A Study of Road Deicer Pathways in a Small Headwater Catchment in Southeastern Massachusetts

Author: David Michael Beutel

Persistent link: http://hdl.handle.net/2345/bc-ir:104633

This work is posted on eScholarship@BC, Boston College University Libraries.

Boston College Electronic Thesis or Dissertation, 2015

Copyright is held by the author, with all rights reserved, unless otherwise noted.

Boston College

The Graduate School of the Morrissey College of Arts & Sciences Department of Earth and Environmental Sciences

A STUDY OF ROAD DEICER PATHWAYS IN A SMALL HEADWATER CATCHMENT IN SOUTHEASTERN MASSACHUSETTS

a thesis

by

David M. Beutel

submitted in partial fulfillment of the requirements for the degree of Master of Science August 2015

© Copyright by David M Beutel

2015

Abstract

Title: A Study of Road Deicer Pathways in a Small Headwater Catchment in Southeastern Massachusetts Author: David M. Beutel Advisor: Rudolph Hon

Road salt deicers are necessary for road safety, yet pose a risk to wildlife and public water supplies by increasing major ion loads above EPA limits. To better understand the fate of deicers after application, we need to know the migration routes and subsurface pathways that deicers take from their sources to points of discharge. This project used sediment core analysis and major ion chemistry analysis of water quality to evaluate the pathways of NaCl and CaCl₂ through the subsurface of a shallow glacial aquifer in south east New England. Assessment of sediment cores revealed a heterogeneous subsurface with great variation in hydraulic conductivity. Analysis of major ion concentrations and ion ratios showed both short, direct pathways and deeper, longer pathways indicative of yearly salt retention in the aquifer. Ion chemistry also revealed deicer sources by their variable NaCl to CaCl₂ ratios.

Acknowledgements

I would like to thank my advising committee Dr. Rudolph Hon and Dr. Corinne Wong for their guidance and support on this project. I would also like to thank Dr. James Besancon of Wellesley College for his technical support and assistance with sample analysis throughout my time at Boston College. Without their patience, hard work, and leadership, this project would never have been possible.

Second, I would like to thank Jack McInnis, Peter Dillon, and everyone at the Norwell Water Department for their generosity and access to resources needed to complete this project.

Thanks to Laila Parker and Michelle Craddock from the DER.

Thank you to my classmates, specifically Bianca Bello, Kendall Valentine, and Stephen Hilfiker for incredible support and positive vibes every step of the way.

Finally, thanks to my wife Dr. Kristen Bottema-Beutel for happily listening to hundreds of hours of me rambling on about groundwater chemistry.

Table of Contents

Acknowledgements	i
List of Figures	iii
List of Tables	iv
List of Equations	iv
Section 1. Introduction	1
_1.2 Current State of Groundwater in New England	3
Section 2. Field Site	9
Section 3. Objective	15
Section 4. Methods	16
_4.1 Surface Water Sampling	16
_4.2 Ground Water Sampling	16
_4.3 Water Sample Analysis	17
_4.4 Sediment Core Analysis	21
_4.5 Pump testing – drawdown characterization	22
Section 5. Results	23
_5.1 Analysis of Subsurface Pathways	23
_5.2 Drawdown measurements	29
_5.3 Estimating salt inputs and evaluating impact on water quality	30
Section 6. Discussion	45
_6.1 Differential Deicer Pathways	45
_6.2 Water chemistry as an indicator of different deicers and source	49
_6.3 Road density regions above the Old Pond Meadow aquifer	54
_6.4 Year-round elevated Cl ⁻ levels in Third Herring Brook	57
_6.5 Water quality differences between NOR-1 and NOR-6	60
Section 7. Conclusion	64
Section 8. References	66

List of Figures

Figure 1 – Percent of total dissolved solids (TDS) attributed to road salt deicers	7
Figure 2 – Chloride concentration of water samples	8
Figure 3 – The Old Pond Meadow Aquifer in Norwell, Massachusetts	10
Figure 4 – Surficial geology of the Old Pond Meadow Aquifer	11
Figure 5 – Monitoring well and public supply well locations.	12
Figure 6 – The THB watershed and OPM aquifer in Norwell, Massachusetts	14
Figure 7 – Cation concentrations of internal standard samples	19
Figure 8 – Anion concentrations of internal standard samples	20
Figure 9 – TDS and specific conductivity of water samples taken from THB	21
Figure 10 – Ground water contours of the Old Pond Meadow aquifer	24
Figure 11 – Sediment core taken in the wetlands next to Monitoring Well 3	25
Figure 12 – Grain size analysis of sediment core taken near MW1	26
Figure 13 – Sediment cores taken from the glacial outwash region	27
Figure 14 – Grain size analysis of sediment core taken near monitoring well 7	27
Figure 15 – Estimated hydraulic conductivity of samples	28
Figure 16 – THB monitoring well response to pumping by NOR-1	29
Figure 17 – Land use map of the watershed.	32
Figure 18 – Land use in the THB watershed	33
Figure 19 – Salted impervious surfaces around Hanover Mall	34
Figure 20 – Six months of specific conductance measurements	35
Figure 21 – Cl ⁻ concentration of THB surface water	36
Figure 22 – Cl ⁻ concentration and Na/Ca ratio of surface water samples	38
Figure 23 - Spatial distribution of average water quality parameters	42
Figure 24 - Cl ⁻ concentration of THB monitoring well samples	43
Figure 25 - Wetland regions adjacent to public supply wells and Third Herring Brook	47
Figure 26 - Nine sediment cores alligned South to North	48
Figure 27 - Na/Ca ratio v Chloride Concentration of water samples	50
Figure 28 - A large pile of rock salt exposed to the elements at the salt storage shed	51
Figure 29 - An empty bag of Peladow deicer found in a snow bank	52
Figure 30 - Na/Ca ratio of monitoring wells along Third Herring Brook	53
Figure 31 - Roadways and impervious surfaces above the OPM	55
Figure 32 - Groundwater pathways	57
Figure 33 - Three water sources within the Old Pond Meadow Aquifer	61
Figure 34 - Modeled pathways of groundwater into NOR-1 and NOR-6	63

List of Tables

Table 1 – Average Ca ²⁺ , Na ⁺ , and Cl ⁻ levels monthly sampling in HBW6	4
Table 2 – Major ion chemistry from the USGS NAWQA NECB land-use project	6
Table 3 – Calculated K values for select horizons from sediment cores	28
Table 4 – Estimated K between 5 THB monitoring wells and NOR-1	30
Table 5 – Annual deicer loading estimates in the Third Herring Brook Watershed	31
Table 6 – Water chemistry of selected surface water samples collected from THB	36
Table 7 – Water quality of selected groundwater samples taken from OPM	37
Table 8 – Average water chemistry parameters for the three sources of water	39
Table 9 – Complete ion chromatography analysis of all THB monitoring well samples.	40
Table 10 - Complete ion chromatography analysis of all surface water samples	44
Table 11 – Average major ions of ocean water	54
Table 12 – Major ion chemistry of groundwater and surface water samples - May	59
Table 13 – Major ion chemistry of groundwater and surface water samples - August	59

