Rothamsted Experimental Station in England , classic drainage experiments were begun in the mid 1800s. The classic drain gauges, installed in 1870 , consisted of 1/1000 acre plots separated from their surroundings by brick and undermined to allow collection of the drainage water. Three such gauges were installed at depths of 20, 40 and 60 inches (Lawes *et al.* 1881a; Lawes *et al.* 1881b). The soil in the gauges was kept in a fallow condition and no fertilizer or manure of any kind was added to the gauges. Measurement of the quantity of drain water was made from the outset and measurement of the nitrate content of the drain water was begun in 1877.

Summaries of the nitrate leaching data from the drain gauges were provided by Miller (1906) and by Russell and Richards (1920). The data summary by Russell and Richards (1920) was used to construct Figure 5.1.1.

The fallow with no fertilizer or manure addition resulted in about 45 lbs N/acre/yr lost to leaching at the begining of the experiment and about 25 lbs N/acre /year at the end of the experiment 45 years later (Fig.4.1.1). *The drainage water from unamended soil in 1877 contained about twice the current EEC allowable nitrate concentration for drinking water.*

More recently, Addiscott (1988b) subjected the Rothamsted drain water data to more rigorous mathematical analysis. He calculated that the half-life of nitrate leakage from the 60 inch drain gauge was 41 years and concluded that the average nitrate leakage from the first seven years of the experiment was little different from estimates of current nitrate leakage from well fertilized winter wheat crops.

