elsewhere is very difficult and can provide only a rough estimate. Using Garrels et al.'s (1975) proposed global stream flux of 2.05 g/m^2 per year, total aluminum releases (including particulate material) were estimated to be approximately 20.45 million tonnes per year for Canada. Studies of weathering flux in selected Canadian and U.S. catchments (e.g., Likens et al. 1977; Kirkwood and Nesbitt 1991) yield similar or somewhat lower estimates (2 to 20 million tonnes per year) when extrapolated to the whole of Canada.

2.2.2.2 Anthropogenic sources

Very limited information is available on historical releases of the three aluminum salts. Accidental releases are reported to Environment Canada's National Analysis of Trends in Emergencies System (NATES) database and, more recently, the National Enforcement Management Information System and Intelligence System (NEMISIS). Between 1974 and 1991, 24 events released 316.2 tonnes of aluminum sulphate, mainly to land, and approximately 80% of the spilled material was recovered. Four accidental releases of aluminum chloride occurred in 1986 and 1987, and the product was not recovered on two occasions, resulting in a total release of 18.18 tonnes (Environment Canada 1995). Six spills involving the three aluminum salts subject to this assessment were reported from 1992 to 2008, all for aluminum sulphate. Approximately 40,000 liters of aluminum sulphate were released during these events, to both land and surface water, with no identified recovery of the spilled material. None of the reported incidents related to municipal or industrial effluent discharges (Environment Canada 2008b).

Municipal drinking water and wastewater treatment plants are the main users of aluminum sulphate, aluminum chloride and other aluminum-based polymeric products. Aluminum salts are used as coagulants and flocculants to cause fine materials that are suspended, soluble or both to agglomerate, for subsequent removal via sedimentation and filtration. As part of this agglomeration or coagulation process, most of the aluminum associated with the added aluminum salt hydrolyses to aluminum hydroxide, which precipitates and becomes part of the floc structure. As such, it makes up a part of the sludge generated by the treatment process. A small amount of the aluminum added may stay with the finished water in either colloidal particulate ($Al(OH)_3$) or soluble form (e.g., $AlOH^{2+}$, $Al(OH)_2^+$, $Al(OH)_3$, $Al(OH)_4^-$), dictated by the conditions of the treatment process and in particular, the pH (see Figure 2.1 below and from Stumm and Morgan 1981) .

While no comprehensive inventory of releases of aluminum associated with commercial use of aluminum salts exists, order-of-magnitude estimates derived from information provided by Canadian producers and users confirm that most releases are associated with wastewater treatment processes (approximately 43% in 2006), with drinking water treatment plants accounting for the majority of the remainder (about 36%; Table 2.3; Cheminfo Services Inc. 2008). All other sources are relatively minor. Again, most quantities are reported in terms of the elemental aluminum present in the respective salts. Approximately three quarters of the releases are to land, including: landfill, application on farms, and permanent lagoons. It is estimated that 5% of the aluminum used at pulp and paper mills for paper sizing is released to water courses (rivers or lakes), while 95% is contained on the paper, which is assumed to receive eventual disposal to landfills and composting in a minor, but growing proportion (2008 email from Canadian Wastewater Association to J. Pasternak, Environment Canada; unreferenced).

Table 2.3 Estimated total releases in Canada of aluminum from aluminum salts[1] for 2006, by application
(kilotonnes aluminum; Cheminfo Services Inc. 2008)

	Drinking Water	**Receiving Water**	**Storage in Lagoon**	**Landfill**	**Farms**	**Total**
	Water	Water	Land	Land	Land	
Municipal Drinking Water Treatment Plants[2]	0.1	3.2	0.1	2.2		5.7
Municipal Wastewater Treatment Plants[3]		0.4	0.06	2.0	4.5	6.9
Industrial Fresh Water Treatment	0.02	0.5	0.02	0.4		1.0
Industrial Wastewater Treatment		0.06	0.01	0.3	0.6	0.9
Pulp and Paper Additive		0.1		1.2		1.2
Miscellaneous				0.2		0.2
Total	0.12	4.3	0.2	6.3	5.1	16.0
Percent of Total						
Municipal Drinking Water Treatment Plants	1%	20%	1%	14%		36%
Municipal Wastewater Treatment Plants		3%	0.4%	12%	28%	43%
Industrial Fresh Water Treatment	0.1%	3%	0.1%	2%		6%
Industrial Wastewater Treatment		0.3%	0.05%	2%	4%	6%
Pulp and Paper Additive		0.4%		7%		8%
Miscellaneous				2%		2%
Total	1%	27%	1%	39%	32%	100%

[1] Includes aluminum sulphate, aluminum chloride, polyaluminum sulphate, polyaluminum chloride, aluminum chlorohydrate and sodium aluminate.

[2] This excludes aluminum that is contained in effluents sent to wastewater treatment plants

[3] This includes aluminum that is contained in effluents obtained from drinking water treatment plants

Most of the aluminum releases are from the use of aluminum sulphate, which is the aluminum salt having the highest quantity of consumption in Canada (Table 2.4; Cheminfo Services Inc. 2008).