List of Equations

Equation 1 – U.S. Bureau of Reclamation formula for estimating K values	26
Equation 2 – Thiem equilibrium method for an unconfined aquifer.	30

Section 1. Introduction

Before the 1940's, state highway departments relied mostly on abrasives such as sand and cinders to increase drivability of roads during winter months. Since the end of World War II, the New England, Middle Atlantic, Great Lakes, and Plains states have increasingly used sodium chloride (NaCl) salt as a deicing agent on roadways in lieu of abrasives (Transportation Research Board, 1991). Throughout the 1950's and 1960's, use of salt on roadways in the northern United States doubled every five years (Transportation Research Board, 1991). Total US deicing salt use leveled off in the 1970's and now varies between 10 million and 20 million metric tons per year, depending on seasonal snowfall (Kostick, 2007). In Massachusetts and other New England states, winter application of salt to highways averages 20 tons of total salt per lane mile per year (Huling and Hollacher, 1972; Heath and Morse, 2013).

Salt works as a road deicer by lowering the freezing point of water. A 25% NaCl salt solution has a eutectic temperature of -21°C (-6°F), although NaCl loses its effectiveness as temperatures decrease and is not considered effective below -9°C (Kelting and Laxon, 2010). If temperatures drop below -9°C, highway departments typically will switch to other chloride salt deicers such as CaCl₂ or MgCl₂ because they depress the freezing point of water further (Fay and Shi, 2012).

With each application of salt, the dissolved portion runs off the roads and into the adjacent soils and surface waters; ultimately the brine will infiltrate the vadose zone and groundwater. The result of each salting event is a pulse of salt into the ecosystem and aquifer; in recent years, the impacts of these salt pulses have been studied extensively. Sodium chloride and other deicer salts are corrosive and pose a threat to industrial

operations and infrastructure (Kelly et al., 2012). The Cl⁻ concentration of salt plumes running off roads can be as high as 9400 mg/L (Harte and Trowbridge, 2010), and such concentrated road salt runoff causes ecological damage to wildlife in rivers, streams and wetlands (Sun et al., 2010; Wilcox, 1986), threatens vital bog bryophytes *Sphagnum recurvum* (Wilcox, 1984), and is associated with poor physiological traits and growth suppression of spruce trees *Picea abies* and *Picea glehnii* (Kayama, 2003). The USEPA limit for short-term (less than one hour) wildlife exposure (based on fish survival rates) to chloride is 860 mg/L and the long-term exposure (four day average concentration) limit is 230 mg/L (USEPA, 1988).

Elevated sodium in drinking water can have negative health impacts on human health as well. High sodium is associated with hypertension (American Heart Association, 2014). The Massachusetts Department of Environmental Protection has set a drinking water guideline for sodium at 5 mg per 8 oz. serving (20 mg/L) and the current EPA secondary maximum contaminant level (SMCL) for sodium is 20 mg/L (MassDEP, 2014; USEPA 2006). The federal SMCL for Cl⁻ is 250 mg/L (USEPA, 2006).

The harmful effects of road deicers are especially important in communities where the drinking water supply comes entirely from ground water. In areas with heavy road salt application during winter months, the groundwater retains much of the salt and shows little seasonality with chloride concentrations (Kelly, 2008). Howard and Haynes (1997) found that only 45% of road salt is flushed from the Metropolitan Toronto region each year in surface waters, while the remaining 55% is retained in the sub-surface. Waters draining the Mohawk River Basin in New York have seen a 243% increase in Cl⁻ concentration since 1952 (Godwin, 2003). While this area has seen a decline in

2

population in addition to environmental legislation such as the Clean Water Act and Safe Drinking Water Act, Cl⁻ continued to rise in the basin throughout the 1990's (Godwin, 2003). Models show that if all salting were halted, it would take decades for all retained salt to be flushed from the aquifer - it could take an estimated 30 years for lakes in Minnesota (Novotny, 2010) to return to natural levels, and up to 100 years for the groundwater in southwestern Ontario to rid itself from all excess Na⁺ and Cl⁻ after 57 consecutive years of salting the roads (Bester, 2006).

Use of road deicers is necessary to ensure safety for those traveling on roadways during winter months. However, deicers are also a pollutant with negative environmental impacts (Sun et al., 2010) and health effects (American Heart Association, 2014). The pathways of the deicers from their sources and through the aquifer are not known. This study uses sediment core and water chemistry analyses to evaluate these pathways of deicers that are impacting a small headwater catchment in southeastern Massachusetts. For this study, we define pathways as the general migration route of road salt deicers from their source to the point of discharge – not particle tracking. Understanding the pathways of deicers through the subsurface is critical to linking deicer sources to water quality in streams, wetlands, and public water supplies.

1.2 Current State of Groundwater in New England

To accurately assess the magnitude of road salt deicer contamination, water samples must be evaluated against the natural sodium, calcium, and chloride levels. The Hubbard Brook Experimental Forrest (HBEF) is a 3,160 hectare reserve in the White Mountain National Forest, New Hampshire. This study analyzes water quality data from HBEF watershed number six (HBW6) – a control watershed that has not been treated

3

experimentally. In HBW6, hydrology and water quality data have been collected monthly since 1964 (Table 1; Likens, 2015). Because the HBEF is remote, it is completely isolated from anthropogenic influences such as road deicers, septic or other wastewater systems, and land use changes. For this study, the water chemistry of HBW6 is used as a baseline, or "pristine" water from New England. Deviations in specific conductivity, TDS, or major ion concentrations from this baseline are indicative of anthropogenic influence.

Table 1 – Average Ca²⁺, Na⁺, and Cl⁻ levels from 46 years of monthly sampling in HBW6 (Likens, 2015).

