
Agricultural contaminants in Quaternary aquitards: A review of occurrence and fate in North America

S.J. Rodvang · W.W. Simpkins

Abstract The intensity of agriculture has increased significantly during the past 30 years, resulting in increased detection of agricultural contaminants (nutrients, pesticides, salts, trace elements, and pathogens) in groundwater. Till, glaciolacustrine, and loess deposits of Quaternary age compose the most common surficial deposits underlying agricultural areas in North America. Quaternary aquitards generally contain higher concentrations of solid organic carbon (SOC, as much as 1.4%), dissolved organic carbon (DOC, as much as 205 mg/L), and reduced sulfur (as much as 0.9%) than do aquifers. Their potential to sorb pesticides increases with the percent of older SOC, because diagenesis increases K_{oc} . Denitrification consistently reduces nitrate to non-detectable levels in unweathered Quaternary aquitards. Organic carbon of Quaternary age is a more labile electron donor than carbon from shale clasts. Pyrite is a more labile electron donor than carbon in many instances. Unweathered Quaternary aquitards provide a high degree of protection for underlying aquifers, due to their large reserves of SOC and reduced sulfur for sorption and denitrification, combined with their typically low hydraulic conductivity. In contrast, agricultural contaminants are common in weathered Quaternary aquitards. Lower reserves of reduced sulfur and sorptive/labile organic carbon, and a higher bulk K due to fractures, limit their ability to attenuate nitrate and pesticides. Subsurface drainage, which is common in Quaternary aquitards because of high water tables, bypasses the attenuation capacity of Quaternary aquitards and facilitates the transport of agricultural contaminants to surface water.

Résumé L'agriculture s'est significativement accrue au cours des dernières 30 années, provoquant une détection plus fréquente dans les eaux souterraines de contaminants agricoles (engrais, pesticides, sels, éléments en traces et germes pathogènes). Les moraines, les formations glacio-lacustres et les loess d'âge quaternaire sont les dépôts superficiels les plus courants sur lesquels sont implantées les régions agricoles d'Amérique du Nord. Les imperméables quaternaires contiennent généralement des concentrations en carbone organique particulaire (COP), jusqu'à 1,4%, en carbone organique dissous, jusqu'à 205 mg/L et en soufre réduit, jusqu'à 0,9%, plus élevées que dans les aquifères. Leur potentiel à adsorber les pesticides augmente en même temps que le pourcentage en COP plus ancien, parce que la diagenèse fait croître K_{OC} . La dénitrification réduit logiquement les nitrates à des niveaux non détectables dans les imperméables quaternaires non altérés. Le carbone organique d'âge quaternaire est un donneur d'électrons plus labile que le carbone des débris schisteux. La pyrite est un donneur d'électrons plus labile que le carbone dans de nombreux cas. Les imperméables quaternaires non altérés constituent une protection très efficace pour les aquifères sous-jacents, du fait de leur importante réserve en COP et en soufre réduit, qui interviennent dans la sorption et la dénitrification, et du fait de leur conductivité hydraulique typiquement faible. Au contraire, les contaminants agricoles sont communs dans les imperméables quaternaires altérés. Leur plus faible réserve en soufre réduit et en carbone organique labile impliqué dans la sorption, ainsi qu'une conductivité globale plus forte due aux fractures, limite leur aptitude à atténuer les nitrates et les pesticides. Le drainage souterrain, qui est courant dans les imperméables quaternaires à cause des niveaux élevés des nappes, court-circuite la capacité d'atténuation des imperméables quaternaires et facilite le transport des contaminants agricoles vers les eaux de surface.

Received: 13 September 2000 / Accepted: 12 November 2000
Published online: 11 January 2001

© Springer-Verlag 2001

S.J. Rodvang (✉)
Groundwater Unit, Irrigation Branch, Alberta Agriculture,
Food and Rural Development, Agriculture Center, 100,
5401-1st Ave. S., Lethbridge, Alberta T1J 4V6, Canada
e-mail: joan.rodvang@gov.ab.ca
Fax: +1-403-3815765

W.W. Simpkins
Department of Geological and Atmospheric Sciences,
253 Science I, Iowa State University, Ames, Iowa 50011, USA

Resumen La intensidad de la agricultura ha aumentado de forma significativa durante los últimos 30 años, provocando una afección creciente de contaminantes de origen agrícola (tales como nutrientes, pesticidas, sales, elementos traza y patógenos) en las aguas subterráneas. Los depósitos cuaternarios de till, de origen glaciolacustre y de loess constituyen la mayor parte de los terrenos aprovechados desde el punto de vista agrícola en Norte-

américa. Los acuitardos cuaternarios contienen normalmente concentraciones más elevadas que los acuíferos en carbono orgánico sólido (COS, con hasta un 1,4%), carbono orgánico disuelto (COD, hasta 205 mg/L) y sulfuro reducido (hasta un 0,9%). Su potencial para absorber pesticidas aumenta con el porcentaje de COS más antiguo, ya que la diagénesis incrementa el coeficiente de partición, K_{oc} . El nitrato se reduce por desnitrificación hasta alcanzar valores no detectables en acuitardos cuaternarios no meteorizados. El carbono orgánico de la Edad Cuaternaria es un dador de electrones más lábil que el carbono presente en los clastos de esquisto. La pirita es un dador de electrones más lábil que el carbono en muchas circunstancias. Los acuitardos no meteorizados del Cuaternario proporcionan un alto grado de protección para los acuíferos subyacentes, puesto que tienen grandes reservas de COS y sulfuro reducido para sorción y desnitrificación, además de conductividades hidráulicas normalmente bajas. Por el contrario, los contaminantes agrícolas son más habituales en acuitardos meteorizados del Cuaternario, donde la capacidad para atenuar nitratos y pesticidas se ve limitada por unas reservas menores de sulfuro reducido y de carbono orgánico sorbible/lábil, así como por la elevada conductividad hidráulica promedio debido a las fracturas. El drenaje subsuperficial, que es común en los acuitardos cuaternarios que tienen niveles freáticos altos, evita la capacidad de atenuación propia de dichos acuitardos y facilita el transporte de los contaminantes de origen agrícola hacia las aguas superficiales.

Keywords groundwater · agricultural contamination · glacial till · nitrate · pesticide sorption

Introduction

The occurrence of groundwater contamination from routine crop and livestock production (herein termed agricultural contamination) is increasing worldwide, as a result of a significant increase in agricultural production since the 1960s and 1970s (Keeney 1986; Hallberg 1989). For example, between 1945 and 1993, the use of nitrogen in commercial fertilizer in the United States increased 20-fold, and phosphorus increased threefold (Puckett 1995). Agricultural and urban use of pesticides was rare before the 1960s, but has now become common practice, with more potent generations of pesticides entering the marketplace. Livestock production is increasingly concentrated in small geographic areas, with the resulting manure nitrogen, phosphorus, microorganisms, antibiotics, growth hormones, and salts stored and applied to adjacent lands. Agricultural contamination of groundwater usually results from routine applications on cropped fields, rather than from spills or other point sources. As such, it is classified as a non-point source (NPS). The diffuse, widespread nature of NPS contamination makes determination of sources, in addition to control and remediation, extremely difficult.

Most studies of agricultural contamination have focused on aquifers (e.g., Kolpin et al. 1998). However, aquitards of Quaternary age deposited by continental glaciation (herein termed Quaternary aquitards) are the most common surficial deposit in agricultural areas of Canada and the northern United States, as shown in Fig. 1a, b. They overlie many important aquifers, and sand layers within them often produce enough water for domestic wells (Meyboom 1967; Kross et al. 1990; Fenelon and Moore 1998). Groundwater-quality problems may just be emerging in these systems, because groundwater residence times in them are generally much longer than the duration of intensive agriculture. The following review presents the current state of knowledge regarding the occurrence and fate of some common agricultural contaminants in Quaternary aquitards in North America.

Characteristics of Quaternary Aquitards

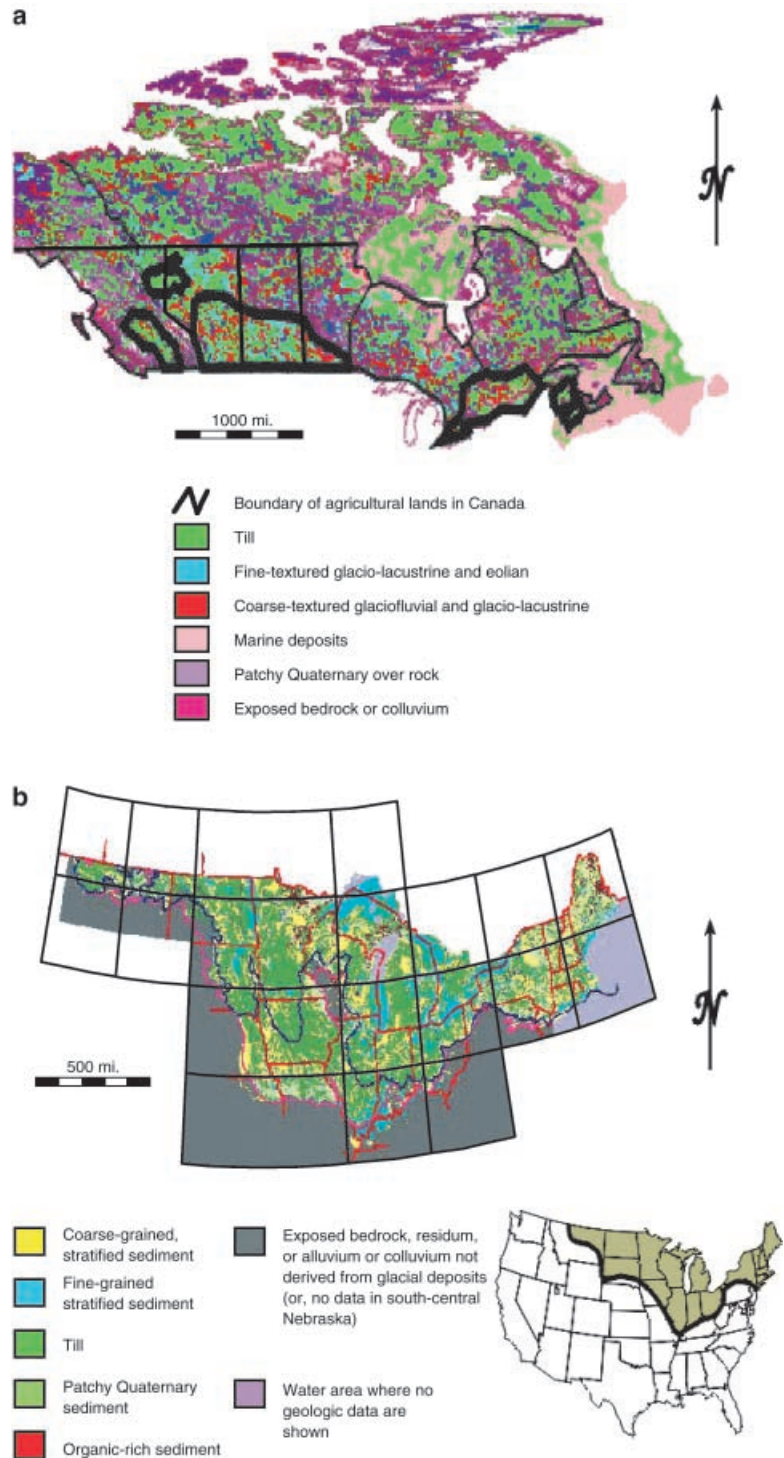
Extent and Thickness

Glacial deposits underlie about 13 million km² in North America (Stephenson et al. 1988; Fig. 1a, b). Till is a genetic term for sediment deposited directly by glacial ice without significant re-sorting (Dreimanis 1982). Till is a poorly sorted, poorly stratified mixture of sand, silt, and clay, and hence is often referred to by the descriptive term diamicton or diamict (Stephenson et al. 1988). Matrix textures commonly range from clay loam to sandy clay loam. Glaciolacustrine (lake) deposits are composed of silt and clay with some sand. They are well sorted, and may be stratified. Loess consists of silt with some sand, transported by wind from sparsely vegetated outwash plains.