Table 2.4 Estimated total releases of aluminum, by salt, for 2006 (kilotonnes aluminum; Cheminfo Services Inc. 2008)

	Drinking Water	**Receiving Water**	**Storage in Lagoon**	**Landfill**	**Farms**	**Total**
Aluminum Sulphate	0.1	3.6	0.2	5.0	3.1	12.0
Polyaluminum Chloride	0.02	0.7	0.03	0.9	0.6	2.3
Aluminum Chlorohydrate	0.01	0.1	0.01	0.2	0.1	0.5
Polyaluminum Sulphate	0.003	0.1	0.005	0.1	0.1	0.3
Sodium Aluminate	0.01	0.2	0.01	0.3	0.2	0.7
Aluminum Chloride	0.004	0.1	0.00	0.1	0.1	0.3
Total	0.2	4.8	0.2	6.6	4.2	16.0

Approximately 2% of the total aluminum used by municipalities for drinking water treatment (6.8 kilotonnes; see Table 2.2) ends up in drinking water (Table 2.3; Cheminfo Services Inc. 2008). A survey of 102 Canadian water treatment facilities conducted in 2006 found that over 80% of drinking water treatment plants (DWTPs) that use aluminum salts as coagulants and flocculants measure the concentration of aluminum in the treated water. The survey considered data from municipal drinking water and wastewater treatment facilities across Canada, primarily from larger municipalities (population > 100,000), although a small sample of small-to-medium sized municipalities was included (population range 20,000-100,000; Cheminfo Services Inc. 2008). Outlet concentrations in drinking water at the surveyed DWTPs which used aluminum ranged from 0.005 to 0.2 mg/L, with an average value of 0.067 mg/L. For comparison, Health Canada's *Guidelines for Canadian Drinking Water Quality* are 0.1 mg/L for conventional treatment plants using aluminum-based coagulants and 0.2 mg/L for other treatment systems using aluminum-based coagulants (Health Canada 2007a).

Less than half of the aluminum used at drinking water plants is released to receiving waters – mostly as solid aluminum hydroxide sludge (Cheminfo Services Inc. 2008). Notable examples of this practice occur in water treatment plants in Toronto. Most of the remaining aluminum is contained in sludge that is sent to landfill. Some of the sludge from drinking water facilities (commonly called "filter backwash solids"), in dilute form, may also be sent to wastewater treatment facilities in the municipality. Results from the 2006 survey suggest that approximately 16% of the aluminum used at drinking water treatment facilities is contained in sludge sent to nearby wastewater treatment facilities. A very small portion (~2%) remains permanently stored in lagoons, which for assessment purposes has been assumed to be a land destination. The 2006 survey did not identify any sludge from drinking water treatment plants going to farms; however, it is possible that some disposal by this method may be occurring in Canada as a small proportion of DWTP sludge was identified for landfarming in the earlier survey conducted for 1995 and 1996 (Germain et al. 2000).

In a study done with sludge from Calgary and Edmonton, AEC (1987) found that less than 0.02% of aluminum bound with sludge (containing 78,187 mg Al/kg dw) was released in water (i.e., 0.20 to 0.32 mg/L). Srinivasan et al. (1998) studied the speciation of aluminum at six different stages of water treatment at Calgary's DWTP. Total aluminum concentrations ranged from 0.038 to 5.760 mg/L, and dissolved inorganic aluminum concentrations varied from 0.002 to 0.013 mg/L. George et al. (1991) measured monomeric aluminum concentrations of less than 0.06 mg/L in alum sludge from ten different DWTPs containing up to a total of 2,900 mg Al/L; Calgary's DWTP was one of the plants studied.

Calgary's DWTP reported the aluminum content in backwash water following the cleaning of its filters. Dissolved aluminum levels ranged from 0.07 to 0.44 mg/L, and total aluminum concentrations varied from 0.76 to 3.3 mg/L. The backwash waters from this DWTP were not released to the river but were treated and sold as fertilizer (Do 1999).

Most of the aluminum discharged from municipal wastewater treatment plants (MWWTPs) surveyed in the 2006 study is associated with sludge. Approximately two thirds of the aluminum in MWWTP sludge is applied to farmland, with most of the balance (around 30%) being sent to landfill. About 5% of total aluminum releases are to surface waters and a very small proportion (less than 1%) is stored permanently in lagoons (Table 2.3). In Quebec City, the sludge from the drinking water treatment plant is directed to MWWTP where the resulting sludge is dried and incinerated with residential waste (co-incineration). The mineral and non-combustible component of the sludge is then landfilled (2008 email from Canadian Wastewater Association to J. Pasternak, Environment Canada; unreferenced). In most cases, the sludge sent to landfills was first sent for anaerobic digestion (where methane gas is generated from the organic content and used for plant energy) and the remaining solids concentrated to remove excess water. Some provinces (e.g., Alberta, Ontario and Quebec) have guidelines for the disposal of sewage sludge on agricultural land; spreading on agricultural land is permitted only when the pH is greater than 6.0 or when liming and fertilization (if necessary) are done. Although not a common practice, a few of the municipalities participating in the 2006 survey provided measured concentrations for aluminum present in sludge solids from their plants. In general, these values were in the range of 10 to 60 mg per gram of solids (dry basis) (Cheminfo Services Inc. 2008).

Final effluent concentrations of aluminum were not always available for MWWTPs participating in the 2006 survey (Cheminfo Services Inc. 2008). Where data were available, reported concentrations ranged from 0.013 to 1.200 mg/L, with an average value (weighted by water volume treated) of 0.816 mg/L. The form of the aluminum measured was not specified. Many of the MWWTPs surveyed relied on substances other than aluminum to treat wastewater, such as iron salts (ferrous and ferric chloride) and/or polyacrylamides, while others did not use any chemicals in their water treatment process.

Only two respondents to the 2006 survey provided information on aluminum concentrations in receiving waters in the vicinity of their effluent outfalls. The typical background level of dissolved aluminum in Lake Ontario in the vicinity of Toronto was reported to be approximately 0.010 mg/L, while typical concentrations in the North Saskatchewan River near Edmonton were 0.020 to 0.040 mg/L (Cheminfo Services Inc. 2008). These data are insufficient to determine in a useful way the contribution of aluminum from aluminum salt consumption in receiving waters. In the original State of the Science (SOS) report (Environment Canada and Health Canada 2000), it was determined that while extensive data on total aluminum concentrations in Canadian surface water are available, few data exist in areas close to sites where releases occur. The situation for sediment and soil is similar, in that data exist for the Canadian environment in general, but not for areas where releases occur. The state of available relevant concentration data has not changed since 2000.