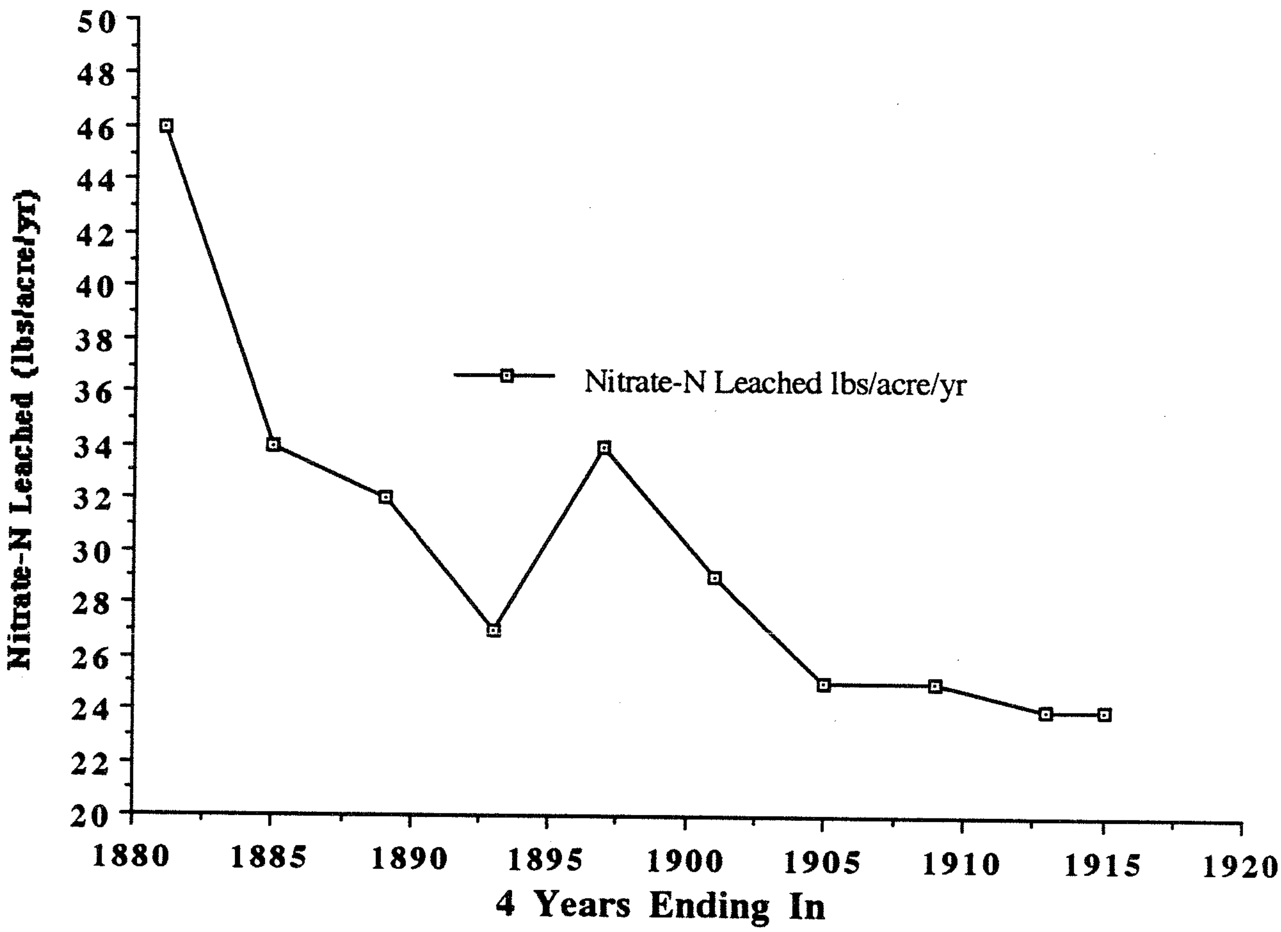

Figure 5.1.1 Nitrate leached from unmanured, uncropped soil at Rothamsted. (SOURCE: Russell and Richards, 1920)

NITRATE LEACHING FROM FERTILIZED AND CROPPED LAND

Broadbalk field at Rothamsted was supplied with drain tiles in 1849. In the summer months when a crop was actively growing drainage rarely took place . The drains usually began to run in October (Lawes *et al.* 1881b). Within Broadbalk field several separate plots were available with separate drain tiles and separate fertilizer treatments were applied for many years. The loss of nitrate to drainage for a selection of fertility treatments is provided in Table 5.1.1.

Table 5.1.1 Loss of nitrate to drainage as affected by fertilizer treatment.				
	.............lbs /acre applied /year...........			lbs/acre/yr
Plot No.	N	P2O5	K2O	Nitrate-N leached.
3,4,16	0	0	0	11
5	0	64	100	12
6	43	64	100	19
7	86	64	100	31
8	129	64	100	43
10	86	0	0	43
(Source; (Lawes *et al.* 1882))				

Further analysis of the many Rothamsted experiments has shown that the nitrate that is actually leached comes from mineralization of organic N after the crop is harvested . The leaching then takes place in the winter months when the land is bare (Addiscott and Powlson 1989; Addiscott 1988a). These studies included N-15 labelled fertilizer N which showed that the N applied to the crop in the spring was not directly leached.

5.2 Watershed Studies:Measurement of Springs and Stream Base Flow

Inorganic N levels were measured in springs and stream baseflow for different land use patterns in Ohio (Chichester 1976). Springs from a watershed planted to conventional corn with cumulative N application rates over 5 years of 869 kg/ha were reported to contain inorganic N levels of up to 50 ppm. In the same area spring flow below mixed woodland and pasture with no N fertilizer applied had about 2 ppm of inorganic N .

A study with corn in Iowa showed 5.8 ppm of nitrate-N in stream base flow from a watershed in which the corn had received 168 kg N/ha/yr and 21 ppm of nitrate-N when the corn had received fertilizer N at 448 kg N /ha/yr (Burwell *et al.* 1976). The firm conclusion from that study was to keep N fertilizer rates for corn in line with crop removal to avoid nitrate pollution of the groundwater.

A study of the important watersheds on very different agricultural land use patterns in Kentucky showed little effect of land use or fertilizer use on the nitrate content of streams (Thomas and Crutchfield 1974). However, none of the nitrate -N values exceeded 6 ppm and the fertilizer rates on corn were not excessive (about 100 kg N/ha/yr).