				Na / Ca ratio
	Ca^{+2} (mg/L)	$Na^{+}(mg/L)$	Cl ⁻ (mg/L)	(meq)
46 year average	0.97	0.84	0.46	0.75

HBW6 can be compared to groundwater more typical to eastern Massachusetts that likely reflects anthropogenic influence, such as data from USGS groundwater land use studies. Groundwater data from the 1999 USGS New England Coastal Basin (NECB) National Water-Quality Assessment (NAWQA) program was reviewed for all constituent ions and total dissolved solids (TDS) (USGS, 1999). In 1999, 29 groundwater samples were taken throughout eastern Massachusetts in areas of varying land use in an attempt to understand the human and natural factors in each setting that affect ground water quality. For 7 of the 29 samples, less than 50% of total dissolved solids (TDS) came from road salt deicers. In 13 of the 29 samples, 61% - 80% of the dissolved solids are attributed to road salt deicers; and for 9 sites, greater than 81% of the TDS are from road salt deicers (Table 2; Fig. 1). Percent of salt attributed to deicers is calculated by subtracting natural Cl⁻ concentration (HBW6) from Cl⁻ concentration of a given sample and then converting to grams of salt (using the molar mass of NaCl and dividing by 0.61, as Cl⁻ is 61% of NaCl by mass). This is then divided by the TDS of the water.

The values for percent of TDS attributed to road salt deicers in Table 2 are greater than those reported in USGS SIR 2014-5012, which states that only 21% of TDS in New England surface water can be attributed to road deicers (Anning and Flynn, 2014). However, SIR 2014-5012 averaged all of New England waterways, including large empty areas of Maine that have no roads and no deicer application. Our calculations based on the 1999 NECB NAWQA data represent water from the metro Boston area with many more roads and significantly more deicer application.

When these samples are represented with absolute concentration of ions as opposed to percent of TDS from deicers, 20 of 29 samples exceeded the MassDEP and USEPA SMCL for sodium (20 mg/L), 3 samples exceeded the USEPA long-term Cl⁻ exposure limit for wildlife (230 mg/L), and 2 samples exceeded the USEPA SMCL for Cl⁻ in drinking water (250 mg/L) (Fig 2).

Monitoring Well				Na / Ca ratio	Percent of TDS
ID	Ca^{2+} (mg/L)	Na^{+} (mg/L)	Cl (mg/L)	(meq)	from road salt
MA-A8W 36	13	6.1	10	0.41	24%
MA-MDW 238	14	14	23	0.87	41%
MA-PEW 351	4.3	10	13	2.03	42%
MA-EBW 233	5.2	8.7	14	1.46	43%
NH-NAW 308	16	16	31	0.87	50%
MA-CDW 150	3	8.7	14	2.53	54%
MA-EMW 294	4.7	18	25	3.34	60%
MA-S9W 279	18	29	46	1.40	61%
MA-F2W 64	12	24	39	1.74	62%
MA-BJW 295	33	28	61	0.74	62%
NH-NAW 309	15	39	62	2.27	67%
MA-N5W 371	9.5	26	46	2.39	67%
MA-D4W 243	2.6	25	35	8.38	68%
MA-RAW 139	19	60	110	2.75	70%
MA-TNW 236	26	47	92	1.58	71%
MA-PWW 731	4.8	17	34	3.09	71%
MA-BCW 376	10	47	71	4.10	71%
MA-NMW 9	15	24	52	1.39	72%
MA-HFW 141	3	39	60	11.33	78%
MA-MHW 296	8.9	42	70	4.11	78%
MA-LWW 171	12	54	94	3.92	80%
MA-CTW 215	19	140	210	6.42	81%
MA-WRW 148	12	56	94	4.07	83%
MA-TQW 107	22	57	110	2.26	84%
MA-CDW 149	1.3	5	33	3.35	85%
MA-D4W 244	9.4	58	110	5.38	87%
MA-TNW 235	19	210	340	9.63	90%
MA-WTW 151	70	380	730	4.73	93%
MA-HFW 149	8.5	140	240	14 36	96%

Table 2 – Major ion chemistry from the USGS NAWQA NECB land-use project. Groudwater was sampled from 29 sites in eastern Massachusetts and New Hampshire. Na/Ca ratio and TDS calculations were done for this project and were not part of the original data set (USGS, 1999).



Figure 1 – Percent of total dissolved solids (TDS) attributed to road salt deicers in monitoring wells throughout eastern Massachusetts (USGS, 1999). 24 of the 29 samples have greater than 50% of TDS coming from road salt deicers. TDS calculations were done for this project and were not part of the original data set.

All of the groundwater samples from the 1999 NAWQA NECB program have higher Cl⁻ than Hubbard Brook Watershed Six, ranging from 20x natural levels to over 1000x natural levels (Table 2). The wide range of Cl⁻ concentrations in groundwater samples throughout eastern Massachusetts (Fig. 2) raises questions about both salt loading (amount of salt used and different types of salt used) and about the fate of deicers after application. This leads to a question of pathways for the salt – mainly, where exactly do all these deicing salts go once they are applied to roads, highways, and impervious parking surfaces each winter?



Figure 2 – Chloride concentration of water samples taken from monitoring wells throughout the eastern part of Massachusetts (USGS, 1999).

Section 2. Field Site

The Old Pond Meadow (OPM) aguifer in SE Massachusetts is one aguifer that is impacted by heavy application of road salt deicers (Anderson, 2013). OPM lies within the towns of Hanover and Norwell, Massachusetts (Fig. 3). The town of Norwell provides public water from groundwater from this aquifer to its 10,506 residents. The South Street public water well field consists of two wells, NOR-1 and NOR-6, that can each pump up to 300,000 gallons of water per day. Since 1987, the Norwell Water Department has been monitoring the chloride concentration of water being pumped by their two wells. In 1987, the water being abstracted by NOR-1 averaged 100 mg/L chloride; by 2014 the water from NOR-1 was producing water with Cl⁻ between 180 mg/L and 200 mg/L chloride (Anderson, 2013; Hon et al., 2014). NOR-1 consistently produces water with 150 - 200 µS/cm greater specific conductivity (45 - 60 mg/L Cl⁻) than NOR-6 (Anderson, 2013). The water quality heterogeneity between these two production wells shows the complexity of the deicer contamination and it shows why a study of deicer pathways if important to understanding the link between potential sources and their respective points of discharge.

Pumping wells NOR-1 and NOR-6 feed water into the South St. water treatment facility, close to the Norwell town border with Hanover, Mass; the two cities are separated by a small stream called Third Herring Brook (THB). The watershed defined by where THB crosses underneath South St. has a drainage area of 6.7 km². Based on surficial and subsurface geology, we assume the THB watershed to be the primary recharge zone for the underlying aquifer that the town of Norwell uses for drinking water supply. This region of eastern Massachusetts receives the water equivalent of 41.51 inches of precipitation per year on average (NOAA, 2001).

9



Figure 3 – The Old Pond Meadow Aquifer in Norwell, Massachusetts.