In addition, changes in policies and procedures relating to the direct release of treatment plant effluents into surface waters have occurred since the publication of the original SOS report. In 1993, a total aluminum concentration of 36 mg/L was measured just downstream of the Regional Municipality of Ottawa-Carleton's (RMOC) DWTP discharge pipe, while the concentration 200 m downstream of the plant was 0.5 mg/L (Germain et al. 2000). Similarly, in 1998, sediment concentrations in the Ottawa River were 125,160, 51,428 and 41,331 mg/kg dw at points closest to, 300 m, and 500 m downstream of the DWTP, respectively, and were significantly elevated compared with control and upstream values of 17,543 and 20,603 mg/kg dw, respectively. In 2008, all wastes from the plant were diverted to a nearby MWWTP, effectively eliminating the direct discharge of aluminum-bearing sludge into the river (Environment Canada 2008c). However, it will likely take some time before conditions in bottom sediment in the vicinity of the DWTP outfall return to those in line with non-impacted areas.

Germain et al. (2000) reported mean total aluminum levels in the effluent of some MWWTPs using aluminum salts. Concentrations varied from 0.03 to 0.84 mg/L, and the maximum value reported by one plant reached 1.8 mg/L. These figures are in the same order of magnitude as those reported by Orr et al. (1992) for 10 Ontario MWWTPs and by MEF and Environnement Canada (1998) for 15 Quebec MWWTPs, and agree well with those of Cheminfo Services Inc. (2008) reported above. Some plants do not use aluminum-based coagulants and flocculants but still reported aluminum levels in their effluents; their mean total aluminum levels ranged from 0.003 to 0.90 mg/L (Germain et al. 2000). Many wastewater treatment plants, such as those in Quebec, receive influents from combined sewers which collect both wastewater and stormwater. In these cases, part of the solids content of the influent will come from urban drainage that could contain aluminum-bearing solids from erosion processes and other sources. The content of wastewater treatment plant influents is determined by the nature and proportions of their primary inputs (i.e., residential, commercial, institutional, industrial) and contaminants present in these waters may also appear in the effluent, depending on the treatment process (2008 email from Canadian Wastewater Association to J. Pasternak, Environment Canada; unreferenced).

Federal, provincial/territorial and municipal governments all play a role in managing treated drinking water quality in Canada (Cheminfo Services Inc. 2008). Voluntary guidelines have been established for aluminum concentrations in drinking water, and while provincial/territorial and municipal government authorities recognize these guidelines, they have not been adopted as mandatory standards. For example, in British Columbia, Alberta, Newfoundland and Manitoba, the *Guidelines for Canadian Drinking Water Quality - Technical Documents: Aluminum* as specified by Health Canada (i.e., 0.1 mg/L for conventional treatment plants using aluminum-based coagulants and 0.2 mg/L for other treatment systems using aluminum-based coagulants) are recognized, but specific standards have not yet been fully incorporated into operating permits for treatment facilities. In Ontario, Certificates of Approval with a limit of 0.1 mg/L are issued to drinking water treatment plants; however, this limit is included as a guideline rather than a standard. In Quebec, no limits on aluminum content in drinking water are found in the provincial regulations (including the

Regulation Respecting the Quality of Drinking Water), and operating approvals are not required by wastewater treatment facilities (Cheminfo Services Inc. 2008).

Similarly, no federal legislation specific to municipal wastewater effluent discharges is in place (Cheminfo Services Inc. 2008). The federal government enforces CEPA (1999) that governs the releases of toxic substances to the environment, and the *Fisheries Act* that protects Canadian waters against the deposit of deleterious substances into fish habitat. In recent years, federal, provincial, and territorial governments have been working to develop a *Canada-wide Strategy for the Management of Municipal Wastewater Effluent* through the Canadian Council of Ministers of the Environment (CCME 2008); however, release standards for aluminum are not currently proposed or under development under the Strategy.

Less information is available on industrial releases of aluminum salts. The pulp and paper sector is the primary industrial user of aluminum salts, with applications in water treatment and as a paper additive. Alum is more commonly used for water treatment at mills in the warmer months of the year, while polyaluminum chloride (PAC) and polyaluminum silicate sulphate (PASS) have been found to be more effective winter coagulants. Recent quantitative release data for industrial uses are not available, although average concentrations of residual aluminum in treated water are estimated to be in the range of 0.02 mg/L (Cheminfo Services Inc. 2008). A 35% to 40% decrease in use of aluminum salts as a pulp and paper additive has been reported for the period 2000 to 2006, indicating a significant reduction in demand for this application (Cheminfo Services Inc. 2008).

Germain et al. (2000) reported mean total aluminum levels ranging from 0.46 to 4.8 mg/L in wastewaters released into rivers by the pulp and paper industry over the period 1990 to 1997. Mean total aluminum levels measured for other types of industries ranged from 0.01 to 2.3 mg/L. Since 1995, pulp and paper mills have been subject to the *Pulp and Paper Effluent Regulations* passed in 1992 under the *Fisheries Act*. In Quebec, for example, implementation of these regulations has led to a mean reduction of approximately 60% in total aluminum concentrations present in effluents (Germain et al. 2000). Environmental Effects Monitoring (EEM) reports published by the pulp and paper industry provide information on the distance from point of discharge that is required to dilute an effluent to less than 1% in the receiving water body. In some cases, only a few metres were needed, while in others, up to 300 km was required. In these cases, water input from other watercourses was needed to achieve dilution to 1%.

Sludge containing aluminum from the salts used in industrial water treatment can be sent to landfill or to steam boilers and co-generation units that handle bark, sludge, or other fuels (Cheminfo Services Inc. 2008). Aluminum may be present in the fly ash after burning of the sludge, although a small portion may also be emitted to air along with particulate matter (PM) emissions. No data are available on aluminum concentrations in fly ash; however, potential PM emissions are usually controlled with baghouses, electrostatic precipitators or other PM control systems.