5.3 Tile Drain Studies in the U.S. Corn States, California and Ontario

Before reviewing the extensive literature from tile drain measurements it is useful to reflect on their meaning. A study in Kentucky found that in a completely tiled field only a small proportion (1/3 or less) of the total flow in the ditch came from tile effluent (Thomas and Barfield 1974). They also found that *the nitrate content in the tile flow was much higher than that in the ditch. Thus, they conclude that the use of tile effluent samples to monitor nitrate contributions to water supplies could be misleading if the entire drainage picture is not known. The reader should keep the Kentucky study in mind when reviewing the following findings which are all based on nitrate measurements of tile drain effluent.*

Work in Iowa found tile drains with nitrate-N content varying from 10 to 30 ppm nitrate-N under a corn , oats and soybean rotation which received only a total of 224 kg /ha of fertilizer N over a 5 year period (Baker *et al.* 1975). They found large variations in the nitrate content of the drainage water and concluded that the nitrate moves down the soil profile in waves or pulses. Their data show the danger inherent in drawing conclusions based only on a few grab samples from tile drains.

A subsequent study with a corn-oats rotation in Iowa related the nitrate content of drain tile water to the N fertilizer levels applied to crops (Baker and Johnson 1981). Where approximately 100 kg/ha of N fertilizer was applied every other year to the corn part of the rotation, the nitrate-N content of the drain water was 20 ppm and the annual loss of nitrate-N to the drain water was 27 kg/ha. Where about 250 kg/ha of N fertilizer was applied every other year to the corn part of the rotation the nitrate-N content of the drain water was 40 ppm and the annual loss of nitrate-N to the drain water was 48 kg/ha. Grab samples taken 3 years after the last differential fertilization still showed the effect of the higher rate of N fertilization.

Work with continous corn in Minnesota measured nitrate-N loss to tile drains of 19,25,59 and 120 kg/ha for annual application rates of 20,112, 224 and 448 kg/ha of fertilizer N for 3 years (Gast *et al.* 1978). Thus, at the recommended rate of 112 kg N /ha the nitrate-N losses to the tile drains were only slightly elevated due to fertilizer.

Recent data from Indiana corn production measured annual nitrate-N loss to tile drains of 42 kg/ha (Kladivko *et al.* 1991). The annual N applications to the corn were 285 kg/ha and the soil was a low organic matter, poorly structured silt loam .

On an irrigated fine sand soil in Nebraska , nitrate-N loss due to leaching varied from 12 to 146 kg/ha depending on the irrigation scheme and year (Hergert 1986). Hergert concluded that to reduce nitrate leaching it was necessary to maintain N fertilizer rates at the level of crop removal. Furthermore, *for sandy soils more precise irrigation scheduling was essential to prevent excessive downward flux.*

An early study in California showed large nitrate-N losses to tile drains and suggested reducing N rates (Johnston *et al.* 1965). A more recent study has related these losses to the soil characteristics (Devitt *et al.* 1976). In coarse textured profiles nitrate leached was directly related to the nitrate available for leaching and the amount of water passing through the soil. Where subsoil layers included fine textured material,conditions favoring increased denitrification were created and less nitrate was available for leaching.

In a clay soil in Ontario N losses to tile drains were about 15 kg/ha/yr under continuous corn fertilized at 112 kg N /ha/yr (Bolton *et al.* 1970). Under bluegrass sod the losses were less than 1 kg N /ha/yr. The predominant factor inflencing the magnitude of N loss under a particular cropping system was the amount of water passing through the soil profile.

In a more recent Ontario study losses of nitrate-N to drain tiles in mineral soils were from 4 to 64 kg/ha/yr and the larger losses were associated with N fertilizer additions greater than the recommended rates (Miller 1979). In the same study losses under organic soils were from 37 to 245 kg N/ha/yr.

5.4 Lysimeter Studies

A lysimeter N-15 balance study with continuous corn in Ohio indicated that about 30% of the 336 kg/ha N application as calcium nitrate was leached (Chichester and Smith 1978). The conditions for creating leaching losses were at a maximum in that Ohio study.

A lysimeter study in Kentucky found higher leaching losses of nitrate under a no tillage system than under conventional tillage (Tyler and Thomas 1977). Their study also confirmed that the leaching losses could take place in natural soil cracks and channels(i.e. macropores).