The town of Norwell and the town of Hanover (pop. 13,879) pump the bulk of their distributed water from the Old Pond Meadow (OPM) aquifer within the THB watershed (Fig. 3). In addition to THB, another small stream, Wildcat Brook (WB) flows above this aquifer. OPM is a shallow glacial basin formed by the retreat of the Wisconsinan glaciation (Reed, 1995) and contains several glacial surface and subsurface topographical features including moraines, drumlins, an esker, and several kettle ponds that have since been filled with fine sediments and organic material (Fig. 4). The subsurface shows great

variation and consists of glacial sediments ranging from areas of course sand and pebbles to significant layers of silt and peat (Reed, 1995).



Figure 4 – Surficial geology of the Old Pond Meadow Aquifer in Norwell, Massachusetts. Taken from Reed (1995).

A shallow basin in the northern section of the OPM was dammed to form a small

pond (Jacob's Pond) that acts as the headwaters for THB. South of NOR-1, WB flows

into THB and they continue south to eventually join the Indian Head River to form the North River. From Jacob's Pond to where it reaches the North River, THB loses approximately 150 feet of elevation. The South St. water treatment plant in Southern Norwell uses the two previously mentioned production wells, NOR-1 and NOR-6. These wells extend to bedrock 20 meters below. NOR-1 lies along THB, with 9 fully screened monitoring wells between NOR-1 and the stream in a north-south array - 250 meters separate the southernmost monitoring well (#7) from the northernmost (#11). These monitoring wells extend from the surface to bedrock, which ranges from 12 meters to 20 meters. NOR-6 is 325 meters east of this monitoring well array. 500 meters further east, closer to WB, lies the 1998 series of monitoring wells. These wells extend to three different depths (3.5m, 14m, and 24m) and are not fully screened, but instead screened 1.5 m from the bottom (Fig 5).



Figure 5 – Monitoring well and public supply well locations around the South St. treatment plant, Norwell, Massachusetts. Public Supply Wells NOR-1 and NOR-6. MW 98-2 was installed in 1998. Monitoring wells 3 through 6 were installed in the fall of 2013 and monitoring wells 7 through 11 were installed in the spring of 2014.

The area of the Old Pond Meadow aquifer near Norwell's South St. treatment plant has many attributes that make this a site of interest for a study of road salt contaminant pathways. It lies under a small headwater catchment with intense seasonal salt loading from a few known sources, which allows for evaluation of the extent of influence from each of the individual sources. Sources of road deicer in the catchment include Massachusetts Route 3 that consists of two lanes each way totaling 5.65 lane miles, a large cloverleaf interchange, Highway 53 with 2 lanes each way totaling 22.75 lane miles, the Hanover Mall parking lot covering 43 acres, a state owned salt storage shed, and residential deicer use on surface streets and driveways. The extensive array of observation wells between the sources and production well NOR-1 can act as a screen with which we can monitor the pathways and sources of road salt deicers moving through the subsurface.



Figure 6 – The THB watershed and OPM aquifer in Norwell, Massachusetts. The aquifer is defined by where Third Herring Brook passes under South St., just south of the South St. treatment facility of the Norwell Water Department. This delineation was chosen to encompass the extensive monitoring well array along THB just north of this point (inset). Pumping well NOR-6 and the 1998 series of monitoring wells lie outside of this watershed and are more influenced by the drainage of nearby Wildcat Brook.

Section 3. Objective

The purpose of this study is to evaluate deicer pathways through the subsurface in a glacial basin. One area of interest is the contrast in chemistry of water derived from two public supply wells (NOR -1 and NOR-6). A second area of interest is dissolved deicer contaminants in near-surface groundwater that discharge into a local stream as baseflow. Specifically, the project will create a model of deicer pathways using a combination of water quality distribution patterns created by road deicers, and an analysis of subsurface geological complexities.

This objective has relevance beyond the Third Herring Brook watershed and underlying aquifer since this region has hydrologic conditions that are typical of other areas in the northeastern United States. This study of water chemistry distribution and deicer pathways in this region is applicable to many other small glacial aquifers throughout New England. Understanding deicer fate is important to evaluation of water resources in areas where road salts can impact local water quality and the local environment.

Section 4. Methods

Two separate types of sampling and analysis will be used to characterize the pathways of road salt deicers.

• Surface water and ground water sampling, coupled with ion chromatography analysis will provide concentrations of constituent ions, which will provide geochemical characterization of potential salt sources and document the variations in groundwater chemistry.

• Sediment core documentation, sampling, and sieve analysis allows a qualitative (through visual evidence of Redox environment) and quantitative (through calculation estimated hydraulic conductivity) assessment of sedimentation from which preferred pathways of groundwater near NOR-1 and NOR-6 can be inferred.

4.1 Surface Water Sampling

Surface water samples were taken at 10 select sites (Fig 21) from Third Herring Brook, Jacob's Pond, and Wildcat Brook throughout the watershed – both north and south of Massachusetts Route 3. Samples were collected weekly or biweekly from May through November of 2014. All surface water samples were collected in new, 250 ml HDPE bottles. Bottles were filled with minimal head-space and were refrigerated, unfiltered, at 4°C. Samples were brought to room temperature before analysis.

4.2 Ground Water Sampling

Groundwater samples were taken from a series of 9 monitoring wells arranged in a North / South array along Third Herring Brook near public supply well NOR-1 (Fig 5). Samples were also collected from the 1998 series of monitoring on the eastern side of the OPM aquifer. Samples were collected weekly or biweekly from May to November of 2014.

Monitoring wells were sampled with an open top, PVC 700 ml bailer that was lowered into the well to 4.5m below the water table. Because these wells are fully screened, and because hydraulic conductivity is quite high throughout the region, the water in the well is considered a representative sample of the groundwater and no purging of the well was done. This is in accordance with USEPA No Purge Sampling Procedures SESDPROC-301-R3.

In two of the monitoring wells (MW6 and MW11), permanent, flexible HDPE (ID 0.25', OD 0.375') tubing was installed to 4 depths: 2.5m, 5m, 7.5m, 10m. Samples were taken through this tubing with a Geotech Geopump Series II peristaltic pump in general accordance with the USEPA Low Stress Purging and Sampling Procedure. All ground water samples were collected in new, 250 ml HDPE bottles. Bottles were filled with minimal head-space and were refrigerated, unfiltered, at 4°C. Samples were brought to room temperature before analysis.

4.3 Water Sample Analysis

Ion Chromatography (IC)

Ion chromatography is an analytical technique that separates and measures the concentration of major ions based on their size and charge. Samples collected were analyzed for anions (chloride, sulfate, nitrate, and fluoride) and cations (sodium, calcium, and magnesium) with Dionex ICS-2100 (for anions) and Dionex ICS-1000 (for cations) ion chromatography columns. In IC, the sample and eluent enter a column and interact

with oppositely charged ions. Naturally, different columns are required for cation and anion analysis. Based on size and charge, ions move through the column at different rates and arrive at the detection point at different times. The timing of ions reaching the detector is distinct for each ion species. Electrical conductivity of each ion in the analyte is then measured to determine concentration. Both columns were equipped with an AS40 automated sampler and analysis was done using Dionex Chromeleon 7.2 processing software.