Sixty percent of the Canadian interior plains is covered by till, 40% by glaciolacustrine deposits (predominantly clay), and less than 1% by outwash deposits (Meyboom 1967; Fig. 1a). The overall average thickness of till on the Canadian prairies is about 23 m, but the average thickness increases markedly from west to east (Meyboom 1967). Sequences of multiple till, glaciolacustrine, and loess deposits in the midwestern United States commonly range from less than 1 m to more than 300 m thick (Hallberg 1980). Glacial sequences in continental North America span an age range from Pre-Illinoian (>500 ka B.P.) to the late Wisconsinan, which ended about 10 ka B.P. Older units are often thinner because they have been subjected to erosion.

Land used for agricultural purposes occurs throughout the United States but is mainly restricted to the southern parts of Canada (Fig. 1a). In the area of the United States covered by continental glaciers, approximately 25% is planted to corn/soybeans, 25% is in mixed cattle and grain, 20% is in dairy, and 10% each is in livestock, horticulture, and small grains (Sommer and Hines 1991).

Fig. 1 Maps showing: **a** surficial geology of Canada, showing agricultural areas. Data from Fulton (1995). **b** Quaternary sediments in the glaciated United States east of the Rocky Mountains. Data from Soller (1992)



Hydraulic Properties and Groundwater Use

Fine-textured glacial deposits are considered aquitards because of low hydraulic conductivity (K) and storativity values. K of till and loess deposits ranges from 10^{-11} – 10^{-5} m/s, whereas K of lacustrine silt and clay ranges from 10^{-11} – 10^{-8} m/s (Freeze and Cherry 1979; Stephenson et al. 1988). By comparison, glacial outwash has K values of 10^{-7} – 10^{-3} m/s. Despite these low K values, many shallow domestic wells are completed in Qua-

ternary aquitards due to the expense of drilling to aquifers that are much deeper in many areas. Meyboom (1967) estimated that 60% of all farm water supplies in the prairie provinces of Canada are obtained from till, even though most of these shallow wells yield less than $30 \text{ m}^3/\text{d}$. Approximately 52% of domestic wells in southern and western Iowa are less than 15 m deep and are completed in “drift aquifers,” which consist of sandy zones within till deposits (Kross et al. 1990). Drift aqu-

fers are also common in other areas of the glaciated midwestern United States (e.g., Fenelon and Moore 1998).

Weathering and Fractures

The upper portions of Quaternary aquitards are weathered, which is the result of oxidation of minerals and organic carbon and subsequent accumulation or migration of weathering products (such as sulfate). Hendry et al. (1984, 1986) concluded that weathering occurred above the water table during the Altithermal period, when the water table declined significantly throughout North America. The weathered zone is generally referred to as "oxidized" because it is a brown color (i.e., hue of 5 or 10 YR and values >5 on the Munsell Chart) due to Fe-sesquioxide formation. The thickest weathered zones (as much as 25 m thick) occur in topographic highs, whereas weathered zones are often thin to absent in topographic lows (Eidem et al. 1999). Thinner aquitards may be weathered throughout their thickness, and weathered and unweathered zones of differing ages may alternate at a single location. The part of the till that is not weathered has been termed "unoxidized" or "reduced" by various researchers to reflect the weathering history and prevailing redox conditions. The terms "weathered" and "unweathered" are used in this paper to describe the two major zones. The boundary between the weathered and unweathered zones coincides or occurs in close proximity to the change from oxidized to reduced conditions and is sometimes called the "redoxcline" (Postma et al. 1991).

Fractures are a common feature in weathered zones of Quaternary aquitards, due to desiccation, unloading, glacial shear, neotectonics, mineral dissolution, or some combination of these processes (Ruland et al. 1991). Fractures increase the K of weathered zones (Keller et al. 1988; McKay and Fredericia 1995) and are widely recognized as the primary pathways for solute transport (McKay et al. 1993). Distance between fractures generally increases with depth. Solute transport is controlled by diffusion in some unweathered Quaternary aquitards, suggesting they are effectively unfractured (e.g., Keller et al. 1989; Remenda et al. 1996; Hendry and Wassenaar 1999). Diffusion of solutes into matrix blocks between fractures causes the transport of dissolved contaminants to be greatly retarded relative to advective flow through fractures, but transport rates are still much higher than in equivalent unfractured sediments. Colloid-sized contaminants (particles having a dimension of 1–1,000 nm in at least one direction) travel faster than non-reactive solutes, because they do not diffuse as readily into the clay matrix (e.g., McKay et al. 1993; Jorgensen et al. 1998). Colloids include clays, metal oxides, organic macromolecules, and bacteria.

Sulfur Content

Pyrite is a common constituent of unweathered Quaternary aquitards, particularly in till and glaciolacustrine deposits. Pyrite crystals have been observed in unweathered till in Britain (Klinck et al. 1996) and central Iowa (Simpkins

and Parkin 1993). Black shale clasts are the dominant source of pyrite in till from southwestern Ontario (Abbott 1987) and Saskatchewan (Keller et al. 1991). The majority of pyrite in weathered till from both the Canadian prairies (Van Stempvoort et al. 1994) and Ontario (Abbott 1987) has been oxidized to sulfate. Where leaching rates are not sufficient to remove sulfate, it is precipitated as gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and bassanite ($\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$) (Miller et al. 1989; Fortin et al. 1991). Gypsum crystals occur commonly in weathered till in Ontario (Abbott 1987) and on the Canadian prairies (Van Stempvoort et al. 1994).

Organic Carbon Content

Organic carbon is generally oxidized and lost by conversion to CO_2 gas in the weathered zone (Keller 1991) but is preserved in the unweathered zone because of anaerobic conditions; data are summarized in Table 1. Unweathered Quaternary aquitards contain high concentrations of solid organic carbon (SOC; Table 1). [The term SOC as used by Keller (1991) is nearly synonymous with the Particulate Organic Carbon (POC) used by Simpkins and Parkin (1993). We will use SOC to describe both types in this paper.] Wassenaar et al. (1990a) concluded that SOC in unweathered till at three sites in southern Alberta originated from Quaternary organic matter and Cretaceous-age coal clasts. Till in Iowa also contains SOC from Cretaceous shale clasts (Hallberg 1980). Allen-King et al. (1997) postulated that upper Devonian carbonaceous shale is a probable source of a significant proportion of the SOC in a till in southwestern Ontario.

SOC in the midwestern United States is often derived from Quaternary forests or paleosols. Late Wisconsinan till and underlying loess in central Iowa contains SOC from intact spruce logs and disseminated organic matter. The SOC ranges in age from 14–17 ka B.P. and was incorporated from a coniferous forest established on the loess when ice advanced from the north (Simpkins and Parkin 1993). Glaciolacustrine sediments contain variable amounts of organic carbon, depending on the biological productivity of the watershed.

Dissolved organic carbon (DOC) concentrations may be high in both weathered and unweathered Quaternary aquitards (Table 1). DOC in Alberta and Saskatchewan is derived from organic matter emplaced during deglaciation, with additional DOC in weathered till derived from the partial oxidation of SOC in coal and shale clasts (Wassenaar et al. 1990a; Keller 1991). Keller and Bacon (1998) observed a depletion of SOC from 0.55% at 10 m to 0.2% near the surface in a Quaternary aquitard in southern Saskatchewan that contains Cretaceous shale as the dominant form of carbon. The depletion is hypothesized to be the result of in situ oxidation over the last 12,000 years. High DOC concentrations (mostly humic and fulvic acids) in late Wisconsinan till and underlying loess in Iowa are derived from wood and disseminated organic material from a coniferous forest that was established on the loess (Simpkins and Parkin 1993; Parkin and Simpkins 1995).

Table 1 Concentrations of reduced sulfur, SOC, and DOC in till (mean value in parentheses)

Formation, age, and location			Reduced S (wt%)	SOC (wt%)	DOC (mg/L)
Weathered till	Late Wisconsinan (~12,000 to 19,000 years B.P.)	S Alberta ^{a, b}	≤0.01	0.04–0.75	9–205 (55)
		S Ontario ^c	≤0.01	0.05–0.2	<0.5
		Central Iowa, Dows Fm ^d	–	0.16–0.66 (0.3)	2–21 (8)
		SE Wisconsin, Oak Creek Fm	0.02	0.5	4.6
	Wisconsinan (~38,000 years B.P.)	Saskatchewan, Floral Fm ^b	≤0.01	0.35–0.44	–
Pre-Illinoian (>500,000 years B.P.)>	Central Iowa, Wolf Creek Fm ^d	–	0.00–0.06 (0.03)	2–7 (4)	
	NE Iowa, Wolf Creek Fm ^{e, f}	–	0.2–0.7	1.5–1.7	
Unweathered till	Late Wisconsinan (~12,000 to 19,000 years B.P.)	S Alberta ^{a, b}	0.35–0.37 (0.36)	0.24–1.28	4–113 (42)
		S Ontario ^c	0.03–0.4	0.05–0.2	<0.5
		SE Wisconsin, Oak Cr. Fm ^c	0.22–0.57	1.05	3.5
		Central Iowa, Dows Fm ^d	–	0.34–0.76 (0.6)	4–41 (18)
	Wisconsinan (~38,000 years B.P.)	Saskatchewan, Floral ^b Fm	0.27–0.35 (0.31)	0.46–0.7 (0.62)	–
		Saskatchewan, Warman Fm ^b	0.65–0.86 (0.75)	1.02–1.31 (1.16)	–
		Saskatchewan, Dundern Fm ^b	0.27–0.29 (0.28)	0.69–0.76 (0.73)	–
	Pre-Illinoian (>500,000 years B.P.)	Central Iowa, Wolf Creek Fm ^d	–	0.9–1.48 (1.16)	5–16 (8)
NE Iowa, Wolf Creek Fm ^{e, f}		–	0.39–1.07	6–12	
Borden and Alliston sand aquifers, oxidized, SW Ontario			–	0.02% ^g	Usually <3 ^h
Sand aquifer below the redoxcline, Denmark			0.043 ⁱ	–	–

^a Wassenaar et al. (1990a) and Rodvang et al. (1998)^b Van Stempvoort et al. (1994)^c Robertson et al. (1996)^d Johnson (1995)^e Moorman et al. (unpublished data)^f Simpkins (1989)^g Brown and Burris (1996)^h Wassenaar et al. (1990b)ⁱ Postma et al. (1991)**Table 2** Mean values for chemical parameters in weathered till and fine-textured glaciolacustrine sediments in southern Alberta, grouped by source of nitrate. (From Rodvang et al. 1998)

Chemical parameter	Source of nitrate		
	No nitrate (<i>n</i> =42)	Agricultural (<i>n</i> =40)	Geological (<i>n</i> =69)
Nitrate-N (mg/L)	0.1	32	164
N ₂ O (mg/L)	0.01	0.17	3.0
δ ¹⁸ O(H ₂ O) (‰)	–16.7	–16.4	–19.3
δ ¹⁵ N(NO ₃ -N) (‰)	–	25	27
Na ⁺ (mg/L)	1373	853	1892
Cl ⁻ (mg/L)	58	72	241
DOC (mg/L)	35	39	57
Dissolved O ₂ (mg/L)	0.6	2.6	0.7

The high DOC of till groundwater may increase colloidal transport rates. The presence of organic matter can greatly increase colloidal stability and result in a “blocking” effect, in which a single layer of colloids attaches to the matrix surface and thus prevents other colloids from attaching. The remaining colloids then move faster than water because they are excluded from part of the water-filled pore space. In the absence of organics, colloid suspensions tend to settle out, resulting in high filter efficiencies and low solute-transport rates (Kretzschmar et al. 1995).