Work with a swelling clay soil in Texas also showed nitrate movement through large pores . The differential movement resulted in detection of leaching losses of nitrate at the125 cm depth after the first large rainstorm (Kissel *et al.* 1974).

6. Nitrate in Groundwater

6.1 Overview Documents

UNITED STATES

An overview of the groundwater nitrate issue in the U.S. has been provided by Madison and Brunett (1985) and by Hallberg (1988). In the document by Madison and Brunett 123,656 wells had been analyzed and 6.4% had nitrate-N values exceeding 10 ppm. An additional 13.2% of sampled wells had nitrate-N values above 3 ppm. A concentration of 3 ppm is usually used as the value which is indicative of additions related in some way to human activity. The data source used in that study was not a statistical sample but rather a compilation of data from a variety of sources with different original objectives.

The United States Environmental Protection Agency (EPA) recently completed a 5 year statistically valid program of sampling 564 community wells and 783 rural wells (United States 1990). This was the first comprehensive well survey conducted in the U.S. It showed that only 1.2 % of the community wells and 2.4 % of rural wells contain nitrate-N levels above 10 ppm .

BRITAIN

Overview documents dealing with nitrate levels in groundwater in Britain have been provided by Foster *et al.* (1982) and more recently by Croll and Hayes (1988). In Britain , 50% of potable groundwater comes from Cretaceous Chalk , 35% from Triassic Sandstone and the remainder from smaller aquifers (Foster *et al.* 1982). In parts of the country the major aquifers outcrop , but in other areas they are covered by by thick deposits of glacial drift.

In areas of aquifer outcrop, elevated nitrate levels were found (Croll and Hayes 1988). That same study provided data from typical wells under arable land for Chalk and Sandstone aquifers. The nitrate-N values of outcrop portions of the major aquifers were typically <10 ppm prior to 1960 and are typically >10 ppm since 1975. The area of contamination is the area of recharge and the area where well yields are the highest and where, nitrate aside, the water is of highest quality. However, when the aquifers move under clay cover the well yields are reduced, the water becomes anaerobic, troublesome levels of iron and manganese are present, and nitrate levels are low (Croll and Hayes 1988).

6.2 Contamination of Wells- (Point Source)

Contamination of wells by point sources such as septic tanks or livestock operations has been documented for decades. In section 2.2 (Nitrate in Well Water) of this review , nitrate contamination of wells was documented for a wide geographical area of the world. The documented cases were from Saskatchewan, Manitoba, Ontario, Iowa, Minnesota, Kansas, California, Ohio, Belgium, Israel and Namibia. The reader is referred to Section 2.2 for the detailed citations involved. Contaminated wells that were studied in the 1940s and 1950s , had been discovered for the most part because of medical problems that had arisen. The medical problems were mostly with infants but occassionally with ruminant animals.

There are numerous reports in the literature of point source contamination of wells leading to high nitrate levels. Only a few examples will be reported here. In Manitoba, Hedlin (1971) reported on work that had been completed in the Neepawa area of Manitoba in the early 1950s. That work clearly documented the contamination of a shallow surface aquifer from human and livestock activities in two separate farmsteads. The contamination extended only a short distance from the farmsteads. The work reported by Hedlin also examined groundwater nitrate in shallow surface aquifers under summerfallow, bromegrass, alfalfa-grass, grain and an old mink ranch slaughter site. Elevated nitrate values were found under the fallow and slaughter sites but not under the other land uses examined.

In Illinois , Walker (1969) also documented contaminated wells associated with feedlots and a mink ranch.

In a very recent water well survey in Montana , 5% of 1300 private well samples had more than 10 ppm nitrate-N (Bauder *et al.* 1991). In the Montana study it was considered that about 50% of the high nitrate wells received nitrate from point sources and the remaining 50% were as a result of long term summerfallowing.

6.3 Contamination of Aquifers (Non-Point Sources)

A large number of recent publications exist which examine the issue of nitrate content of aquifers over time, and the role of non-point contributions from N fertilizers and spreading of animal manures. The following discussion will summarize the current information on non-point contamination of aquifers with nitrate.