Each time samples were analyzed by IC, internal standards of were also analyzed as a quality control measure. The internal standard was Boston MWRA tap water collected in January of 2014. Figures 7 and 8 show the measured ion concentration of this internal standard water as compared to the reported concentrations of major ions for January 2014. All samples of Fl⁻, Na⁺, and Cl⁻ were at or under 5% error. Ca²⁺ samples ranged from 1 to 11% error. These measurements give us confidence that we have reliable results throughout this project.



Figure 7 – Cation concentrations of internal standard samples tested by Ion Chromatography in Boston College's Environmental Geology Laboratory compared to the MWRA reported concentrations. Na⁺ samples showed 2-4% error, while Ca²⁺ samples showed 1-11% error.



Figure 8 – Anion concentrations of internal standard samples tested by Ion Chromatography in Boston College's Environmental Geology Laboratory compared to the MWRA reported concentrations. Both FI⁻ and CI⁻ samples showed 0% - 5% error.

Total Dissolved Solids (TDS)

For TDS analysis, 25 samples with a wide range of specific conductivity values were selected. This analysis was done according to EPA Method 160.1 for Total Dissolved Solids. Samples were passed through a filter of 0.45 microns pore size, poured into a pre-weighed evaporating dish and evaporated to constant weight at 180 C. The

evaporating dish was weighed and the result were used to calculate the TDS of the sample. The strong correlation coefficient between specific conductivity and TDS (R^2 =0.96) allows us to calculate TDS from specific conductivity measurements (Fig 9).



Figure 9 – TDS and specific conductivity of water samples taken from THB and monitoring wells near THB. The strong correlation allows us to use specific conductivity as a proxy for TDS.

4.4 Sediment Core Analysis

Nine sediment cores were taken in 2013 and 2014, using GeoProbe[®] sediment core sampling equipment, adjacent to the monitoring wells along Third Herring Brook. These cores were analyzed, documented, photographed and sampled. Coloration of sediment can be used as an indicator of redox environment (Wheeler et al., 1999). Several unique sediment horizons were sampled from each core and sieve analysis was done using 1¢ intervals from -1¢ (2,000 μ m) to 4¢ (62.5 μ m) using a Ro-Tap[®] RX-94 Duo model sieve shaker. Samples from cores were selected from the middle of each unique lithology observed. Complete statistical grain size analysis was done using GRADISTAT software (Blott and Pye, 2001).

4.5 Pump testing – drawdown characterization

In-Situ Inc. AquaTROLL 200 probes were temporarily (1 to 5 days) placed down 5 of the THB monitoring wells (MW5, MW7, MW8, MW9 and MW10). These probes recorded water depth, temperature, and specific conductance. An identical probe was also placed in a deep (20 meters) monitoring well in close proximity to public supply well NOR-1. Drawdown in monitoring wells in response to withdraw from NOR-1 was calculated manually from the AquaTROLL data. Using this drawdown data, transmissivity between the wells and NOR-1 can be estimated using the Thiem equilibrium method (Equation 2).

Section 5. Results

Data is organized into two parts. The first part includes a description of the subsurface based upon qualitative and quantitative analysis of samples from borings located along THB near the monitoring well array, and the results of pump testing done using the same monitoring wells. This analysis will examine the cores for signs of preferential pathways for water and Cl⁻ contaminants from the sources to the South St. well field. The second part will be an analysis of the potential pathways of water and dissolved road salt contamination through the aquifer using water quality data. Pathways will be separated and described by both magnitude of salt loading, and by water chemistry based on a semi-unique ion ratio from different sources.

5.1 Analysis of Subsurface Pathways

Groundwater level surveys done by Reed (1995), show the pre-pumping groundwater gradient of the Old Pond Meadow Aquifer (Fig. 10). High hydraulic head is in the northwest region of the basin, and low hydraulic head in in the southeast – toward the junction of Third Herring Brook and Wildcat Brook.



Figure 10 – Ground water contours of the Old Pond Meadow aquifer when the NOR-1 and NOR-6 public supply wells are not pumping groundwater. High hydraulic head is in the northwest of the aquifer and low head is in the southeast. Stars show the locations of NOR-1 and NOR-6. Taken from Reed (1995).

Analysis of sediment cores reveals two unique deposits – those in the wetlands adjacent to THB (MW1, MW2, MW3, MW5) and those outside of the wetlands along South Street (MW7, MW8, MW9, MW10, MW11) (Fig. 5). MW1 and MW2 were lost during the winter of 2013 and no longer exist. The cores from the wetland areas show significant (5-6 m thick) peat layers overlying silt and fine sand. These compacted peat and silt horizons are gray in color (Fig. 11).



Figure 11 – Sediment core taken in the wetlands next to Monitoring Well 3. This core has 5 meters of peat overlying 5 to 6 meters of silty peat and silt. The silt layers from 5 meters of depth to bedrock are gray in color.

Sediment core samples were taken from the middle of each unique horizon in each core. Sieve analysis of these unique horizons taken from cores near MW1 and MW3 show that these deposits are predominantly fine sand and silt (Fig. 12). When hydraulic conductivity (K) is estimated using the U.S. Bureau of Reclamation formula for estimating hydraulic conductivity (Equation 1), we find that all samples from these cores in the wetlands have low relative K values; four of seven K values were below 1 meter/day, 3 of seven were between 1 and 6 meters/day (Table 3).



Figure 12 – Grain size analysis of sediment core taken near monotoring well 1 at 8.8 meters of depth. This sample is representative of samples in sediment cores taken from wetland areas along THB by NOR-1. A small d20 value equates to a very small estimated conductivity value.

Equation 1 – U.S. Bureau of Reclamation formula for estimating K values

$$K = \frac{g}{v} \times 4.8 \times 10^{-4} d_{20}^{0.3} \times d_{20}^{2}$$

where

K is hydraulic conductivity (m/day) g is the acceleration due to gravity v is the kinematic velocity (m/day) d₂₀ is the effective grain size at 20% in the cumulative distribution (mm)

In contrast to the sediment facies in the wetlands, those taken near monitoring wells outside of the wetlands (MW 7, 8, 9, 10) show a very different lithology. This core reveals a thin layer (< 1 meter) of topsoil and sand overlying thick layers (13 meters) of course sand intermixed with pebbles and cobbles. These thick sand/pebble layers are reddish brown in color (Fig. 13). Sieve analysis of this core revealed larger grains (Fig. 14), and thus the estimated K value of the coarse sand horizon of MW7 using the USBR formula was much greater (300% greater) than those from the wetland cores (Table 3).