Nitrogen Content

Organic-rich sedimentary rocks often contain a high concentration of organic N, which is mineralized to ammonium during diagenesis (Holloway and Dahlgren 1999). When the ammonium is nitrified, it produces “geologic”

nitrate. The occurrence of geologic nitrate associated with organic-rich shale has been documented at several locations in the United States, including North Dakota and eastern Montana (Power et al. 1974), Nebraska and South Dakota (Boyce et al. 1976), Colorado (Reeder and Berg 1977), and California (Strathouse et al. 1980; Holloway and Dahlgren 1999).

Geologic nitrate is common in weathered till and fine-textured lacustrine sediments in southern Alberta, where concentrations in groundwater range from about 100–400 mg/L nitrate-N (Hendry et al. 1984; Rodvang et al. 1998). Geologic nitrate was probably derived from organic-rich coal and shale incorporated into the till from underlying bedrock. Rodvang et al. (1998) determined that “geologic” nitrate in Quaternary aquitards can usually be distinguished from “agricultural” nitrate. Agricultural nitrate occurs at depths less than 6 m and is associ-

Table 3 Pesticide loss to surface water during the growing season. (From Bengtson et al. 1990)

Pesticide	Undrained field	Drained field	
	Surface runoff	Surface runoff	Subsurface drainage
Atrazine	3.2%	1.4%	0.04%
Metolachlor	2.45%	1.07%	0.13%
Water loss (mm)	412	254	152

ated with tritium, dissolved oxygen, and $\delta^{18}\text{O}(\text{H}_2\text{O})$ signatures characteristic of modern groundwater, as shown in Table 2. Concentrations of agricultural nitrate-N are usually less than 100 mg/L and increase with higher rates of fertilizer or manure application. In contrast, geologic nitrate usually occurs below 6 m (below the actively flushed zone) in groundwater that lacks tritium and contains isotopically lighter $\delta^{18}\text{O}(\text{H}_2\text{O})$ values, indicating the water is “pre-bomb” and “pre-fertilizer.” Geologic nitrate is associated with high concentrations of chloride and other salts (Table 2).

Solute Leaching and Subsurface Drainage

When rainfall or irrigation is sufficient, solutes leach rapidly through macropores in shallow oxidized till. Schuh et al. (1997) observed that a bromide tracer was detected throughout 6.5 m of fractured till and in the underlying aquifer in North Dakota almost immediately following the first rainfall after application. Infiltration to weathered till is usually much greater than recharge to deeper groundwater, particularly in the Northern Great Plains (the Canadian prairies and the north-central United States), where annual evapotranspiration exceeds precipitation. Rapid infiltration combined with low recharge rates to deeper groundwater result in shallow solute-accumulation zones near the bottom of the root zone that serve as feeder zones for sporadic pulses of solute transport to underlying layers during recharge events (Schuh et al. 1997).

Irrigation in Canada is mainly limited to southern Alberta, with minor amounts of irrigation in other locations. Irrigation is not conducted over Quaternary aquitards in the United States. Chang and Entz (1996) studied nitrate leaching in southern Alberta, where annual evapotranspiration exceeds precipitation by a factor of three. Under non-irrigated conditions, leaching below 150 cm was minimal except during a year with unusually high precipitation. Addition of only 167 mm/year of irrigation water caused all applied chloride to be leached below 150 cm.

Leaching tends to be much more extensive below minor topographic depressions (Keller et al. 1988; Fortin et al. 1991). Hayashi et al. (1998) described recharge through a till on the Canadian prairies that was oxidized to a depth of 4–6 m. Snowmelt and rainfall runoff that accumulated in a wetland infiltrated and flowed laterally through the oxidized till to the upland, where it was consumed by evapotranspiration. Only 1% of annual precipitation to the wetland (3.7 mm) recharged to the unoxi-

dized till. Similar cycles of runoff, infiltration, lateral flow, and evapotranspiration occur even in very flat landscapes, where topographic depressions of as little as 3 cm act as locations for depression-focused recharge (Keller et al. 1991; Schuh et al. 1997).

Subsurface (tile) drains have been installed for agronomic purposes in most humid areas underlain by Quaternary aquitards, particularly in eastern Canada (Madramootoo et al. 1992) and the north-central United States (Moorman et al. 1999). Subsurface drains are installed to lower the water table, which is usually shallow in Quaternary aquitards. Subsurface drainage reduces runoff relative to infiltration, and thus provides a greater opportunity for loss via degradation and sorption in the subsurface. For example, Bengtson et al. (1990) concluded that drainage on a clay-loam soil significantly reduced pesticide losses to surface water, as summarized in Table 3. P leaching through undrained soils is typically an order of magnitude less than P losses in runoff, with intermediate losses in drained soils (Scott et al. 1998).

Tile drains help to prevent recharge to groundwater below the drains, but they facilitate the transport of chemicals to surface water (Eidem et al. 1999). Hatfield et al. (1999) determined that tile drains capture 95% of potential recharge in the Walnut Creek Watershed. Martin et al. (1996) observed that although intertill aquifers in Indiana had low-nitrate, tile-drain effluent caused streams draining areas underlain by stratified-drift aquifers to have higher nitrate concentrations than other areas. Subsurface drainage may partially explain why nitrate levels in shallow groundwater under drained sites in Sweden and Iowa were much lower than those measured at an undrained site in southern Alberta, even though fertilizer application rates and levels in the soil zone were similar, as shown in Table 4.

Although tile drainage is common in Quaternary aquitards, solutes reach shallow groundwater in many areas. For example, Steinheimer et al. (1998) studied continuous corn on loess in southwestern Iowa, where nitrogen fertilizer was applied at recommended rates for 26 years. Nitrate in natural groundwater discharge from the field increased gradually from 0.7 mg/L as N in year 1, to 23 mg/L as N by year 25. This study illustrates that in Quaternary aquitards contamination may take a long time to emerge and may then supply solute-rich groundwater discharge for long periods of time.

Table 4 Nitrate concentrations in glacial aquitards at three locations

Study	Fertilizer rate (kg N/ha)	NO ₃ ⁻ -N in soil (kg/ha)		NO ₃ ⁻ -N in piezometers [% exceeding 10 mg/L NO ₃ ⁻ -N; <u>average</u> and max. conc. (mg/L)]		NO ₃ ⁻ -N in subsurface drainage ^a	
		0–2 m	2–4 m	2 m	4 m	Loss as a % of applied	Av. conc. (mg/L)
		Rodvang et al. (1998) (Alberta)	0 0 100 200	67 95 237 483	98 75 107 96	67%, <u>26</u> , 51 100%, <u>63</u> , 88 100%, <u>71</u> , 134 100%, <u>48</u> , 69	100%, <u>20</u> , 22 0%, <u>5</u> , 6 67%, <u>22</u> , 44 100%, <u>29</u> , 37
Bergstrom and Brink (1986) (Sweden)	0 50 100 150 200	45 – 70 – 348	– – – – –	<u>6</u> <u>5</u> <u>7</u> <u>7</u> <u>8</u>	<u>3.3</u> <u>1.2</u> <u>1.3</u> <u>1.3</u> <u>4.1</u>	– 8–24% 8–12% 17–23% 31–45%	1.3 2.7 3.3 9 16
Cambardella et al. (1999) (Iowa)	90–140	–	–	44%, 10, 52	16%, 4, 32	17–27%	8.8

^a Range indicates difference between losses in low-precipitation vs. high-precipitation years

Occurrence and Fate of Nitrogen

Occurrence

Nitrate in drinking water has been linked to blue-baby syndrome (methemoglobinemia), certain types of cancer, and negative reproductive outcomes (Weisenburger 1990; Drury et al. 1993; Morales-Suarez et al. 1993; Levallois and Phaneuf 1994). Discharge of nitrate-rich groundwater to surface water may also reduce surface-water quality for drinking and aquatic life (Smith et al. 1999). Inorganic fertilizer and manure applied to cropland are the most common sources of nitrate to groundwater (Keeney 1986; Hallberg 1989). Nitrate is highly soluble and readily leaches to groundwater or drainage tiles when fertilizer or manure application rates are greater than plant nutrient needs. Manure is often applied at greater than agronomic rates in areas with high livestock densities, because transportation costs limit the amount of exported manure (Gretz and Nair 1995). Mineralization of organic N in fertilizer and manure occurs at all times of the year, and the highest rates of nitrate leaching tend to occur when plants are not available to use the nitrate (e.g., Milburn and Richards 1994; Cambardella et al. 1999).

Groundwater nitrate concentrations tend to be lower in areas of the United States that are underlain by fine-textured Quaternary aquitards. Higher concentrations typically occur where sand and bedrock aquifers occur at the surface, and where aquifers are overlain by coarse-textured materials (Kross et al. 1990; Mueller et al. 1995; Nolan et al. 1997; Tesoriero and Voss 1997). Only 7% of rural wells in clayey aquitards throughout Ontario are contaminated with nitrate, in contrast to 27% of wells in sand and gravel (Goss et al. 1998).

Despite lower nitrate impacts relative to aquifer studies, agricultural contamination is common in weathered Quaternary aquitards. About 20–50% of samples taken from Quaternary aquitard systems in intensive agricul-

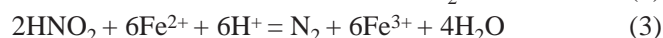
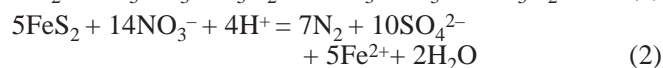
tural areas contain nitrate concentrations above the maximum contaminant level (MCL) of 10 mg/L NO₃⁻-N (Kross et al. 1990; Spalding and Exner 1993; Ray and Schock 1996; Zhang et al. 1996; Goss et al. 1998; Eidem et al. 1999). Spalding and Kitchen (1988) and Geyer et al. (1992) observed significant nitrate contamination to depths of 16 m in oxidized loess. Shallow, large-diameter wells in loess and glacial till in eastern Nebraska exhibit a higher percentage of nitrate contamination above the MCL (27%) than in other areas of the state, where wells are deeper and in coarse-textured sediments (Gosselin et al. 1997).

Denitrification

Processes

Denitrification occurs when bacteria obtain energy by catalyzing a redox reaction in which an electron donor is oxidized while nitrate is reduced to nitrogen (N₂) or nitrous oxide (N₂O) gas. Denitrification requires: (1) the presence of denitrifying bacteria; (2) the near absence of oxygen; and (3) an electron donor. Studies in till and loess have shown that denitrifiers are present at all depths, and that they become active under the appropriate conditions (e.g., Hendry et al. 1984; Lind and Eiland 1989; Geyer et al. 1992).