IOWA

In a recent review of the situation in Iowa , Hallberg (1988) stated "*While septic tanks, chemical spills and poor well construction cause local problems , they are no longer a significant factor. Nitrate problems have become regional in scope, resulting from the widespread application of fertilizer.*" The Iowa work included intensive investigations in the Big Spring Basin of northeastern Iowa. The Big Spring Basin is a 103 square mile area with a responsive hydrologic system and one in which discharge can be determined quantitatively. The basin is entirely agricultural, with no industries, landfills or municipal wastes to complicate the picture. In the 1950s and 1960s groundwater nitrate was 3 ppm nitrate-N but by 1983 it had escalated to 10.1 ppm. The increase in groundwater nitrate paralled the increase in N fertilizer use associated with increase in per acre rate and an increase in corn acreage. The association between fertilizer N use and groundwater nitrate was such that a significant reduction in fertilizer N use because of the government PIK program resulted in a sharp drop in groundwater nitrate (Hallberg 1988) .

In another Iowa study, municipal wells from across the state showed only a slight increase in nitrate from 1950 to 1979 (McDonald and Splinter 1982), and then only for wells less than 30 feet deep. However, the same study showed about 4.5 ppm nitrate-N increase in two river systems from the early to late 1970s.

NEBRASKA

A Nebraska study conducted in Merrick county, showed groundwater nitrate-N values of about 3 ppm in 1947-51 and about 12 ppm in 1974 (Spalding *et al.* 1978). Where contamination was present the nitrate levels were relatively homogenous , suggesting large diffuse non-point sources. That study concluded that the combination of irrigation and fertilizer N was responsible for the increase in nitrate.

In a study involving three Nebraska counties, and utilizing N15 measurements ,the primary source of contamination in most wells was concluded to be fertilizer (Gormly and Spalding 1979). The authors concluded that N-15 was a useful technique for irrigated coarse textured soils, with a very permeable unsaturated layer. Under such conditions isotopic fractionation is at a minimum. It was also concluded that in fine textured soils with shallow water tables the N-15 technique was unable to assist in identifying the source of nitrate (Gormly and Spalding 1979).

A very recent Nebraska study has examined fertilizer rates and found that a large portion of excess N application came from 14% of the area where N rates were ≥ 100 kg N/ha more than the recommended rate (Schepers *et al.* 1991). The authors also reported that " *Efforts on the part of the Central Platte Natural Resource District to reduce nitrate leaching involve a series of voluntary and mandatory N and water management practices. Producers on coarse textured soils are not permitted to apply N fertilizer in the fall and are limited to applications made after November 1 on other soils, and then only when an approved nitrification inhibitor is used*".

GEORGIA

A study of the surficial Claiborne aquifer located in Georgia found slightly elevated nitrate-N levels (1-1.5 ppm) when the aquifer was exposed and the land use was mostly irrigated agriculture (Beck *et al.* 1985). When the same aquifer outcropped in forested areas the nitrate-N level was < 0.25 ppm. It is interesting to note that the irrigated area in Georgia increased from about 150,000 acres in 1970 to over 1,000,000 acres in 1980 (Beck *et al.* 1985).

DELAWARE

In Kent and Sussex counties of Delaware ground water is the only source of water and most of it comes from surficial aquifers (Ritter and Chirnside 1984). Depending on the county, from 8% to 32% of wells were found to have >10 ppm nitrate-N , while nitrate-N levels under forested areas were < 1.5 ppm . Nitrate contaminated wells were in areas of intensive broiler chicken production or intensive crop production on sandy soils. Based on N-15 analyses it was concluded that poultry manure was the main source of nitrate but that septic tanks and fertilizers were also contributing factors. In the study average annual precipitation is 109 cm and about 50% of the precipitation contributes directly to groundwater recharge.

In another groundwater nitrate study in Delaware, an interesting negative correlation was found between nitrate and iron levels (Robertson 1979). The reducing environment which resulted in the high iron levels was considered to be the reason for low nitrate levels. The area of high iron had the highest percentage of cultivated land and numerous chicken farms but the aquifer had low nitrate values (Robertson 1979).