Figure 13 – Sediment cores taken from the glacial outwash region, outside of the wetland region, near monitoring wells 8 and 10. This core shows a thin layer of topsoil over 13 meters of course sand and pebbles. The sand from 7 meters of depth to bedrock at 13 meters of depth is dark reddish brown in color.



Figure 14 – Grain size analysis of sediment core taken near monitoring well 7 at 15 meters of depth. This sample is representative of samples taken outside of wetland areas along THB. A large d20 value equates to a larger estimated conductivity value.

Table 3 – Calculated K values for select horizons from three sediment cores taken near monitoring v	vells
between THB and South St. Estimations were made using grain size data (d20) and using the USB	R
hydraulic conductivity formula.	

Sample	Estimated K		
Depth (m)	(m/day)		
6.5	3.96		
8.2	2.85		
8.8	0.48		
3.9	0.32		
4.9	6.02		
5.2	0.05		
5.8	0.19		
5.2	1.22		
13.8	19.51		
14.6	3.96		
	Sample Depth (m) 6.5 8.2 8.8 3.9 4.9 5.2 5.8 5.2 5.8 5.2 13.8 14.6		

Estimated K values of samples taken in the wetlands show hydraulic conductivity similar to silt, while one of the estimated values for MW7 (located outside the peat deposits) has an estimated K value closer to that of sandy gravel (Fig. 15). Each core shows heterogeneity, containing horizons with higher K than the others.



Figure 15 – Estimated hydraulic conductivity of samples from MW1, MW3, and MW7 as compared to typical values for unlithified sediments. The subsurface at MW1 and MW3 have 100 to 1000 times less estimated conductivity than the subsurface at MW7.
5.2 Drawdown measurements

Over the course of 3 weeks, water level measurements from five fully screened THB monitoring wells (MW5 in the wetlands and MW7, MW8, MW9, and MW10 in the riparian areas) were taken using temporarily placed AquaTroll 200 probes – at the same time as water level measurements at a deep monitoring well next to public supply well NOR-1. Drawdown was measured manually from AquaTROLL readouts. Using this data, we were able to quantify the magnitude of the cone of depression with respect to the monitoring wells along THB (Fig. 16).



Figure 16 – THB monitoring well response to pumping by NOR-1 plotted against distance from NOR-1. Wells 7 through 10 show a linear relationship of well drawdown and distance from the well. These wells are situated in areas of glacial outwash, not in the peat deposits. Monitoring well 5 is in the peat deposits between THB and NOR-1 – this well has much less response to the NOR-1 pumping than any of the other wells, indicating that the peat has lower hydraulic conductivity than the outwash areas.

Also, with the magnitude of drawdown at each monitoring well (in response to pumping at NOR-1), we used the Thiem equilibrium method (Equation 2) to estimate hydraulic conductivity between NOR-1 and each monitoring well (Table 4). MW 7 and MW 10 show the highest estimated K (over 16 m/day), MW 8 and MW 9 have estimated K values just over 12 m/day, and MW 5 – in the wetlands between THB and NOR-1 – had the lowest estimated K value, 6.44 m/day.

Equation 2 – Thiem equilibrium method for an unconfined aquifer.

$$\mathbf{K} = \frac{Q}{\pi (h_2^2 - h_1^2)} \ln \frac{r_2}{r_1}$$

where K is hydraulic conductivity (m/day)
r is the radial distance to the point of head measurement (m)
h is hydraulic head (m)
Q is well discharge (m³ per day)

Table 4 – Estimated K between 5 THB monitoring wells and NOR-1 using the Thiem equilibrium method. *MW5* is in the wetland region and has much lower estimated conductivity than the other subsurface at other areas outside the wetlands.

	Estimated K
	(m/day)
MW5	6.44
MW7	16.35
MW8	12.45
MW9	12.93
MW10	16.90

5.3 Estimating salt inputs and evaluating impact on water quality

Estimates of road salt deicer loading to the Third Herring Brook watershed, which covers the recharge area for OPM, were approximated using application rates from Heath and Morse (2013), road density data, and land use data (Fig 17). Road density and land use for the THB watershed was analyzed using the land use layer from MassGIS (Figs. 17 and 18). Commercial, industrial, and urban/public institution (schools, libraries, etc.) received an estimated 1 ton Cl⁻ per acre annually (Heath and Morse, 2013). For the Hanover Mall and the South Shore YMCA (directly across the street from Hanover Mall), 65% of the impervious surface is parking, while the remaining 35% is rooftop that would not be salted. Since these are the two largest regions of impervious surface in the watershed (80% of all impervious surface), the 65% salted, 35% not salted conversion will be applied to all commercial, industrial, and urban/public institutions in the watershed. Estimates of annual deicer loading into the Third Herring Brook watershed are shown in Table 5.

Table 5 – Annual deicer loading estimates in the Third Herring Brook Watershed. Estimates are based on Heath and Morse (2013)

Source	NaCl (tons)	CaCl ₂ (tons)	Na [⁺] (g)	Ca ²⁺ (g)
Commercial	59.1	88.6	2.09E+07	2.89E+07
Public Institution	10.3	15.4	3.64E+06	5.03E+06
Industrial	0.75	1.12	2.65E+05	3.66E+05
Mass Route 3	113	0	4.00E+07	0
Route 53 / surface				
streets	277.6	0	9.82E+07	0
Totals	460.75	105.12	1.63E+08	3.43E+07
Na / Ca ratio	4.75			



Figure 17 – Land use map of the watershed defined by where THB crossed underneath South St. This catchment is the primary recharge area for the Old Pond Meadow aquifer.

The THB watershed contains 5.65 lane miles of state owned expressway (Massachusetts Route 3) and 22.75 lane miles of road consisting of highway 53 and residential roads. These sources receive 20 tons of deicer per lane mile per year and 12.2 tons of deicer per lane mile per year, respectively (Huling and Hollacher, 1972; Heath and Morse, 2013).



Figure 18 – Land use in the THB watershed. This area is the primary reacharge zone for the Old Pond Meadow aquifer. Transportation, commercial, and residential land uses make up 33% of the watershed, and contribute to road salt deicer loading into the aquifer.

The area directly upgradient of the South Street public supply well field has undergone significant development over the past decades. The major development in the area is Hanover Mall, which was built in 1971. Hanover Mall is a 700,000 ft² shopping complex that lies only 1,128 meters north east of public supply well NOR-1. Around the mall are 3,585 parking spaces that cover over 43 acres of paved surface (CBL and Associates, 2014). This parking lot is heavily salted throughout the winter months, receiving approximately 1 ton of salt per acre per year (Heath and Morse, 2013). Since 2001, this area has continued to see development and increased impervious land cover (Fig. 19).