Denitrification processes are as follows:



Heterotrophic denitrification, which uses organic carbon as an electron donor [Eq. (1)], was historically thought to be thermodynamically favored over autotrophic denitrification, which uses reduced sulfur [Eq. (2)] or reduced iron

Table 5 Organic-carbon content and laboratory denitrification rates measured in Quaternary aquitards

Parameter	Geology	Cambardella et al. (1999)	Johnson (1995)	Fujikawa and Hendry (1991)	Lind (1985)
Organic carbon	Weathered Wisc. till	0.06–0.2%	0.3%	0.4%	–
	Unweathered Wisc. till	0.15–0.55%	0.6%	0.5%	–
	Unweathered Peoria Fm loess	0.5–2%	0.68%	–	–
Denitrification rate (ng N ₂ O-N/g per day)	Weathered Wisc. till	52	0.0	19,200	4.1
	Unweathered Wisc. till	8	5.8	44,880	61.2
	Unweathered Peoria Fm loess	258	6.7	–	–

Table 6 Changes in groundwater chemistry across the redoxcline in till at three locations. Concentrations in mg/L, except for tritium in TU. Above, Below position of sample in relation to redoxcline

Parameter	Robertson et al. (1996), Ontario		Simpkins and Parkin (1993) Nest 3, central Iowa		Rodvang et al. (1998), Alberta. Geologic nitrate, average of four sites in two watersheds	
	Above (3 m)	Below (5.6 m)	Above (2.5 m)	Below (4.3 m)	Above (9–19 m)	Below (12–23 m)
NO ₃ ⁻ -N	8.3	<0.05	17.4	<0.1	221	0.06
N ₂ O-N	–	–	–	–	3.4	0.07
NH ₄ ⁺ -N	<0.05	<0.05	2.2	1.9	1.15	7.47
Diss. O ₂	–	–	4.1	<0.1	–	–
SO ₄ ²⁻	20	52	45	2.2	3544	2545
Tritium	27	32	20	9	0	0
HCO ₃ ⁻	146	171	437	492	648	1326
Fe ²⁺	0.03	0.25	0.02	8	0.003	1.63
Mn ²⁺	0.01	0.08	0.003	0.329	1.35	3.95
As ³⁺	–	–	–	–	0.73	9.47
DOC	<0.5	<0.5	4.6	18.6	42.2	47.4
Ca ²⁺	85	86	130	97	533	457
Mg ²⁺	26	31	36	33	307	198
Cl ⁻	17	13	9	3	309	24
Na ⁺	3.8	5	6	17	1030	746

[Eq. (3)], but some studies have concluded that pyrite is more labile for denitrification than organic carbon (Kolle et al. 1985; Boettcher et al. 1991; Postma et al. 1991).

Heterotrophic denitrification is part of a redox sequence in which organic carbon is oxidized by oxygen, then nitrate, followed by manganese, iron, and sulfate. Reduced iron and sulfide can in turn reduce nitrate [Eqs. (2) and (3)]. Conversion of organic carbon to methane (CH₄) does not occur until SO₄²⁻ concentrations have been reduced to <1 mmol/L (Simpkins and Parkin 1993).

Denitrification rates are usually greater in topographically low areas than in higher landscape positions (Gambrell et al. 1975; Geyer et al. 1992; Farrell et al. 1996). Shallow water tables are more common in low areas, and, in addition to the more anaerobic conditions, modern organic carbon is more likely to reach shallow water tables (Starr and Gillham 1989). Clay-rich sediments allow for reduced oxygen and more stabilized organic matter, thus promoting increased denitrification (Lund et al. 1974; Vinten et al. 1994). However, denitrification rates in the vadose zone of fine-textured soils are highly dependent on moisture content. For example, Tindall et al. (1995) concluded that denitrification is unlikely to occur along preferential flow paths in a struc-

tured clay soil except when the macropores are filled with water. Water-saturated zones are more likely to develop in unfractured soils, even those with a relatively high K.

Laboratory studies of Quaternary aquitard material indicate that denitrification is an active process (Lind 1985; Fujikawa and Hendry 1991; Cambardella et al. 1999). As shown in Table 5, short- and long-term rates measured for late Wisconsinan till and loess in central Iowa and in Denmark are similar to each other and within the range given in Korom (1992). Denitrification rates cited by Fujikawa and Hendry (1991) are anomalously high.

In the unweathered zone

Consistent with laboratory studies showing that denitrification rates are higher in unweathered till than in weathered till (Table 5), field studies show that nitrate consistently decreases to non-detectable levels at the redoxcline in Quaternary aquitards. Evidence indicates that the loss of nitrate at the redoxcline is the result of denitrification. As shown in Table 6, the disappearance of nitrate is accompanied by decreased dissolved oxygen, in-

creased Fe^{2+} , and other indications of decreasing redox potential that are discussed in more detail below. Hydraulic barriers alone cannot explain the decrease of nitrate concentration across the redoxcline. For example, tritium does not decrease with nitrate across the redoxcline in southern Ontario (Table 6). Where multiple sequences of weathered and unweathered material occur, the disappearance of nitrate in an unweathered aquitard can occur even when it overlies weathered till (Klinck et al. 1996; Rodvang et al. 1998).

Role of electron donors

The loss of nitrate at the redoxcline coincides with an increase in pyrite and/or organic carbon (Table 1), both of which are potential electron donors. DOC and SOC from Quaternary sources appear to be labile for denitrification. Simpkins and Parkin (1993) concluded that the oxidation of DOC from wood in late Wisconsinan till in central Iowa catalyzes the reduction of nitrate, manganese, iron, sulfate, and finally methane. Fe^{2+} , Mn^{2+} , H_2S , and CH_4 all increase across the redoxcline in central Iowa till (Table 6), indicating nitrate would not be stable in unweathered till, because reduced iron, sulfur, and methane act as electron donors for denitrification (Mechsner and Hamer 1985; Korom 1992; Parkin and Simpkins 1995). Laboratory studies on the same till showed denitrifying activity was correlated with DOC and SOC, even though most of the DOC appears to consist of high molecular weight humic and fulvic acids that are notoriously difficult for microorganisms to utilize (Table 5; Johnson 1995). In contrast, the underlying pre-Illinoian till, which is older than 500,000 years, showed no denitrification activity, despite an average SOC content of 1.16%. This suggests that the older SOC is not labile for denitrification. Consistent with this hypothesis, late Wisconsinan Quaternary deposits in central Iowa exhibit a lower percentage of nitrate contamination (7.4%) than do older Quaternary deposits in other parts of the state (Kross et al. 1990).

DOC and SOC derived from Devonian shale clasts in southern Ontario till (Allan-King et al. 1997) do not appear to be labile for denitrification. Robertson et al. (1996) observed that the attenuation of nitrate at the redoxcline in a till in southern Ontario corresponded to an increase in sedimentary sulfur and pore water SO_4^{2-} , whereas SOC and HCO_3^- changed only slightly across the redox boundary (Tables 1 and 6). This suggests that pyrite is the dominant electron donor for denitrification, and that the bulk of the SOC constitutes compounds of higher molecular weight, such as humic substances, that are not readily labile for denitrification (Robertson et al. 1996). Evidence of sulfate reduction or methane production in unweathered till in Saskatchewan is lacking (Hendry and Wassenaar 2000). In contrast, H_2S and methane are often detected below the redoxcline in central Iowa (Simpkins and Parkin 1993), reinforcing the hypothesis that organic carbon of Quaternary age in Iowa is much more labile than the shale clasts in Saskatchewan.

In late Wisconsinan till in southern Alberta, DOC is high in both weathered and unweathered tills (Table 1), suggesting that it is not highly labile for denitrification. Both SOC and pyrite increased at the redoxcline in southern Alberta till (Table 1), and the disappearance of nitrate coincided with an increase in HCO_3^- (Rodvang et al. 1998; Table 6), suggesting that SOC from coal clasts may be the dominant electron donor. The disappearance of nitrate below the redoxcline was also accompanied by increases in As^{3+} , Fe^{2+} , and Mn^{2+} (Table 6). This is probably the result of denitrification via oxidation of either SOC or pyrite, because arsenic is strongly sorbed to iron and manganese oxides and also substitutes for Fe in pyrite (Hem 1989). Simultaneous nitrate attenuation using both carbon and pyrite has been documented in aquifers in Ontario (Aravena and Robertson 1998) and Denmark (Postma et al. 1991). Concentrations of NH_4^+ increased with HCO_3^- across the redoxcline in southern Alberta (Table 6; Rodvang et al. 1998). The source of NH_4^+ could be the breakdown of organic matter or dissimilatory nitrate reduction to ammonium (DNRA). The lack of detectable NH_4^+ across the redoxcline in southern Ontario (Table 6) is consistent with the lower organic carbon at that site (Table 1), because DNRA does not occur when carbon supplies are limited (Tiedje et al. 1982).

Mass-balance calculations indicate that reserves of pyrite and organic carbon in Quaternary aquitards have the potential to denitrify agricultural nitrate for a very long time. Robertson et al. (1996) showed that denitrification of nitrate from manure and fertilizer increases the rate of pyrite oxidation in southern Ontario, and this increases the vertical migration rate of the redoxcline from the pre-anthropogenic rate of about 0.4 mm/year to about 1 mm/year. Cambardella et al. (1999) determined that organic carbon in till and loess in central Iowa had a lifetime capacity to denitrify 20,340 kg N/ha.

In the weathered zone

Studies have also demonstrated indirect evidence of denitrification in weathered zones of Quaternary aquitards. In southern Alberta, groundwater with geologic and agricultural nitrate contained $\delta^{15}\text{N}(\text{NO}_3)$ ranging from 13–74‰ (30 samples) (Rodvang et al. 1998; Table 2). $\text{N}_2:\text{Ar}$ ratios were 71 and 77 (two samples), suggesting that N_2 was produced by denitrification (Wilson et al. 1990). Similar $\text{N}_2:\text{Ar}$ ratios, ranging from 34.7–71.7, occurred due to denitrification in till groundwater in the UK (Feast et al. 1998). Denitrification is also indicated by above-ambient concentrations of dissolved N_2O in groundwater containing nitrate in weathered till (Rodvang et al. 1998; Table 2).

In all cases, weathered till containing high $\delta^{15}\text{N}(\text{NO}_3)$, $\text{N}_2:\text{Ar}$ ratios, and N_2O also contained nitrate, and as much as 5 mg/L dissolved oxygen (Rodvang et al. 1998; Table 2), even though Spalding and Parrott (1994) suggest that denitrification does not occur above oxygen concentrations of 0.2 mg/L. This contradiction suggests that denitrification in weathered zones is “patchy”. Parkin

(1987) concluded that spatially variable denitrification under mostly oxidizing conditions is the result of particles of SOC dispersed in the matrix, which serve as loci for denitrification.