The use of sludge derived from aluminum-based water treatment facilities as a soil amendment is the primary pathway by which aluminum salts enter the terrestrial environment. It is likely that the amount of aluminum added to soil through this practice is small in comparison with aluminum naturally present in soil. Sludge disposal guidelines specifying maximum application rates and soil pH requirements exist for a number of provinces. In Ontario, sludge application rates cannot exceed 8 tonnes solids/ha/5 years and the pH of the receiving soil must be greater than 6.0 or liming is required (ME and MAFRA 1996). Still, potential exists for the release of aluminum into soil due to high amounts of the metal present in sludge residuals (Mortula et al. 2007). In addition, a shift in soil pH at the site of sludge application could mobilize aluminum in the sludge by shifting the chemical equilibrium towards more soluble forms of the metal. Soil acidification may occur during high water discharge events (e.g., storm events), when water entering the sludge deposition area has interacted with organic matter or travelled through more acidic upper mineral soils (Pellerin et al. 2002). Aluminum solubilized in this process is then available to be transported to adjacent soils or water bodies along shallow flow paths in the soil.

2.3 Exposure Characterization

2.3.1 Environmental Fate

The sections below summarize the information available on the distribution and fate of aluminum and the three aluminum salts, aluminum chloride, aluminum nitrate and aluminum sulphate, in the environment. A more detailed discussion on environmental fate can be found in Bélanger et al. (1999), Germain et al. (2000) and Roy (1999a).

2.3.1.1 Air

In air, hydrated aluminum chloride will react with moisture to produce hydrochloric acid and aluminum oxide (Vasiloff 1991). Aluminum nitrate and aluminum sulphate are likely to react in the same way, forming nitric and sulfuric acids, respectively. As the three aluminum salts that are the subject of this assessment are not usually emitted to air, the amount of aluminum present in air due to these salts is expected to be negligible compared with amounts coming from the natural erosion of soil (Environment Canada and Health Canada 2000).

2.3.1.2 Water

Natural sources of aluminum release to aquatic systems include weathering of rocks, glacial deposits and soils and their derivative minerals, and atmospheric deposition of dust particles. The most obvious increases in aluminum concentrations have consistently been associated with environmental acidification (Driscoll and Schecher 1988; Nelson and Campbell 1991). For this reason, recently observed changes in global climate and alterations in the acidity of atmospheric and oceanic systems, both resulting at least in part from human activities, have the potential to influence the presence and mobility of aluminum in the environment (Pidwirny and Gow 2002; Crane et al. 2005). The relationship is complex, however, and more research is needed in order to elicit the nature of potential impacts and their consequences for biota. Crane et al. (2005) postulated that increasingly severe weather patterns occurring as a consequence of global climate change, such as an increased incidence of prolonged heavy rainfall in some areas, may intensify physical and chemical weathering processes. When combined with the effects of acidification of waters, this could lead to significant changes in the speciation and mobility of aluminum and other metals.

Soil minerals such as gibbsite ($Al(OH)_3$) and jurbanite ($AlSO_4(OH)\cdot 5H_2O$) are considered the primary sources of aluminum release to the aqueous environment, especially in poorly buffered watersheds (Driscoll and Schecher 1990; Campbell et al. 1992; Kram et al. 1995). In more buffered watersheds, a solid-phase humic sorbent in soil is involved in the release of aluminum (Cronan et al. 1986; Bertsch 1990; Cronan and Schofield 1990; Cronan et al. 1990; Seip et al. 1990; Taugbol and Seip 1994; Lee et al. 1995; Rustad and Cronan 1995).

The three aluminum salts—chloride, nitrate and sulphate—are highly soluble and will form various dissolved species on contact with water. The fate and behaviour of aluminum in the aquatic environment are very complex. Aluminum speciation, which refers to the partitioning of aluminum among different physical and chemical forms, and aluminum solubility are affected by a wide variety of environmental parameters, including pH, solution temperature, dissolved organic carbon (DOC) content, and the presence and concentrations of numerous ligands. Metals in solution may be present as dissolved complexes, as "free" or aquo ions, in association with particles, as colloids or as solids in the process of precipitating. Colloidal particles (i.e., those in the range of 0.001 to 1 µm) are important in the transport of metals in stream ecosystems (Kimball et al. 1995; Schemel et al. 2000), as well as the accumulation of metals in sediment (Church et al. 1997) and biofilm (Besser et al. 2001), and the transfer to biota. Farag et al. (2007) proposed that colloids and biofilm may play critical roles in the pathway of metals to the food chain. The reactivity of aluminum, as well as geochemical behaviour, bioavailability and toxicity, are dependent upon its speciation (Neville et al. 1988; Gagnon and Turcotte 2007).

There are two general types of ligands that can form strong complexes with aluminum in solution. Inorganic ligands include anions such as sulphate (SO_4^{2-}), fluoride (F^-), phosphate (PO_4^{3-}), bicarbonate (HCO_3^-) and hydroxide (OH^-), among others. Organic ligands include oxalic, humic and fulvic acids (Driscoll et al. 1980; Sparling and Lowe 1996). The relative concentrations of the inorganic and organic ligands generally determine the proportions and type of complexes that are formed in solution.

Interactions with pH (Campbell and Stokes 1985; Hutchinson and Sprague 1987; Schindler 1988; Driscoll and Postek 1996) and DOC (Hutchinson and Sprague 1987; Kullberg et al. 1993) are of primary importance to the fate and behaviour of aluminum. DOC will complex with aluminum in water, forming aluminum-organic complexes and reducing concentrations of monomeric forms of aluminum (Farag et al. 1993; Parent et al. 1996). At a pH of 4.5, a concentration of 1 mg DOC/L can complex approximately 0.025 mg Al/L, with this complexing capacity increasing as pH increases (Neville et al. 1988). Fractions of dissolved organic aluminum were estimated for various rivers in Canada using the MINEQL+ (Schecher and McAvoy 1994) and WHAM (Tipping 1994) models; the results suggested that the importance of complexation with dissolved organic material (DOM) decreased over the pH range 7.0 to 8.5, likely due to reduced concentrations of the Al^{3+} and $AlOH^{2+}$ species which can associate with DOM (Fortin and Campbell 1999).