WISCONSIN

In irrigated sand plains of Wisconsin , where water is obtained from a surficial glacial outwash aquifer nitrate-N values in the aquifer exceeded 10 ppm in 15 of 33 irrigation wells (Saffigna and Keeney 1977). The area included 83,000 sprinkler irrigated acres growing potatoes, corn and vegetable crops. Even though the preciptitaion of the area exceeds evaporation, irrigation is required to maintain crop production on the very sandy soils. Under these conditions rapid changes could be expected. Indeed , in two wells the nitrate-N level dropped 50% between 1972 and 1974 . The reason for the decline was not known . However, the authors speculated that a cattle barn , whose use was discontinued, and which was located upgradient from the wells ,might have been a contributing factor to the decline (Saffigna and Keeney 1977).

ONTARIO

In the Alliston region of Ontario a shallow water table aquifer underlies a sand plain . The nitrate-N level exceeded 10 ppm in 68 of 164 groundwater samples (Hill 1982). The high nitrate levels were related to potatoe production with high rates of N fertilizer application. Beneath forest or permanent pasture , low nitrate values were found in the groundwater.

SUMMARY

In summary, non-point contamination of aquifers with nitrate from N fertilizers or spreading of animal manures occurs in humid or irrigated areas where sandy soils are underlain by sand or gravel deposits which form surface aquifers. The agronomy includes the use of high rates of N fertilizers or manures , usually well in excess of crop uptake.

6.4 Studies Using N-15 to Trace the Nitrate Source

The use of N-15 analyses of nitrate from water has been suggested as one means to aid in identifying the source of nitrate contamination. One of the early studies in this regard was that of Kohl *et al.* (1971) who reported delta N-15 (dN-15) for fertilizer N to be +3 and for soil N to be +15. On that basis the authors concluded that nitrate added to an Illinois surface water came mostly from fertilizer. Since that time the dN-15 values used by Kohl *et al.* (1971) for soil and fertilizer have both been questioned (Bremner and Tabatabai 1973; Freyer and Aly 1974) .

In recent years much more extensive use of the N-15 technique has provided some guidelines to aid in its interpretation. Based on papers by Flipse and Bonner (1985), Ritter and Chirnside (1984) and Gormly and Spalding (1979) it can be stated that dN-15 values for nitrate derived primarily from fertilizer would be generally < +3.5 ; while dN-15 values of nitrate derived largely from animal manures would be generally > +10. Isotopic fractionation due to denitrification of fertilizer derived nitrates would tend to slightly increase the dN-15 value to the +4 to +8 range. Thus, in high organic matter soils , or where denitrification is active it can be difficult to distinguish soil derived nitrate from fertilizer derived nitrate.

In situations where sandy soils overly surficial sand or gravel aquifers, the N-15 technique can be used to assist in identifying the nitrate source. This has been done in Nebraska to identify fertilizer as the major contributor (Gormly and Spalding 1979); in Delaware to identify poultry manure as the main contributor (Ritter and Chirnside 1984) ; in New York to determine that the nitrate source was not animal in origin (Flipse and Bonner 1985) , and in British Columbia to identify poultry manure as a major contributor to groundwater nitrate problems (Kohut *et al.* 1989) .

6.5 Denitrification in Groundwater

Denitrification in soils is recognized as a loss mechanism which can reduce the efficiency of applied fertilizer N for incresing crop growth. Thus, the conditions which favor denitrification reactions in soils have been the subject of numerous investigations, with the objective being to manage the crop production system in such a way as to reduce denitrification to a minimum value. Some of the works in the soils literature dealing with denitrification include Aulakh and Rennie (1987); Aulakh *et al.* (1982); Aulakh *et al.* (1983); Aulakh *et al.* (1984); Dowdell (1982); Dowdell and Webster (1984); and Malhi *et al.* (1990).