Spatially variable denitrification in weathered till is probably also controlled by oxygen diffusion. Studies in thick, weathered loess in Washington State suggest that denitrification occurs in water-saturated anaerobic microsites that are heterogeneously distributed throughout the loess (Geyer et al. 1992). These authors suggest that oxygen transport to the microsites is controlled by diffusion. Denitrification may also occur in some areas of the matrix of weathered till, whereas more oxygenated, nitrate-rich water moves through the fractures (Helmke et al. 1999). Wolf and Russow (2000) concluded that N_2O produced in an oxygenated system is stable when it diffuses out of the anaerobic microsites. A limited quantity or quality of organic carbon during denitrification results in a high ratio of N_2O to N_2 (Ottow et al. 1985). N_2O is not detectable below the redoxcline in southern Alberta (Table 6), which suggests that denitrification at the redoxcline occurs in anaerobic conditions and is not limited by electron donors. High concentrations of N_2O may also reflect nitrification under conditions of low oxygen and high NH_4^+ (Goreau et al. 1980; Ottow et al. 1985; Ueda et al. 1991, 1993). Blackmer et al. (1980) demonstrated significant N_2O production by ammonia-oxidizing chemoautotrophic bacteria in loamy till soil.

Occurrence and Fate of Phosphorus

Phosphorus (P) is the principal limiting nutrient in fresh waters, and in excess it is responsible for anthropogenic eutrophication (Downing and McCauley 1992; Smith et al. 1999). The output of P in crop and animal produce averages only 30% of the input in fertilizer and feed, resulting in an average annual P surplus of 33 kg/ha over the total utilizable agricultural land area in the United States. P surpluses tend to be greatest in areas with a high density of livestock operations, due to the reliance on imported feed (Sharpley et al. 1999).

P is adsorbed strongly to most sediments and is capable of combining with various metal cations, particularly iron, aluminum, manganese, and calcium, to form minerals that are stable in low-temperature aqueous environments (Robertson et al. 1998). Information on P occurrence and transport in till groundwater is limited. Robertson et al. (1998) studied septic system plumes in nine sand aquifers and a sandy till. Migration rates were significantly retarded by sorption, with retardation factors as great as 100. Mineral precipitation resulted in c/co values as low as 0.004. The highest P concentrations occurred in oxidizing conditions at near-neutral pH. P concentrations in reducing and acidic plumes are probably controlled by precipitation of vivianite, strengite, and variscite (Robertson et al. 1998).

Numerous studies have demonstrated significant P leaching through macropores in fine-textured sediments,

including calcareous clay-loam till (e.g., Stamm et al. 1998; Jensen et al. 1999). P leaching tends to increase significantly once binding sites in soil become saturated (e.g., Mozaffari and Sims 1994; Simard et al. 1995), but substantial P leaching can occur even before saturation is reached (Heckrath et al. 1995). Whalen and Chang (in press) concluded that about 20% of applied manure P was lost from an irrigated flat-lying calcareous clay-loam till in southern Alberta that received annual applications of manure for 16 years. Soil tests suggested a substantial portion of the loss was due to leaching below 150 cm. Several studies have demonstrated higher P leaching losses from clay than from sand due to preferential flow (e.g., Culley and Bolton 1983; Beauchemin et al. 1998). Macropore flow appears to particularly promote leaching of particulate P (bound to organic matter and sediment) (Beauchemin et al. 1998). Scott et al. (1998) noted that rapid leaching of particulate P through macropores was eventually surpassed by soluble P in drainage from the matrix.

Drainage tiles in aquitard settings often contribute high concentrations of P to surface water, with values ranging from 7–900 $\mu\text{g/L}$ in Canada (Bolton et al. 1970) and the midwestern United States (Baker et al. 1975; Schwab et al. 1980; Bottcher et al. 1981). The United States Environmental Protection Agency (USEPA) states that P concentration should not exceed 0.05 mg/L for streams entering lakes and reservoirs (Daniel et al. 1998). P loss in tile drainage from watersheds in clay soils in southwestern Ontario accounted for 50–68% of ortho-P loss from watersheds (Culley and Bolton 1983; Gaynor and Findlay 1995).

Occurrence and Fate of Pesticides

Occurrence

Pesticides, including herbicides and insecticides, are increasingly detected in groundwater and surface water in agricultural areas. The European Union has adopted a maximum admissible concentration of 0.1 $\mu\text{g/L}$ for individual pesticides and 0.5 $\mu\text{g/L}$ for the sum of the concentrations of pesticides (Leistra and Boesten 1989). Canada and the United States rely on guidelines for individual pesticides; many of these guidelines have not yet been developed. Allowable concentrations are generally much higher than in Europe. For example, the MCLs for atrazine and dicamba are 3 and 10 $\mu\text{g/L}$, respectively. Guidelines have rarely been set for the degradates of pesticide parent compounds, even though a 1995–1998 USGS survey of groundwater in Iowa showed eight of the ten most common herbicides occurred as degradation products (Kolpin et al. 2000).

Contamination of groundwater by pesticides is common in agricultural areas. Kolpin et al. (1998) observed that pesticides occurred in 54% of recently recharged groundwater in the United States ($n=1,034$), but only a small percentage of the detections exceeded USEPA MCLs. Pesticide detections in shallow groundwater oc-

Table 7 Range of K_{oc} values measured in Quaternary aquitards for various adsorbants

Reference	Location	Adsorbant	Sediment	Primary source of SOC	Depth (m)	K_{oc} (L/kg)
Allan-King et al. (1997)	Ontario	TCE	Unweathered till	Upper Devonian carbonaceous shale	12 and 15	7,744–15,700
			Data from four studies, compiled for sand aquifers			
Binger et al. (1999)	Ontario	PCE	Surficial (weathered) till	Upper Devonian carbonaceous shale	1.5	2,230 and 2,609
			Unweathered till		5 and 6	24,000–38,810
Moorman et al. (unpublished data) ^a	Central Iowa	Atrazine	Clarion and Nicollet soil developed in late Wisconsinan till (Dows Fm)	Late Wisconsinan coniferous forest	0–1	117–173
			Weathered late Wisconsinan till (Dows Fm)		1–3.5	48–563
			Unweathered late Wisconsinan till (Dows Fm)		6	994
	Western Iowa	Atrazine	Peoria Fm. loess	Late Wisconsinan coniferous forest	0–3	61–565
	NE Iowa	Atrazine	Weathered pre-Illinoian till (Wolf Creek Fm)	–	0–8.7	112–492
			Unweathered pre-Illinoian till (Wolf Creek Fm)	–	8.7–12.2	535–1,468
Roy and Krapac (1994)	Illinois	Atrazine	Wedron Fm till	–	3	806 and 858

^a Moorman TB, Jayachandran K, Reungsang A, unpublished data, Agricultural Research Service, US Dept. Agric, National Soil Tilth Lab, Ames Iowa

cur more often in areas with permeable soils than in areas covered by till, clays, and other low-permeability deposits (USGS 1999). The frequency of herbicide detection in Iowa aquifers is 82.5% for alluvium, 81.8% for bedrock/karst, 40% for glacial drift, and 25% for bedrock/non-karst-type (Kolpin et al. 1998). Most studies demonstrate strong attenuation of pesticides with depth. Kruger et al. (1996) reported that the mobility of eight pesticides increased with decreasing soil organic matter and increased sand content in till-derived soil in Iowa. Lampman (1995) observed significantly more attenuation of herbicides to 6 m depth in silty clay soils than in sandy soils in southwestern Ontario.

In contrast to the above studies, Hallberg (1989) cited examples where pesticide detections were more frequent in fine-textured till than in shallow sand and gravel aquifers. Statewide surveys in Iowa showed that about 18% of rural wells covered by 15 m of aquitard material contained detectable concentrations of one or more pesticides (Kross et al. 1990). Hill et al. (1996) and Miller et al. (1995) detected herbicides in 9–61% of samples collected from water-table wells installed at 4–6 m in a clay-loam till in southern Alberta. Atrazine and metribuzin were detected in 26 and 13%, respectively, of groundwater samples collected in till to a depth of 2.6 m

in Iowa (Moorman et al. 1999). Both the Alberta and Iowa studies showed that although detections tend to be greatest following herbicide application, herbicides were also detected in years they were not applied. In the Iowa study, herbicide detections ranged from 10–15% in the upper 3 m of till, decreasing to 4% below 3 m (Moorman et al. 1999).

Pesticide Sorption

Sorption is the primary mechanism for attenuation of pesticides with depth. Sorption is promoted by organic carbon, iron oxides, and clay minerals, all of which are important constituents of Quaternary aquitards. Even in systems dominated by preferential flow, strongly adsorbing chemicals appear at lower concentrations (Bottcher et al. 1981; Smith et al. 1985; Kladvik et al. 1991; Southwick et al. 1995; Abu-Ashour et al. 1998).

Organic carbon in surface soils and sediments has a consistent ability to sorb organic compounds, with organic-carbon-normalized sorption coefficients (K_{oc} values) generally ranging from 50–500 L/kg (Allen-King et al. 1997). However, SOC in till in southwestern Ontario (from shale) tends to be much more sorptive than SOC in soils (Table 7). Allen-King et al. (1997) showed that the

high sorption capability of till is due to the lipophilic nature of the SOC and not due to sorption by the mineral fraction. Sorptive capability increases as oxygen content decreases during diagenesis and catagenesis (Allen-King et al. 1997; Binger et al. 1999). The increase in K_{oc} with diagenesis explains why SOC in till from southwestern Ontario, which is derived from Devonian shale clasts, is much more sorptive than SOC in late Wisconsinan till in central Iowa (Table 7), which is derived mainly from wood that is less than 14,000 years old (Simpkins and Parkin 1993). Unweathered Pre-Illinoian till is also relatively sorptive (Table 7).

Due to sorption, the amount of pesticide leached to groundwater is generally less than the amount lost to surface runoff (Table 3). Total herbicide losses in subsurface drainage on fine-textured soils are usually less than 0.3% of applied (e.g., Muir and Baker 1976; Bengtson et al. 1990; Milburn et al. 1991; Buhler et al. 1993; Masse et al. 1996) but are occasionally as much as 1.5% of applied (e.g., Gaynor et al. 1992; Jayachandran et al. 1994).

Preferential Flow and Biodegradation

Preferential flow in fine-textured soils causes very rapid transport of pesticides to subsurface drains. Concentrations tend to be highest at the beginning of each new drain-flow event, and to decrease rapidly as matrix flow begins to dominate. Biodegradation causes some attenuation of peak concentrations with each successive drain-flow event (Kladivko et al. 1991; Moorman et al. 1999). Binger et al. (1999) reported that sorption was much lower along fracture faces than in the matrix of a till in southwestern Ontario (Table 7). This was due to a weathering-induced increase in the oxygen/carbon ratio of the SOC and a resulting decrease in K_{oc} . Stehouwer et al. (1994) observed that the organic carbon lining on earthworm burrows significantly enhanced herbicide sorption.

Pivetz and Steenhuis (1995) and Pivetz et al. (1996) observed that biodegradation rates were initially slower in macropores but eventually surpassed rates in the matrix, possibly because of the increased availability of oxygen in the vicinity of the macropore and the greater mass of substrate delivered to this area. Pesticides tend to degrade much more quickly in the liquid phase than in the sorbed phase, so adsorption decreases degradation (Guo et al. 2000). Due to diffusion between macropores and matrix and slow release of adsorbed pesticides, pesticides can persist in the environment for several years (Buhler et al. 1993; Moorman et al. 1999).

Occurrence and Fate of Pathogens

Occurrence

Occurrence of bacteria and other pathogens in groundwater is a relatively recent area of investigation. Livestock waste contains many pathogenic microorganisms associated with serious gastrointestinal disease. These organisms include bacteria such as *Escherichia coli* (*E.*

coli) and *Streptococcus*, viruses such as Enterovirus, and protozoa such as *Cryptosporidium* and *Giardia*. The presence of fecal coliform bacteria indicates that other disease-causing organisms may be present (Mawdsley et al. 1995). Many strains of *E. coli* are harmless, but some strains, such as O157:H7, are serious pathogens. Protozoan pathogens are often resistant to standard water treatment methods (Mawdsley et al. 1995).