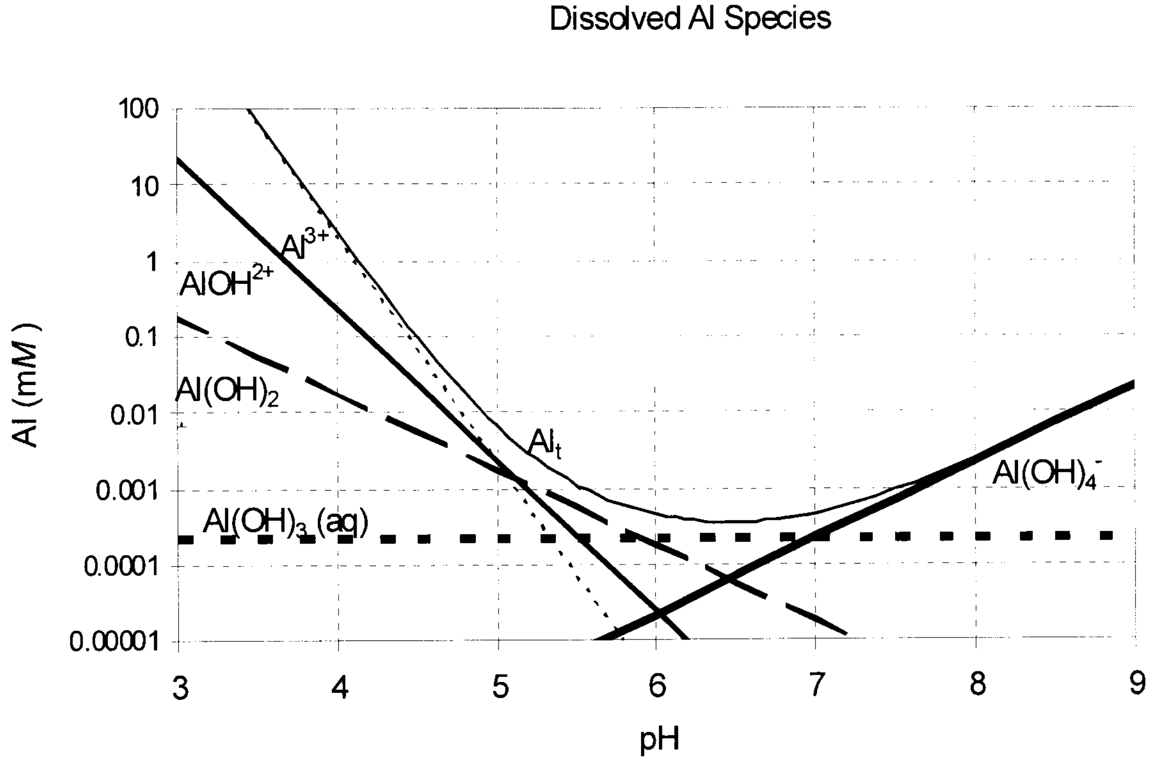
Aluminum is a strongly hydrolysing metal and is relatively insoluble in the neutral pH range (6.0–8.0) (Figure 2.1). In the presence of complexing ligands and under acidic ($pH < 6$) and alkaline ($pH > 8$) conditions, aluminum solubility is enhanced. At low pH values, dissolved aluminum is present mainly in the aquo form (Al^{3+}). Hydrolysis occurs as pH rises, resulting in a series of less soluble hydroxide complexes (e.g., $Al(OH)^{2+}$, $Al(OH)_2^+$). Aluminum solubility is at a minimum near pH 6.5 at 20°C and then increases as the anion, $Al(OH)_4^-$, begins to form at higher pH (Driscoll and Schecher 1990; Witters et al. 1996). Thus, at 20°C and $pH < 5.7$, aluminum is present primarily in the forms Al^{3+} and $Al(OH)^{2+}$. In the pH range 5.7 to 6.7, aluminum hydroxide species dominate, including $Al(OH)^{2+}$ and $Al(OH)_2^+$, and then $Al(OH)_3$. Typically, at a pH of approximately 6.5, $Al(OH)_3$ predominates over all the other species. In this range, aluminum solubility is low, and availability to aquatic biota should also be low. At $pH > 6.7$, $Al(OH)_4^-$ becomes the dominant species. Aluminum-hydroxide complexes predominate over aluminum-fluoride complexes under alkaline conditions. However, the aluminum speciation determined for some rivers in Canada indicated that only one river, of pH less than 7, had a significant concentration (> 1%) of aluminum-fluoride complexes (Fortin and Campbell 1999). It is important to note that the various aluminum species described above are always present simultaneously at any pH value. The influence of pH in aquatic systems is mainly to change the proportion of all the species as the pH changes (2008 email from Canadian Wastewater Association to J. Pasternak, Environment Canada; unreferenced).

Mononuclear aluminum hydrolytic products combine to form polynuclear species in solution (Bertsch and Parker 1996). Aluminum begins to polymerize when the pH of an acidic solution increases to over 4.5:

$$2Al(OH)(H_2O)_5^{2+} \rightleftharpoons Al_2(OH)_2(H_2O)_8^{4+} + 2H_2O$$

Polymerization gradually proceeds to larger structures, eventually leading to the formation of the Al_{13} polycation (Parker and Bertsch 1992a, 1992b). In nature, conditions that favour the formation of polynuclear forms of aluminum can occur during the liming of acidic aluminum-rich watersheds (Weatherley et al. 1991; Lacroix 1992; Rosseland et al. 1992) and possibly during the addition of alum to circumneutral waters (Neville et al. 1988; LaZerte et al. 1997).