It is not the purpose of this document to review the very extensive soils literature dealing with denitrification but a summary statement will be provided. In soil systems, when an abundant supply of nitrate is available and when the soil moisture content exceeds field capacity at a time of year when the soil temperature is conducive to microbial growth, denitrification can be very large and very rapid. The soils most susceptible to denitrification are clay and heavy clay textures which can take a week or more to drain to the field capacity moisture content after a heavy rain or irrigation appplication.

The role of denitrification , in recent years, and in the setting of aquifers rather than soils, has shifted from a negative process which can reduce fertilizer use efficiency to a positive process which has the potential to prevent serious contamination of aquifers by nitrate. It is the purpose of this discussion to review the literature on denitrification in aquifers.

In North Carolina, nitrate contained in shallow groundwater did not move to deeper aquifers (Gilliam *et al.* 1974). It was concluded that denitrification was occurring although no direct measurements were made.

In Ontario, nitrate concentrations in shallow, surface aquifers decreased at greater depth in an aquifer or downgradient from a point source contamination (Egboka 1984). In that study it was concluded that denitrification was responsible for the reduction in nitrates, although no direct measurements were made.

In a subsequent Ontario study a slug of nitrate was directly injected in to a shallow surface aquifer and denitrification was measured directly (Trudell *et al.* 1986). The loss of nitrate was associated with a decline in dissolved oxygen and an increase in bicarbonate concentration. The stoichiometry of nitrate reduction and bicarbonate production was worked out in the study .

In a sand and gravel aquifer located on Cape Cod, Massachusetts , denitrification was found to be the predominant nitrate reducing mechanism (Smith and Duff 1988). The nitrate was essentially depleted in the centre of the contaminant plume 250 m downgradient from the contaminant source. In the Massachusetts study the aquifer had been continuously contaminated with sewage since 1936.

A study of a limestone aquifer in Britain concluded that denitrification was occurring within the aquifer (Foster *et al.* 1985). The aquifer outcrops in the west and moves under a confining claybed downdip towards the east. In the outcrop portion nitrate-N levels were considerably more tha 10 ppm , but in the confined portion of the aquifer the nitrate-N was less than 0.1 ppm. Foster *et al.* (1985) found evidence for the presence of bacteria capable of denitrification at depths up to 50 m. It was concluded that the low nitrate content of confined aquifers was due to denitrification which requires a supply of organic carbon substrate.

Foster *et al.* (1985) presumed that the organic carbon was being generated from geologic sources.

Another British study in a similar geologic environment came to quite different conclusions. In the Chalk aquifer Howard (1985) concluded that the lowering of nitrate concentration in the direction of flow was due primarily to mixing between waters of different origins and that denitrification was not a significant factor.

In the Chalk aquifer in Britain significant nitrate-reducing bacteria were found throughout the vadose zone (Whitelaw and Rees 1980). Denitrification was identified at a permanent grassland site but not at an arable site. The vadose zone was anaerobic at the grassland site but aerobic at the arable site.

THE IRON FACTOR

In a fundamental chemistry study Buresh and Moraghan (1976) found that nitrate reduction took place when high iron concentrations were accompanied by copper to catalyze the rection. They referred to earlier work which pointed out that iron and nitrate do not normally co-exist in soil (Pearsall and Mortimer 1939) .

In a Delaware surface aquifer, it was noted that one major area contained water of variable nitrate content and low iron concentrations ; and a second major area had high iron concentrations (> 2.0 ppm) and little detectable nitrate (Robertson 1979). The area of the aquifer with high iron was one with the highest percentage of cultivated land and with numerous chicken farms.

As described earlier (see section 6.1) it has been reported in Britain that troublesome levels of iron and manganese can be present when nitrate levels are low (Croll and Hayes 1988). Iron and manganeses would be expected to be in solution under anaerobic conditions .

The issue of iron and its role in determining the nitrate concentration of groundwater is one that must receive careful attention in any study of Western Canadian groundwater. Iron is a common constituent of groundwater in Western Canada. If the presence of iron in groundwater is indicative of a situation which will reduce or eliminate nitrate by denitrification, then many Western Canadian groundwater supplies will not be at risk of nitrate contamination.

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