In Ontario, 17 and 20% of farm wells in coarse- and fine-textured sediments were contaminated with fecal coliform and *E. coli*, respectively (Goss et al. 1998). About 5% of wells contained fecal coliform, with 80% of those detections occurring in wells in till that are less than 30 m deep (Kross et al. 1990). Coliform bacteria were present in 17% of domestic water wells in loess and till in eastern Nebraska (Gosselin et al. 1997).

Preferential Flow and Biodegradation

Fecal coliforms have a cell diameter of 3–10 μm (Brush 1997). Due to their large size, coliforms tend to leach most readily through very coarse-textured soils and karst, and through fine-textured soils with macropores and fractures. The presence of surface-connected macropores in soils receiving manure during recharge events allows bacteria to travel rapidly to subsurface drains (Mawdsley et al. 1996; Natsch et al. 1996; McMurry et al. 1998; Scott et al. 1998). Abu-Ashour et al. (1998) reported that *E. coli* was only leached through soil columns with macropores. Gagliardi and Karns (2000) stated that intact clay-loam cores became clogged with fecal coliform shortly after inoculation.

Once bacteria leach to groundwater, they can survive for months, which is considerably longer than survival rates in open water (Burton et al. 1987; Crabill et al. 1998; Filip et al. 1988; Gagliardi and Karns 2000). Bacterial survival rates tend to be higher in fine-textured soils, possibly due to their higher moisture-retention capabilities (Gerba et al. 1975; Burton et al. 1987) or higher content of organic matter and nutrients (Conboy and Goss 2000). The presence of nutrients increases bacterial survival rates, probably because coliforms are facultative anaerobes (Gagliardi and Karns 2000).

Conclusions

The increase in agricultural intensity during the past 30 years has resulted in agricultural contaminants from non-point sources appearing with greater frequency in groundwater. Quaternary aquitards are the dominant surficial material in North America, and these units often represent the only natural protection for major aquifer systems.

Thick, unweathered Quaternary aquitards provide very effective protection for underlying aquifers. Fractures are widely spaced or absent, resulting in slow rates of contaminant transport. The aquitards often contain much higher concentrations of SOC, DOC, and reduced

sulfur than do their weathered counterparts. SOC derived from older shale clasts probably has a much higher ability to sorb pesticides than does SOC of Quaternary age. Denitrification consistently reduces nitrate to non-detectable levels in unweathered Quaternary aquitards. Organic carbon of Quaternary age is a more labile electron donor than Cretaceous or Devonian shale clasts. Pyrite acts as an electron donor when labile organic carbon is not available. Variations in hydraulic conductivity and concentrations of pyrite and labile and highly sorptive organic carbon dictate that the degree of attenuation provided by unweathered Quaternary aquitards varies with location. However, reserves of pyrite and organic carbon at the locations cited indicate that these aquitards have the potential to reduce nitrate and potentially sorb pesticides well into the future.

In contrast to their unweathered counterparts, weathered Quaternary aquitards commonly contain agricultural contamination from non-point sources, including nitrate concentrations greater than the MCL or drinking-water guideline, pesticides and their degradates, fecal coliforms, and P. Solute transport through weathered Quaternary aquitards is increased by the presence of fractures. Weathering of shale clasts reduces K_{oc} , so that pesticide sorption is significantly lower. Dissolved O_2 is commonly present and is the primary electron acceptor. Organic carbon and pyrite have been oxidized to CO_2 and SO_4^{-2} , respectively, such that denitrification occurs only in microsites.

Weathered Quaternary aquitards generally have concentrations of agricultural contaminants that are lower than those in shallow aquifers. This may be due to lower K values, matrix diffusion, higher clay content, and the presence of subsurface drainage, which reduces contaminant leaching by facilitating transport directly to surface water. Agricultural contaminants currently present in weathered Quaternary aquitards will probably eventually enter aquifers and surface water. Future research should therefore be directed toward understanding biogeochemistry and groundwater flow in weathered Quaternary aquitards, where contaminants from the past 30 years of agriculture will provide problems well into the future.

References

- Abbott DE (1987) The origin of sulphate and the isotope geochemistry of sulphate-rich shallow groundwater in the St. Clair clay plain southwestern Ontario. MSc Thesis, Univ Waterloo, Ontario
- Abu-Ashour J, Joy DM, Lee H, Whiteley HR, Zelin S (1998) Movement of bacteria in unsaturated soil columns with macropores. *Trans ASAE* 41(4):1043–1050
- Allen-King RM, McKay LD, Trudell MR (1997) Organic carbon dominated trichloroethene sorption in a clay-rich glacial deposit. *Ground Water* 35(1):124–130
- Aravena R, Roberson WD (1998) Use of multiple isotope tracers to evaluate denitrification in ground water: study of nitrate from a large-flux septic system plume. *Ground Water* 36(6):975–982
- Baker JL, Campbell KL, Johnson HP, Hanway JJ (1975) Nitrate, phosphorus, and sulfate in subsurface drainage water. *J Environ Qual* 4:406–412
- Beauchemin S, Simard RR, Cluis D (1998) Forms and concentration of phosphorus in drainage water of twenty-seven tile-drained soils. *J Environ Qual* 27:721–728
- Bengtson RL, Southwick LM, Willis GH, Carter CE (1990) The influence of subsurface drainage practices on herbicide losses. *Trans ASAE* 33(2):415–418
- Bergstrom L, Brink N (1986) Effects of differentiated applications of fertilizer N on leaching losses and distribution of inorganic N in the soil. *Plant Soil* 93:333–345
- Binger CA, Martin JP, Allen-King RM, Fowler M (1999) Variability of chlorinated-solvent sorption associated with oxidative weathering of kerogen. *J Contam Hydrol* 40:137–158
- Blackmer AM, Bremner JA, Schmidt EL (1980) Production of nitrous oxide by ammonia-oxidizing chemoautotrophic microorganisms in soil. *Appl Environ Microbiol* 40(6):1060–1066
- Boettcher J, Strelbel O, Duynisveld WHM, Frind EO (1991) Reply. *Water Resour Res* 27:3275–3278
- Bolton EF, Aylesworth JW, Hore FR (1970) Nutrient losses through tile drains under three cropping systems and two fertility levels on a Brookston clay soil. *J Soil Sci* 50:275–279
- Bottcher AB, Monke EJ, Huggins LF (1981) Nutrient and sediment loadings from a subsurface drainage system. *Trans ASAE* 24:1221–1226
- Boyce JS, Muir J, Edwards AP, Seim EC, Olson RA (1976) Geologic nitrogen in Pleistocene loess of Nebraska. *J Environ Qual* 5(1):93–96
- Brown MJ, Burris DR (1996) Enhanced organic contaminant sorption on soil treated with cationic surfactants. *Ground Water* 34(4):734–744
- Brush CF (1997) Surface and transport properties of *Cryptosporidium parvum* oocysts. PhD Thesis, Cornell University, New York
- Buhler DD, Randall GW, Koskinen WC, Wyse DL (1993) Atrazine and alachlor losses from subsurface tile drainage of a clay loam soil. *J Environ Qual* 22:583–588
- Burton GA Jr, Gunnison D, Lanza GR (1987) Survival of pathogenic bacteria in various freshwater sediments. *Appl Environ Microbiol* 53:633–638
- Cambardella CA, Moorman TB, Jaynes DB, Hatfield JL, Parkin TB, Simpkins WW, Karlen DL (1999) Water quality in Walnut Creek watershed: nitrate-nitrogen in soils, subsurface drainage water, and shallow groundwater. *J Environ Qual* 28:25–34
- Chang C, Entz T (1996) Nitrate leaching losses under repeated cattle feedlot manure applications in southern Alberta. *J Environ Qual* 25(1):145–153
- Conboy MJ, Goss MJ (2000) Natural protection of groundwater against bacteria of fecal origin. *J Contam Hydrol* 43:1–24
- Crabill C, Donald R, Snelling J, Foust R, Southam G (1998) The impact of sediment fecal coliform reservoirs on seasonal water quality in Oak Creek, Arizona. *Water Res* 33:2163–2171
- Culley JLB, Bolton EF et al. (1983) Suspended solids and phosphorus loads from a clay soil: II. watershed study. *J Environ Qual* 12(4):498–503
- Daniel TC, Sharpley AN, Lemunyon JL (1998) Agricultural phosphorus and eutrophication: a symposium overview. *J Environ Qual* 27(2):251–257
- Downing JA, McCauley E (1992) The nitrogen:phosphorus relationship in lakes. *Limnol Oceanogr* 3:936–945
- Dreimanis AD (1982) Work Group I. Genetic classification of tills and criteria for their differentiation; progress report on activities 1977–1982, and definitions for glacial terms. In: Schluchter C (ed) Commission on genesis and lithology of Quaternary deposits report on activities 1977–1982. International Quaternary Association, Zurich, p 70
- Drury CF, McKenney DJ, Findlay WI, Gaynor JD (1993) Influence of tillage on nitrate loss in surface runoff and tile drainage. *Soil Sci Soc Am J* 57:797–802
- Eidem JM, Simpkins WW, Burkart MR (1999) Geology, groundwater flow, and water quality in the Walnut Creek watershed. *J Environ Qual* 28:60–69