Figure 2.1 Solubility of aluminum species (and total aluminum, Al_t) in relation to pH in a system in equilibrium with microcrystalline gibbsite
(0.001 mM = 0.027 mg/L; Driscoll and Schecher 1990)



Temperature has been shown to influence the solubility, hydrolysis and molecular weight distribution of aqueous aluminum species as well as the pH of solutions. Lydersen et al. (1990b) reported a higher degree of aluminum hydrolysis and greater polymerization to high molecular weight species in inorganic aluminum solutions stored for one month at 25°C compared with those stored for an equivalent period at 2°C. The researchers hypothesized that more advanced polymerization evident at the higher temperature resulted in more deprotonation and condensation reactions, possibly accounting for the observed lower pH of the 25°C test solutions (range 4.83 to 5.07 versus 5.64 to 5.78 in the solutions at 2°C). Solubility and sedimentation were significantly higher at 25°C, with dissolution controlled by microcrystalline gibbsite. While substantial amounts of high molecular weight aluminum species were present in the solution at 2°C, little sedimentation was observed. Dissolution at the lower temperature appeared controlled by an amorphous $Al(OH)_3(s)$ with much higher solubility and, therefore, a high proportion of the high molecular weight inorganic aluminum species remained as colloids in the solution. The effects of low temperature on the coagulation efficiency of aluminum sulphate have been studied in relation to water treatment processes (Braul et al. 2001; Wobma et al. 2001; Kundert et al. 2004). The results provide further evidence that temperature-dependent fluctuations in the predominant aluminum species present in an aquatic system may occur in regions of Canada that experience marked seasonal fluctuations in temperature.

When released into water, for example within a drinking water treatment plant (DWTP), most of the aluminum associated with the aluminum salts considered in this report hydrolyses to form aluminum hydroxides (Hossain and Bache 1991). Reactions between aluminum salts, water and associated "impurities" result in the formation of a floc, which separates from the water phase to form alum sludge. A small fraction of the aluminum can stay in the water in either colloidal or dissolved form. Barnes (1985) describes the different reactions involved in the formation of aluminum hydroxide in aqueous solution; the overall reaction can be represented by the following equation:

$$Al_2(SO_4)_3 + 6H_2O \rightleftharpoons 2Al(OH)_3^0 + 3H_2SO_4$$

The aluminum hydroxide present in sludge is expected to remain mostly solid following release into surface water. Ramamoorthy (1988) showed that less than 0.2% of the aluminum hydroxide present in sludge was released in supernatant water at a pH of 6 and less than 0.0013% was released at pH 7.65. In both cases, aluminum hydroxide was present mostly in particulate form. At these pH values, aluminum solubility is low and kinetics favour the formation of solid aluminum hydroxide.

When used to treat sewage water, alum will also react with phosphate, as shown in the following reaction (Romano 1971; Barnes 1985):

$$Al_2(SO_4)_3 + 2PO_4^{3-} \rightleftharpoons AlPO_4(s) + 3SO_4^{2-}$$

This process has been used for many years to treat phosphorus in wastewaters, as well as to reduce phosphorus levels in runoff from land fertilized with poultry litter and restore phosphorus-enriched eutrophic lakes (Lewandowski et al. 2003).

Kopáček et al. (2001) examined the possible role of aluminum in influencing the natural cycling of phosphorus, which is often a limiting nutrient in aquatic systems. The researchers postulated that aluminum from nearby lower pH soils may enter circumneutral water bodies during episodic acidification events, such as spring melt, leading to the formation of colloidal aluminum oxyhydroxide flocs which will strongly adsorb orthophosphate in the water column. The phosphate-bound particulate aluminum settles onto the lake bottom, removing the bioavailability of this phosphorus to organisms in the water column. The increasing sediment concentrations of aluminum-phosphorus floc disrupt the redox-dependent cycling of phosphorus in the lake, indicating that while aluminum does not enter directly into biotic cycles, it is capable of influencing the biogeochemical cycles of substances that are integral to living systems. Based on the solubility characteristics of aluminum (see Figure 2.1), this process may also occur when acidic waters, which generally contain the most aluminum (Gensemer and Playle 1999), enter downstream waters of higher pH.

The cycling and availability of other trace elements (e.g., nitrogen) and of organic carbon may also be influenced by the adsorption and coagulation properties of aluminum (Driscoll and Schecher 1990; Lee and Westerhoff 2006). Dissolved organic carbon (DOC) has been shown to provide an important weak acid/base buffering system that aids in the regulation of pH in dilute acidic waters and removal of DOC by adsorption to aluminum could adversely affect pH conditions in a water body (Johannessen 1980; Driscoll and Bisogni 1984). As well, coagulation and removal of DOC and other light attenuating materials may alter patterns of water column heating, resulting in decreased thermal stability in a water body (Almer et al. 1974; Malley et al. 1982). Changes to the heating pattern and thermal stratification of a lake can profoundly impact ecosystems by altering the vertical transport of solutes and restricting coldwater fisheries (Driscoll and Schecher 1990).

Aluminum is highly reactive in seawater and will be rapidly scavenged by particulate matter when released into this medium (Nozaki 1997). The mean oceanic residence time for aluminum is predicted to be short compared to some other elements, in the range of 100 to 200 years, with vertical distribution dictated by terrestrial and atmospheric inputs at the surface, intense particle scavenging throughout the water column, and some regeneration in bottom waters (Orians and Bruland 1985). The higher ionic strength and relative magnitude of individual ion concentrations in saline waters compared with freshwaters lead to differences in coagulation reactions with aluminum salts. Duan et al. (2002) identified distinctly different characteristics between the two water types with respect to colloid destabilization, coagulation mechanisms, and colloidal removal. These differences can become important when water treatment processes include release of effluent or backwash materials into marine or brackish waters.