Figure 19 – Salted impervious surfaces around Hanover Mall and the South St. treatment facility in 2001 and in 2013. 18 acres of additional impervious surface was added between these orthophotos.

From 2001 to 2013, an additional 18 acres of impervious parking surface (that is salted in winter months) has been added to the region between Hanover Mall and the South Street well field – this is a 41% increase in salted parking areas over these 12 years. The Hanover Mall and surrounding impervious parking areas are directly upgradient and within 1200 meters of NOR-1. This proximity to the public supply well is reflected in the chemistry of NOR-1 and NOR-6. NOR-1 produces water with 150 μ S/cm greater conductivity (45 – 50 mg/L Cl⁻) than NOR-6 (Fig. 20).



Figure 20 – Six months of specific conductance measurements at the South St. water treatment plant from July 2013 though January 2014. The treatment plant does a periodic backflush and during these times only water from one of the pumping wells is represented in the specific conductivity readings. The peaks on the above chart show when NOR-1 was the only well being pumped through the treatment plant, and the valleys show when NOR-6 was the only well being pumped through the plant. In this way we can track the specific conductivity of each public supply well. NOR-1 routinely produces water with 150-200 μ S/cm greater conductivity than NOR-6.

Sources of deicers can be differentiated by two different metrics – loading of deicers as measured by Cl⁻ concentration, and cation ratios of the water based on differing use of NaCl and CaCl₂ deicer at various sources. Surface water samples collected at the end of August when surface runoff was at an annual minimum (Table 6) suggest that near surface groundwater (baseflow) in THB north of Route 3 have Cl⁻ levels of 109 mg/L. Corresponding THB surface water samples south of Route 3 had Cl⁻ levels between 234 mg/L and 245 mg/L, approaching the USEPA SMCL for Cl⁻ of 250 mg/L.

Table 6 – Water chemistry of selected surface water samples collected from THB sites in August of 2014. Jacob's Pond that the Jacob's Pond Spillway are north of route 3, while the other sites are south (downstream) of route 3.

		Specific				
Date		Conductance	Chloride	Sodium	Calcium	Na/Ca ratio
Collected	Water Source	(uS/cm)	(mg/L)	(mg/L)	(mg/L)	(meq)
8/5/2014	Mill St	862	243.0	124.5	23.8	4.57
8/5/2014	South St Br	870	245.5	124.6	24.7	4.40
8/5/2014	MW 10	869	245.0	125.1	24.6	4.44
8/5/2014	YMCA	851	243.6	122.2	24.2	4.41
8/5/2014	Cinema	846	234.1	121.7	22.7	4.67
8/5/2014	Mill Pond Spillway	868	246.2	126.4	23.5	4.68
8/12/2014	Jamaica Pond	409	109.0	61.2	9.2	5.77
	Jamaica Pond					
8/12/2014	Spillway	408	109.0	61.1	9.2	5.78



Figure 21 – CI^{-} concentration of THB surface water collected in August of 2014. CI levels increase by 110 – 150 mg/L when the stream passes underneath Massachusetts Route 3.

Similarly to the variation in THB surface water, groundwater of the OPM aquifer also shows large difference in chloride concentration from monitoring wells located on opposite sides of the aquifer. MW3 and MW5 have lower chloride concentrations, 60 mg/L and 41 mg/L respectively, relative to the rest of the monitoring wells along THB that have higher Cl⁻ (> 116 mg/L) (Table 7). MW11 has the highest Cl⁻ concentration of all monitoring wells in the aquifer at 282 mg/L. The water samples taken from the east side of the aquifer, from the 1998 series of monitoring wells, have very different water chemistry than the THB monitoring wells, with Cl⁻ levels below 10 mg/L.

		Specific				
Date		Conductance	Chloride	Sodium	Calcium	Na/Ca ratio
Collected	Water Source	(uS/cm)	(mg/L)	(mg/L)	(mg/L)	(meq)
8/5/2014	MW3	285	60.0	24.2	15.9	1.3
8/5/2014	MW4	578	141.6	79.7	13.1	5.3
8/5/2014	MW5	222	41.0	21.0	12.0	1.5
8/5/2014	MW6	548	149.6	79.9	11.3	6.1
8/5/2014	MW7	645	184.4	97.2	13.5	6.3
8/5/2014	MW8	587	163.8	89.1	12.7	6.1
8/5/2014	MW9	665	184.9	95.2	17.4	4.8
8/5/2014	MW10	417	116.5	53.1	8.1	5.7
8/5/2014	MW11	964	282.0	166.4	12.0	12.1
8/5/2014	98 shallow	69	7.6	4.8	3.5	1.2
8/5/2014	98 medium	104	7.9	6.6	6.8	0.8
8/5/2014	98 deep	53	8.1	3.3	1.6	1.8
8/12/2014	NOR-1	594	158.0	83.6	13.0	5.6
8/12/2014	NOR-6	404	101.8	53.8	10.3	4.6

Table 7 – Water quality of selected groundwater samples taken from OPM during August of 2014.

All salting of roads and parking lots adds to the overall Cl⁻ loading of the aquifer, but the ratio of cation loading is not the same for all salting applications. MassDOT applies predominantly NaCl to roads due to lower costs when compared to CaCl₂ or MgCl₂ (MassDOT, 2015) although they do occasionally apply liquid calcium chloride and magnesium chloride solutions to roads before snow events to prevent snow and ice from adhering to pavement, or when pavement temperatures fall below -6°C (Fay and Shi, 2012). Conversely, salting of commercial and industrial parking lots, in addition to residential salt use, has a much higher percentage of CaCl₂ than MassDOT. This can be observed by surface water THB samples taken in August of 2014 (Fig. 22).



Figure $22 - C^{1}$ concentration and Na/Ca ratio of surface water samples taken from THB monitoring sites in August of 2014. Samples were collected during the lowest flows of the year to represent baseflow.

Figure 22 shows that the Cl⁻ concentration increases – almost doubling – when THB crosses under Route 3 and passes by Hanover Mall. Which is consistent with the highway and mall as major loading sources of road salt deicers. Figure 22 also shows that when the waters pass under the highway, the Na/Ca ratio decreases, indicating greater Ca^{2+} relative to Na⁺ concentrations.

In addition to Cl⁻ concentration, ratios of ions can be used as a means to characterize the different salt sources contributing to OPM groundwater. To identify unique sources, Na/Ca ratio was used as an identifying characteristic. Most THB groundwater samples had Na/Ca ratios between 5 and 8 (meq/meq). All MW 11 samples had Na/Ca ratios over 11 (meq/meq). MW 3 and MW 5 had the lowest ratios for wells along THB – falling between 1.2 and 1.6 (meq/meq). Samples from the 1998 series of monitoring wells on the east side of OPM by WCB had ratios between 0.4 and 1.8 (meq/meq). Samples from production well NOR-1 average a Na/Ca ratio of 5.6, while samples from NOR-6 average 4.5. Table 7 shows the major ion concentrations and Na/Ca ratios for each groundwater sampling site at the end of the 2014 summer – these samples were collected on August 5 or August 12, 2014.