- Farrell RE, Sandercock PJ, Pennock DJ, Van Kessel C (1996) Landscape-scale variations in leached nitrate: relationship to denitrification and natural nitrogen-15 abundance. *Soil Sci Soc Am J* 60:1410–1415
- Feast NA, Hiscock KM, Dennis PF, Andrews JN (1998) Nitrogen isotope hydrochemistry and denitrification within the Chalk aquifer system of north Norfolk, UK. *J Hydrol* 211:233–252
- Fenelon JM, Moore RC (1998) Transport of agrichemicals to ground and surface water in a small central Indiana watershed. *J Environ Qual* 27:884–894
- Filip Z, Daddu-Mulindwa D, Milde G (1988) Survival of some pathogenic and facultative pathogenic bacteria in groundwater. *Water Sci Technol* 20:227–231
- Flint RF (1945) Glacial map of North America, 1:4,555,000 scale. Geol Soc Am, New York
- Fortin G, van der Kamp G, Cherry JA (1991) Hydrogeology and hydrochemistry of an aquifer-aquitard system within glacial deposits, Saskatchewan, Canada. *J Hydrol* 126:265–292
- Freeze RA, Cherry JA (1979) *Groundwater*. Prentice-Hall, Englewood Cliffs
- Fujikawa JI, Hendry MJ (1991) Denitrification in clayey till. *J Hydrol* 127:337–348
- Fulton RJ (compiler) (1995) Surficial materials of Canada. Map 1880A, scale 1:5,000,000, paper and digital. Geological Survey of Canada
- Gagliardi JV, Karns JS (2000) Leaching of *Escherichia coli* O157:H7 in diverse soils under various agricultural management practices. *Appl Environ Microbiol* (March 2000):877–883
- Gambrell RP, Gilliam JW, Weed SB (1975) Denitrification in subsoils of the North Carolina Coastal Plain as affected by soil drainage. *J Environ Qual* 4(3):311–316
- Gaynor JD, Findlay WI (1995) Soil and phosphorus loss from conservation and conventional tillage in corn production. *J Environ Qual* 24(4):734–741
- Gaynor JD, MacTavish DC, Findlay WI (1992) Surface and subsurface transport of atrazine and alachlor from a Brookston clay loam under continuous corn production. *Arch Environ Contam Toxicol* 23:240–245
- Gerba CP, Wallis C, Melnich JL (1975) Fate of wastewater bacteria and viruses in soil. *J Irrig Drain Div* 101(2):157–174
- Geyer DJ, Keller CK, Smith JL, Johnstone DL (1992) Subsurface fate of nitrate as a function of depth and landscape position in Missouri Flat Creek watershed, U.S.A. *J Contam Hydrol* 11:127–147
- Goreau TJ, Kaplan WA, Wofsy SC, McElroy MB, Valois FW, Watson SW (1980) Production of NO_2^- and N_2O by nitrifying bacteria at reduced concentrations of oxygen. *Appl Environ Microbiol* 40:526–532
- Goss MJ, Barry DAI, Rudolph DL (1998) Contamination in Ontario farmstead domestic wells and its association with agriculture. I. Results from drinking water wells. *J Contam Hydrol* 32(3–4):63–90
- Gosselin DC, Headrick J, Tremblay R, Chen X, Summerside S (1997) Domestic well water quality in rural Nebraska: focus on nitrate-nitrogen, pesticides, and coliform bacteria. *Ground Water Monit Remed* 17(2):77–87
- Greatz DA, Nair VD (1995) Fate of phosphorus in Florida spodosols contaminated with cattle manure. *Ecol Eng* 5:163–181
- Guo L, Jury WA, Wagenet RJ, Flury M (2000) Dependence of pesticide degradation on sorption: nonequilibrium model and application to soil reactors. *J Contam Hydrol* 43:45–62
- Hallberg GR (1980) Pleistocene stratigraphy in east-central Iowa. *Iowa Geol Surv Tech Info Ser* 10
- Hallberg GR (1989) Pesticide pollution of groundwater in the humid United States. *Agric Ecosys Environ* 26:299–367
- Hatfield JL, Jaynes DB, Burkart MR, Cambardella CA, Moorman TB, Prueger JH, Smith MA (1999) Water quality in Walnut Creek watershed: setting and farming practices. *J Environ Qual* 28:11–24
- Hayashi M, van der Kamp G, Rudolph DL (1998) Water and solute transfer between a prairie wetland and adjacent uplands. I. Water balance. *J Hydrol* 207:42–55
- Heckrath G, Brookes PC, Poulton PR, Goulding KWT (1995) Phosphorus leaching from soils containing different phosphorus concentrations in the Broadbalk experiment. *J Environ Qual* 24:904–910
- Helmke MF, Simpkins WW, Horton R (1999) Use of multiple tracers and measured effective diffusion coefficients to constrain solute transport models in fractured till. *Geol Soc Am, Abstr Prog* 31(7):A-450
- Hem JD (1989) Study and interpretation of the chemical characteristics of natural water, 3rd edn. US Geol Surv Water-Supply Pap 2254
- Hendry MJ, Wassenaar LI (1999) Implications of the distribution of *D in pore waters for groundwater flow and the timing of geologic events in a thick aquitard system. *Water Resour Res* 35(6):1751–1760
- Hendry MJ, Wassenaar LI (2000) Controls on the distribution of major ions in pore waters of a thick surficial aquitard. *Water Resour Res* 36(2):503–513
- Hendry MJ, McCready RGL, Gould WD (1984) Distribution, source and evolution of nitrate in a glacial till of southern Alberta, Canada. *J Hydrol* 70:177–198
- Hendry MJ, Cherry JA, Wallick EI (1986) Origin and distribution of sulfate in a fractured till in southern Alberta, Canada. *Water Resour Res* 22(1):45–61
- Hill BD, Miller JJ, Chang C, Rodvang SJ (1996) Seasonal variation in herbicide levels detected in shallow Alberta groundwater. *J Environ Sci Health B31(4):883–900*
- Holloway JM, Dahlgren RA (1999) Geologic nitrogen in terrestrial biogeochemical cycling. *Geology* 27(6):567–570
- Jayachandran K, Steinheimer TR, Somasundaram L, Moorman TB, Kanwar RS, Coats JR (1994) Occurrence of atrazine and degradates as contaminants of subsurface drainage and shallow groundwater. *J Environ Qual* 23:311–319
- Jensen MB, Hansen HCB, Jorgensen PR, Magid J (1999) Leaching of phosphate in structured soil – a two step process. *Nord Hydrol* 30(4/5):361–378
- Johnson BL (1995) Assessment of the fate and transport of nitrate in groundwater within the Walnut Creek watershed. MSc Thesis, Iowa State Univ
- Jorgensen PR, McKay LD, Spliid NH (1998) Evaluation of chloride and pesticide transport in a fractured clayey till using large undisturbed columns and numerical modeling. *Water Resour Res* 34(4):539–553
- Keeney DR (1986) Sources of nitrate to ground water. *Crit Rev Environ Control* 16: 257–304
- Keller CK (1991) Hydrogeochemistry of a clayey till. 2. Sources of CO_2 . *Water Resour Res* 27(10):2555–2564
- Keller CK, Bacon DH (1998) Soil respiration and georespiration distinguished by transport analyses of vadose CO_2 , $^{13}\text{CO}_2$. *Global Biogeochem Cycles* 12:361–371
- Keller CK, van der Kamp G, Cherry JA (1988) Hydrogeology of two Saskatchewan tills, I. Fractures, bulk permeability, and spatial variability of downward flow. *J Hydrol* 101:97–121
- Keller CK, van der Kamp G, Cherry J (1989) A multiscale study of the permeability of a thick clayey till. *Water Resour Res* 25(11):2299–2317
- Keller CK, van der Kamp G, Cherry JA (1991) Hydrogeochemistry of a clayey till. 1. Spatial variability. *Water Resour Res* 27(10):2543–2554
- Kladivko EJ, van Scoyoc E, Oates KM, Pask W (1991) Pesticide and nutrient movement into subsurface tile drains on a silt loam soil in Indiana. *J Environ Qual* 20:264–270
- Klinck BA, Barker JA, Noy DJ, Wealthall GP (1996) Mechanisms and rates of recharge through glacial till: experimental and modelling studies from a Norfolk site. Fluid Processes Group, Br Geol Surv, Keyworth, Nottingham
- Kolle W, Strebel O, Boettcher J (1985) Formation of sulfate by microbial denitrification in a reducing aquifer. *Water Supply* 3:35–40
- Kolpin DW, Barbash JE, Gilliom RJ (1998) Occurrence of pesticides in shallow ground water of the United States: initial re-

- sults from the national water-quality assessment program. *Environ Sci Technol* 32(5):558–566
- Kolpin DW, Thurman EM, Linhart SM (2000) Finding minimal herbicide concentrations in ground water? Try looking for their degradates. *Sci Total Environ* 248:115–122
- Korom SF (1992) Natural denitrification in the saturated zone: a review. *Water Resour Res* 28(6):1657–1668
- Kretzschmar R, Robarge WP, Amoozegar A (1995) Influence of natural organic matter on colloid transport through saprolite. *Water Resour Res* 31(3):435–445
- Kross BC, Hallberg GR, Bruner DR, Libra RD, Rex KD, Weih MB, Vermace ME, Burmeister LF, Hall NH, Cherryholmes KL, Johnson JK, Selim MI, Nations BK, Seigley LS, Quade DJ, Dudler AG, Sesker MA, Lynch CF, Nicholson HF, Hughes JP (1990) Iowa State Well-Water Survey, water quality data: initial analysis. Tech Info Ser 19. Iowa Dept Natural Res
- Kruger EL, Zhu B, Coats JR (1996) Relative mobilities of atrazine, five atrazine degradates, metolachlor, and simazine in soils of Iowa. *Environ Toxicol Chem* 15(5):691–695
- Lampman W (1995) Susceptibility of groundwater to pesticide and nitrate contamination in predisposed areas of southwestern Ontario. *Water Qual Res J Can* 30(3):443–468
- Leistra M, Boesten JJTI (1989) Pesticide contamination of groundwater in western Europe. *Agric Ecosys Environ* 26:369–389
- Levallois P, Phaneuf D (1994) Contamination of drinking water by nitrates: analysis of health risks. *Can J Public Health* 85(3):192–196
- Lind AM (1985) Nitrate reduction in the subsoil. In: Golterman HL (ed) *Denitrification in the nitrogen cycle*. Plenum Press, New York, pp 145–156
- Lind AM, Eiland F (1989) Microbiological characterization and nitrate reduction in subsurface soils. *Biol Fertil Soils* 8:197–203
- Lund LJ, Adriano DC, Pratt PF (1974) Nitrate concentrations in deep soil cores as related to soil profile characteristics. *J Environ Qual* 3(1):78–82
- Madramootoo CA, Wiyo, KA, Enright P (1992) Nutrient losses through tile drains from two potato fields. *Am Soc Agric Eng* 8(5):639–646
- Martin JD, Crawford CG, Frey JW, Hodgkins GA (1996) Water-quality assessment of the White River Basin, Indiana – analysis of selected information on nutrients, 1980–92. US Geol Surv Water Resour Invest Rep 96–4192
- Masse L, Patni NK, Jui PY, Clegg BS (1996) Tile effluent quality and chemical losses under conventional and no tillage – Part 2: atrazine and metolachlor. *Trans ASAE* 39(5):1673–1679
- Mawdsley JL, Bardgett RD, Merry RJ, Pain BF, Theodorou MK (1995) Pathogens in livestock waste, their potential for movement through soil and environmental pollution. *Appl Soil Ecol* 2:1–15
- Mawdsley JL, Brooks AE, Merry RJ (1996) Movement of the protozoan pathogen *Cryptosporidium parvum* through three contrasting soil types. *Biol Fertil Soils* 21(1/2):30–36
- McKay LD, Fredericia J (1995) Distribution, origin, and hydraulic influence of fractures in a clay-rich glacial deposit. *Can Geotech J* 32:957–975
- McKay LD, Cherry JA, Gillham RW (1993) Field experiments in a fractured clay till. 2. Solute and colloid transport. *Water Resour Res* 29(12):3879–3890
- McMurry SW, Coyne MS, Perfect E (1998) Fecal coliform transport through intact soil blocks amended with poultry manure. *J Environ Qual* 27:86–92
- Mechsner KL, Hamer G (1985) Denitrification by methanotropic/methylotrophic bacterial associations in aquatic environments. In: Golterman HL (ed) *Denitrification in the nitrogen cycle*. Plenum Press, New York, pp 257–271
- Meyboom P (1967) Interior plains hydrogeological region. In: Brown IC (ed) *Groundwater in Canada*. Geol Surv Can Econ Rep 24, pp 131–158
- Milburn P, Richards JE (1994) Nitrate concentration of subsurface drainage water from a corn field in southern New Brunswick. *Can Agric Eng* 36(2):69–78
- Milburn P, O'Neill H, Gartley C, Pollock T, Richards JE, Bailey H (1991) Leaching of dinoseb and metribuzin from potato fields in New Brunswick. *Can Agric Eng* 33:197–204
- Miller JJ, Pawluk S, Beke GJ (1989) Evaporite mineralogy, and soil solution and groundwater chemistry of a saline seep from southern Alberta. *Can J Soil Sci* 62(2):273–286
- Miller JJ, Foroud N, Hill BD, Lindwall CW (1995) Herbicides in surface runoff and groundwater under surface irrigation in southern Alberta. *Can J Soil Sci* 75:145–148
- Moorman TB, Jaynes DB, Cambardella CA, Hatfield JL, Pfeiffer RL, Morrow AJ (1999) Water quality in Walnut Creek watershed: herbicides in soils, subsurface drainage, and groundwater. *J Environ Qual* 28(1):35–45
- Morales-Suarez VM, Llopis-Gonzalez AL, Tejerizo-Perez ML, Ferrandiz-Ferrugud J (1993) Concentration of nitrates in drinking water and its relationship with bladder cancer. *J Environ Pathol Toxicol Oncol* 12:229–236
- Mozaffari M, Sims JT (1994) Phosphorus availability and sorption in an Atlantic coastal plain watershed dominated by animal-based agriculture. *Soil Sci* 157(2):97–107
- Mueller DK, Hamilton PA, Helsel DR, Hitt KJ, Ruddy BC (1995) Nutrients in ground water and surface water of the United States – an analysis of data through 1992. *Water Resour Invest Rep* 95–4031. US Geol Surv, Denver, Colorado
- Muir CB, Baker BE (1976) Detection of triazine herbicides and their degradation products in tile-drain water from fields under intensive corn (maize) production. *J Agric Food Chem* 24:122–125
- Natsch A, Keel C, Troxler J, Zala M, Von-Albertin N, Defago G (1996) Importance of preferential flow and soil management in vertical transport of a biocontrol strain of *Pseudomonas fluorescens* in structured field soil. *Appl Environ Microbiol* 62(1):33–40
- Nolan BT, Ruddy BC, Hitt KJ, Helsel DR (1997) Risk of nitrate in groundwaters of the United States – a national perspective. *Environ Sci Technol* 31:2229–2236
- Ottow JGG, Burth-Gebauer I, Demerdash ME (1985) Influence of pH and partial oxygen pressure on the N₂O-N to N₂ ratio of denitrification. In: Golterman HL (ed) *Denitrification in the nitrogen cycle*. Plenum Press, New York, pp 101–120
- Parkin TB (1987) Soil microsites as a source of denitrification variability. *Soil Sci Soc Am J* 51:1194–1199
- Parkin TB, Simpkins WW (1995) Contemporary groundwater methane production from Pleistocene carbon. *J Environ Qual* 24:367–372
- Pivetz BE, Steenhuis TS (1995) Soil matrix and macropore biodegradation of 2,4-D. *J Environ Qual* 24:564–570
- Pivetz BE, Lelsey JW, Steenhuis TS, Alexander M (1996) A procedure to calculate biodegradation during preferential flow through heterogeneous soil columns. *Soil Sci Soc Am J* 60:381–388
- Postma D, Boesen C, Kristiansen H, Larsen F (1991) Nitrate reduction in an unconfined sandy aquifer: water chemistry, reduction processes, and geochemical modeling. *Water Resour Res* 27:2027–2045
- Power JF, Bond JJ, Sandoval FM, Willis WO (1974) Nitrification in Paleocene shale. *Science* 183:1077–1079
- Puckett LJ (1995) Identifying the major sources of nutrient water pollution. *Environ Sci Technol* 29(9):408A–414A
- Ray C, Schock SC (1996) Comparability of large-scale studies of agricultural chemical contamination of rural private wells. *Ground Water Monit Remed* (Spring 1996):92–102
- Reeder JD, Berg WA (1977) Nitrogen mineralization and nitrification in a Cretaceous shale and coal mine spoils. *Soil Sci Soc Am J* 41:922–927
- Remenda VH, van der Kamp G, Cherry JA (1996) Use of vertical profiles of $\delta^{18}\text{O}$ to constrain estimates of hydraulic conductivity in a thick, unfractured aquitard. *Water Resour Res* 32(10):2979–2987
- Robertson WD, Russell BM, Cherry JA (1996) Attenuation of nitrate in aquitard sediments of southern Ontario. *J Hydrol* 180:267–281