2.3.1.3 Sediment

Sediment, where metals are generally considered less biologically available, is nonetheless an important medium for aluminum (Stumm and Morgan 1981; Campbell et al. 1988; Tessier and Campbell 1990). Aluminum occurs naturally in aluminosilicates, mainly as silt and clay particles, and can be bound to organic matter (fulvic and humic acids) in sediments (Stumm and Morgan 1981). At pH > 5.0, dissolved organic matter (DOM) can co-precipitate with aluminum, thereby controlling its concentrations in lakes with elevated concentrations of DOM (Urban et al. 1990). DOM plays a similar role in peatlands (Bendell-Young and Pick 1995). At pH < 5.0, the cycling of aluminum in lakes is controlled by the solubility of mineral phases such as microcrystalline gibbsite (Urban et al. 1990). Lakes receiving drainage from acidified watersheds can act as a sink for aluminum (Troutman and Peters 1982; Dillon et al. 1988; Dave 1992).

Experimental acidification of lakes and limnocorrals has shown that aqueous aluminum concentrations rapidly increase in response to acidification (Schindler et al. 1980; Santschi et al. 1986; Brezonick et al. 1990). Mass-balance studies have demonstrated that retention of aluminum by sediments decreases as pH decreases (Dillon et al. 1988; Nilsson 1988). Under such conditions, sediments in acidified watersheds can provide a source of aluminum to the water column (Nriagu and Wong 1986). Based on calculation of fluxes in acidic lakes, Wong et al. (1989) suggested that sediment is a source of aluminum to the overlying water column.

The release of aluminum hydroxide sludge from drinking water treatment plants (DWTPs) directly to surface waters is the primary pathway by which aluminum from aluminum salts enters sediment. If water velocity is low at the point of discharge, much of the released sludge will settle onto the surface of local sediment. Since, in Canada, the waters receiving such discharges are typically circumneutral, the solubility of aluminum in the sludge will generally be minimal (Environment Canada and Health Canada 2000).

2.3.1.4 Soil

Atmospheric deposition of aluminum to soil is attributed mostly to the deposition of dust particles and is generally low (Driscoll et al. 1994). Volcanic activity can also act as a major natural source of aluminum to soil (Pichard 2005). Aluminum is the third most abundant element in the earth's crust, making up approximately 8% of rocks and minerals and accounting for about 1% of the total mass of the Earth (Landry and Mercier 1992; Skinner and Porter 1989). Approximately 75% of Canada is covered by glacial till (Landry and Mercier 1992); examples of aluminum-bearing minerals inherited from glacial till (i.e., primary minerals) are feldspars, micas, amphiboles and pyroxenes. Transformation of primary minerals by chemical weathering reactions results in new solid phases (i.e., secondary minerals). Aluminum-bearing secondary minerals such as smectite, vermiculite and chlorite are often found in Canadian soils developed on glacial till.

Inputs of aluminum into soil solutions usually occur by mobilization of aluminum derived from the chemical weathering of soil minerals. The most important reaction in the chemical weathering of the common silicate minerals is hydrolysis. However, aluminum is not very soluble over the normal soil pH range; thus, it generally remains near its site of release to form clay minerals or precipitate as amorphous or crystalline oxides, hydroxides or hydrous oxides. Silica is much more soluble than aluminum at normal soil pH and is always in excess of the amount used to form most clay minerals, so that some is removed from the soil system in leachates (Birkeland 1984). In some parts of the world, the extent of chemical transformation by chelation is believed to exceed that by hydrolysis alone. In forest soils of cold and humid regions, such as those of eastern Canada, aluminum is believed to be transported from upper to lower mineral soil horizons by organic acids leached from foliage and the slow decomposition of organic matter in the forest floor (Courchesne and Hendershot 1997). The movement of aluminum-organic complexes stops when the soil solution becomes saturated (or when the aluminum-to-organic-carbon ratio reaches a critical value), thereby reducing their solubility. In pristine conditions, aluminum is normally retained within the B horizon of the soil. A third important reaction involving aluminum is the transformation of one mineral into another through the exchange of interlayer cations (Sposito 1996).

Although the dissolution and precipitation reactions of aluminum-bearing minerals are often good indicators of the solubility of aluminum in soils, they are by no means the only pedogenic processes controlling the concentrations of aluminum in soil solutions. Many other processes may partly control the uptake of aluminum by plants and soil organisms. Aluminum may be 1) adsorbed on cation exchange sites, 2) incorporated into soil organic matter, 3) absorbed by vegetation or 4) leached out of the soil system (Ritchie 1995). Aluminum can form stable complexes with various types of soluble and insoluble organic matter, from simple low-molecular weight organic acids to humic and fulvic acids (Vance et al. 1996; Ritchie 1995). Organic ligands play an important role in the speciation of aluminum in soil solutions (David and Driscoll 1984; Driscoll et al. 1985; Ares 1986).

In eastern Canada, the atmospheric deposition of strong acids, such as nitric acid and sulfuric acid, has accelerated the natural acidification of soil. The increased H^+ activity (lower pH) in the soil solution creates a new equilibrium where more Al^{3+} is dissolved in the soil solution, cation nutrients (Ca^{2+}, Mg^{2+} and K^{+}) are replaced on the soil exchange complex by Al^{3+} and the base cations are eventually leached out of the soil.

There may be significant variation in Al^{3+} solubility with depth in a soil profile (Hendershot et al. 1995). In the surface horizons, the soil solutions tend to be undersaturated with respect to aluminum-bearing minerals; in the lower B and C horizons, aluminum in soil solutions can be expected to be near equilibrium with some aluminum solids. Although the equilibrium concentration is close to that which would be expected if gibbsite were controlling equilibrium, gibbsite has generally not been identified in Canadian soils. Other forms of aluminum, for example, hydroxy interlayered vermiculite, may control aluminum solubility at values close to those of gibbsite. Amorphous aluminum complexed with organic matter may also have a similar pH solubility curve that is a function of the pH-dependent variation in the number of binding sites.

Fluoride and hydroxide complexes are the two strongest groups of inorganic ion associations with aluminum in soil solutions (Nordstrom and May 1995). In very acidic soils, aluminum in the soil solution is present mainly as free Al^{3+}; as pH increases, free Al^{3+} hydrolyses to form complexes with OH^- ions (e.g., $AlOH^{2+}$, $Al(OH)_2^+$, $Al(OH)_3^0$). Near pH 6.5, aluminum solubility is at a minimum, but it increases at neutral to alkaline conditions because of the formation of $Al(OH)_4^-$ (Driscoll and Postek 1996). According to Lindsay et al. (1989), fluorine, the most electronegative and one of the most reactive elements, is released as fluoride ion through the dissolution of fluoride-bearing minerals. In acidic soils ($pH < 5.5$), low-ligand-number complexes such as AlF^{2+} are normally formed. In neutral to alkaline conditions, it is more difficult for F^- to compete with OH^- for aluminum in the soil solution because of the increased level of OH^- and probably the presence of calcium that tends to link with fluoride (CaF_2). Consequently, aluminum-hydroxide complexes predominate over aluminum-fluoride complexes in alkaline conditions.

The complexation of aluminum with sulphate is weaker than that with fluoride. However, in acidic soils where the sulphate concentration is high, aluminum may also form aluminum-sulphate complexes (Driscoll and Postek 1996). At low sulphate concentrations, $AlSO_4^+$ is the dominant aqueous form, whereas $Al(SO_4)_2^-$ is predominant in soil solutions with higher sulphate concentrations. Brown and Driscoll (1992) showed that several aluminosilicate complexes, including $AlSiO(OH)_3^{2+}$, are present in various regions of the eastern U.S. and Canada.

It has been shown that most dissolved aluminum in soil solution of the forest floor is organically bound and that these aluminum-organic complexes become less abundant with increasing soil depth (Nilsson and Bergkvist 1983; David and Driscoll 1984; Driscoll et al. 1985). In the Adirondacks of New York, David and Driscoll (1984) found that 82% and 93% of the total dissolved aluminum in the organic horizons of conifer and hardwood stands, respectively, were organically complexed. The proportion of organic to inorganic aluminum decreased at both sites from the organic to the upper mineral horizons and from the upper to the lower mineral horizons. In the soil solutions of the mineral horizons, aluminum-organic complexes accounted for 67% and 58% of the total aluminum in the conifer and hardwood sites, respectively, which indicates the importance of aluminum-organic complexes in humus-rich forest soils of eastern North America.

2.3.1.5 Biota

In general terms, a substance is considered to be bioavailable if, under the conditions of exposure, it can be taken up by organisms (Environment Canada 1996). The bioavailability of a substance is determined by its chemical form, the physical and chemical characteristics of the media (e.g., water, soil, food) in which it occurs, the receptor species, and the route of the exposure (e.g., dermal contact, ingestion, inhalation). For metals such as aluminum, the "free" or hydrated dissolved ions (i.e., Al^{3+}, $Al(OH)^{2+}$ and $Al(OH)_2^{+}$) are normally considered to be the principal bioavailable forms (Newman and Jagoe 1994). However, there is evidence that some other forms of a metal, such as organometallic compounds (e.g., of mercury and tin), oxyanions of the metal (e.g., CrO_4^{2-}, AsO_4^{3-}), and dissolved organic and inorganic metal complexes (e.g., colloidal and polynuclear aluminum complexes) can also be taken up by organisms (Parker and Bertsch 1992b; Benson et al. 1994; Campbell 1995).

Bioavailability directly influences the potential for bioconcentration, bioaccumulation and biomagnification of a substance in organisms. ICMM (2007) defines bioconcentration as the increase in concentration of a substance in an organism (or specified tissues thereof) relative to the concentration of the substance in the environmental medium (generally water) to which it is exposed, bioaccumulation as the amount of a substance taken up by an organism from water (bioconcentration) as well as through ingestion via the diet and inhalation, and biomagnification as the process by which the tissue concentration of a bioaccumulated substance increases as it passes up the food chain through at least two levels (Parametrix 1995). The three processes are significant indicators of the propensity of a substance to impart toxicity to individual organisms and at higher trophic levels in the food chain. However, bioaccumulation of essential elements (such as some metals) in organisms is typically subject to metabolic regulation (ICMM 2007).

Bioconcentration factors (BCFs) and bioaccumulation factors (BAFs) are unitless values derived by dividing steady state tissue concentrations of a substance by the steady state environmental concentration (ICMM 2007). For synthetic organic compounds, the use of a BCF and BAF threshold value (such as that of 5000 specified in the CEPA 1999 *Persistence and Bioaccumulation Regulations*; Canada 2000) provides valuable information for the evaluation of hazard and risk. Bioaccumulation is more complex for naturally occurring inorganic substances such as metals, however, as processes such as adaptation and acclimation can modulate both accumulation and potential toxic impact (ICMM 2007). All biota will naturally accumulate metals to some degree without deleterious effect and as some metals are essential elements, bioaccumulation does not necessarily indicate the potential for adverse effects (McGreer et al. 2003). While metal bioaccumulation is homeostatically regulated for metals essential to biological function (Adams et al. 2000), non-essential metals may also be regulated to some degree as these homeostatic mechanisms are not metal-specific (ICMM 2007).

Thus, interpretation of the toxicological significance of bioaccumulation data for metals such as aluminum is complex. A more complete discussion of aluminum bioavailability