- Robertson WD, Schiff SL, Ptacek CJ (1998) Review of phosphate mobility and persistence in 10 septic system plumes. *Ground Water* 36(6):1000–1010
- Rodvang SJ, Schmidt-Bellach R, Wassenaar LI (1998) Nitrate in groundwater below irrigated fields in southern Alberta. CAESA Project #RES-041–93. Alberta Agriculture, Lethbridge, Alberta, Canada. joan.rodvang@gov.ab.ca
- Roy WR, Krapac IG (1994) Adsorption and desorption of atrazine and deethylatrazine by low organic carbon geologic materials. *J Environ Qual* 23:549–556
- Ruland WW, Cherry JA, Feenstra S (1991) The depth of fractures and active ground-water flow in a clayey till plain in southwestern Ontario. *Ground Water* 29(3):405–417
- Schuh WM, Klinkebiel DL, Gardner JC, Meyer RF (1997) Tracer and nitrate movement to groundwater in the Northern Great Plains. *J Environ Qual* 26:1335–1347
- Schwab GO, Fausey NR, Kopcak DE (1980) Sediment and chemical content of agricultural drainage water. *Trans ASAE* 23:1446–1449
- Scott CA, Geohring LD, Walter MF (1998) Water quality impacts of tile drains in shallow, sloping, structured soils as affected by manure application. *Am Soc Agric Eng* 14(6):599–603
- Sharpley AN, Daniel T, Sims T, Lemunyon J, Stevens R, Parry R (1999) Agricultural phosphorus and eutrophication. US Dept Agric, Agric Res Serv, ARS-149
- Simard RR, Cluis D, Gangbazo G, Beauchemin S (1995) P status of forest and agricultural soils from a watershed of high animal density. *J Environ Qual* 24:1010–1017
- Simpkins WW (1989) Genesis and spatial distribution of variability in the lithostratigraphic, geotechnical, hydrogeological, and geochemical properties of the Oak Creek Formation in southeastern Wisconsin. PhD Thesis, Univ Wisconsin-Madison
- Simpkins WW, Parkin TB (1993) Hydrogeology and redox geochemistry of CH₄ in a late Wisconsinan till and loess sequence in central Iowa. *Water Resour Res* 29(11):3643–3657
- Smith MS, Thomas GW, White RE, Ritonga D (1985) Transport of *Escherichia coli* through intact and disturbed soil columns. *J Environ Qual* 14(1):87–91
- Smith VH, Tilman GD, Nekola JC (1999) Eutrophication: impacts of excess nutrient inputs on freshwater, marine, and terrestrial ecosystems. *Environ Pollut* 100: 179–196
- Soller DE (1992) Text and references to accompany 'Map showing the thickness and character of Quaternary sediments in the glaciated United States east of the Rocky Mountains'. US Geol Surv Bull 1921
- Sommer JE, Hines FK (1991) Diversity in U.S. agriculture: a new delineation by farming characteristics. Agric Rural Econ Div, Econ Res Serv, US Dept Agric, Agric Econ Rep No 646
- Southwick LM, Willis GH, Johnson DC, Selim HM (1995) Leaching of nitrate, atrazine, and metribuzin from sugarcane in southern Louisiana. *J Environ Qual* 24:684–690
- Spalding RF, Exner ME (1993) Occurrence of nitrate in groundwater – a review. *J Environ Qual* 22:392–402
- Spalding RF, Kitchen LA (1988) Nitrate in the intermediate vadose zone beneath irrigated cropland. *Ground Water Monit Rev*, Spring 1988, pp 89–95
- Spalding RF, Parrott JD (1994) Shallow groundwater denitrification. *Sci Total Environ* 141:17–25
- Stamm C, Fluhler H, Gachter R, Leuenberger J, Wunderli H (1998) Preferential transport of phosphorus in drained grassland soils. *J Environ Qual* 27(3):515–521
- Starr RC, Gillham WR (1989) Controls on denitrification in shallow unconfined aquifers. In: Kobus HE, Kizzelbach W (eds) Contaminant transport in groundwater. Balkema, Rotterdam, pp 51–56
- Stehouwer RC, Dick WA, Traina SJ (1994) Sorption and retention of herbicides in vertically-oriented earthworm and artificial burrows. *J Environ Qual* 23(2):286–292
- Steinheimer TR, Scoggin KD, Kramer LA (1998) Agricultural chemical movement through a field-size watershed in Iowa: surface hydrology and nitrate losses in discharge. *Environ Sci Technol* 32:1048–1052
- Stephenson DA, Fleming AH, Mickelson DM (1988) Glacial deposits. In: Back W, Rosenshein JS, Seaber PR (eds) Hydrogeology. The geology of North America vol O-2. Geol Soc Am, Boulder, Colorado, pp 301–314
- Strathouse SM, Sposito G, Sullivan PJ, Lund LJ (1980). Geologic nitrogen: a potential geochemical hazard in the San Joaquin Valley, California. *J Environ Qual* 9(1):54–60
- Tesoriero AJ, Voss FD (1997) Predicting the probability of elevated nitrate concentrations in the Puget Sound Basin: implications for aquifer susceptibility and vulnerability. *Ground Water* 35(6):1029–1039
- Tiedje JM, Sexstone AJ, Myrold DD, Robinson JA (1982) Denitrification: ecological niches, competition and survival. *Antonie van Leeuwenhoek* 48(6):569–583
- Tindall JA, Petrusak RL, McMahon PB (1995) Nitrate transport and transformation processes in unsaturated porous media. *J Hydrol* 169:51–94
- Ueda S, Ogura N, Wada E (1991) Nitrogen stable isotope ratio of groundwater N₂O. *Geophys Res Lett* 18(8):1449–1452
- Ueda S, Ogura N, Yoshinari T (1993) Accumulation of nitrous oxide in aerobic groundwaters. *Water Res* 27(12):1787–1792
- USGS (1999) United States Geological Survey, Fact Sheet FS-244-95. National Water Quality Assessment Pesticide National Synthesis Project
- Van Stempvoort DR, Hendry MJ, Schoenau JJ, Drouse HR (1994). Sources and dynamics of sulfur in weathered till, western glaciated plains of North America. *Chem Geol* 111:35–56
- Vinten AJA, Vivian BJ, Wright F, Howard RS (1994) A comparative study of nitrate leaching from soils of differing textures under similar climatic and cropping conditions. *J Hydrol* 159:197–213
- Wassenaar LI, Hendry MJ, Aravena R, Fritz P (1990a) Organic carbon isotope geochemistry of clayey deposits and their associated porewaters, southern Alberta. *J Hydrol* 120:251–270
- Wassenaar L, Aravena R, Fritz P, Barker J (1990b) Isotopic composition (¹³C, ¹⁴C, ²H) and geochemistry of aquatic humic substances from groundwater. *Org Geochem* 15(4):383–396
- Weisenburger DD (1990) Environmental epidemiology of non-Hodgkin's lymphoma in eastern Nebraska. *Am J Ind Med* 18(3):303–305
- Whalen JK, Chang C (in press) Phosphorus accumulation in cultivated soils from long-term annual applications of cattle feedlot manure. *J Environ Qual*
- Wilson GB, Andrews JN, Bath AH (1990) Dissolved gas evidence for denitrification in the Lincolnshire Limestone groundwaters, eastern England. *J Hydrol* 113:51–60
- Wolf I, Russow R (2000) Different pathways of formation of N₂O, N₂ and NO in black earth soil. *Soil Biol Biochem* 32:229–239
- Zhang WL, Tian ZX, Zhang N, Li XQ (1996) Nitrate pollution of groundwater in northern China. *Short Comm, Agric Ecosys Environ* 59:223–231