With respect to specific conductivity and Na/Ca ratio, three unique endmembers arise (Table 8). Endmember 1 (E1) is the low specific conductivity, low Na/Ca waters found east of NOR-6 – taken from the 1998 series of wells. Endmember 2 (E2) is the high specific conductivity (900+ uS/cm), high Na/Ca water produced by MW11, and Endmember 3 (E3) is the surface water of Third Herring Brook – this water has relatively high conductivity (700-800 uS/cm), but a Na/Ca ratio of 4.

Table 8 – Average water chemistry parameters for the three sources of water (endmembers) feeding
into the South St. treatment facility, as well as water chemistry for pumping wells NOR-1 and NOR-6.
Endmember 1 is representative of groundwater from the eastern side of the aquifer. Endmember 2 is
representative of groundwater from monitoring well 11. Endmember 3 is representative of THB surface
water by MW7.

	Sp. Conductivity (uS/cm)	Na:Ca (meq)
Endmember 1	70	0.75
Endmember 2	1000	12
Endmember 3	870	4.4
NOR-1	594	5.6
NOR-6	404	4.5

				Spec. Conductance	Sulfate	FI	CI	Nitrate	Na	Mg	Ca	Na/Ca ratio
Month	Day	Year	Well Name	(uS/cm)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(meq)
6	24	2014	98-1 d	52.6	6.9	0.0	8.1	1.9	3.3	0.5	1.6	1.8
6	24	2014	98-1 m	104.3	12.2	0.1	7.9	3.3	6.6	1.6	6.8	0.8
6	24	2014	98-1 s	68.6	11.6	0.1	7.6	0.3	4.8	0.9	3.5	1.2
6	10	2014	98-2 d	77.8	10.3	0.1	11.1	5.4	6.4	0.3	2.0	2.8
11	21	2014	98-2 m	72.9	8.1	0.2	11.6	0.5	8.7	0.9	2.6	2.9
6	10	2014	98-2 m	71.6	9.1	0.1	11.5	0.4	7.7	0.3	1.9	3.5
6	10	2014	98-2 s	65.6	6.6	0.1	13.0	0.1	6.5	0.2	0.5	12.2
11	21	2014	MW 10	450	11.1	0.2	136.2	0.8	76.6	3.7	13.2	5.1
5	20	2014	MW 10	304	8.3	0.1	79.3	1.2	45.5	2.1	5.0	7.9
6	3	2014	MW 10	671	14.3	0.1	184.4	5.8	105.0	2.7	12.0	7.7
6	18	2014	MW 10	566	11.6	0.2	155.3	0.5	87.2	2.3	11.1	6.8
8	5	2014	MW 10	417	4.5	0.1	116.5	0.1	53.1	2.0	8.1	5.7
11	21	2014	MW 11	873	22.3	0.1	241.8	1.0	169.2	2.9	12.6	11.7
5	6	2014	MW 11	914	11.8	0.1	279.5	0.6	151.9	2.1	10.3	12.9
5	20	2014	MW 11	986	11.5	0.1	291.5	0.4	165.5	2.8	12.1	11.9
7	17	2014	MW 11	1042	13.2	0.1	306.6	0.8	179.9	2.7	13.2	11.9
8	5	2014	MW 11	964	13.4	0.0	282.0	0.2	166.4	2.4	12.0	12.1
6	18	2014	MW 11 10m	982	12.6	0.1	292.3	0.5	168.0	2.3	11.5	12.7
7	10	2014	MW 11 10m	906	13.4	0.0	261.1	0.0	153.8	2.3	11.5	11.7
7	22	2014	MW 11 10m	1031	12.5	0.1	304.2	0.1	177.0	2.8	13.2	11.7
6	12	2014	MW 11 10m	993	12.0	0.1	299.9	0.2	172.4	3.0	13.5	11.1
6	18	2014	MW 11 2.5m	999	12.5	0.1	298.0	0.3	171.7	2.3	11.5	13.0
7	10	2014	MW 11 2.5m	839	13.8	0.0	238.7	0.0	142.4	2.0	10.5	11.8
7	22	2014	MW 11 2.5m	949	13.1	0.1	277.4	0.1	163.4	2.4	12.2	11.7
6	12	2014	MW 11 2.5m	999	12.8	0.1	289.7	0.2	168.6	2.9	13.0	11.3
6	18	2014	MW 11 5m	969	12.9	0.1	288.1	0.4	166.0	2.3	11.4	12.7
7	10	2014	MW 11 5m	883	13.7	0.0	254.0	0.0	150.1	2.3	11.2	11.7
7	22	2014	MW 11 5m	997	13.0	0.1	293.3	0.7	171.6	2.7	12.7	11.8
6	18	2014	MW 11 7.5m	1000	11.9	0.1	295.7	0.1	170.4	2.3	11.7	12.7
7	10	2014	MW 11 7.5m	898	13.1	0.0	256.5	0.1	151.2	2.3	11.3	11.7
7	22	2014	MW 11 7.5m	1020	12.8	0.1	299.1	0.4	174.5	2.7	12.8	11.9
6	12	2014	MW 11 7.5m	1005	11.8	0.1	290.8	0.2	168.4	2.9	13.0	11.3
6	12	2014	MW 11 b5m	1009	12.1	0.1	288.0	0.2	167.6	3.0	13.3	11.0
11	21	2014	MW 3	282	11.8	0.1	58.5	0.9	27.9	6.2	17.8	1.4
8	5	2014	MW 3	285	11.6	0.0	60.0	1.0	24.2	5.1	15.9	1.3
11	21	2014	MW 4	493	26.9	0.1	145.6	1.1	92.4	4.2	13.3	6.1
7	22	2014	MW 4	569	8.2	0.1	164.4	0.3	86.0	3.1	11.5	6.5
8	5	2014	MW 4	578	6.3	0.1	141.6	0.5	79.7	3.5	13.1	5.3

Table 9 – Complete ion chromatography analysis of all THB and '98 series monitoring well samples.

Month	Dav	Vear	Well Name	Spec. Conductance	Sulfate	Fl (mg/L)	Cl (mg/L)	Nitrate	Na (mg/L)	Mg (mg/L)	Ca (mg/L)	Na/Ca ratio (meg)
11	Day	2014		(us/ciii)	(IIIg/L) 14 F	(IIIg/L) 0.1	(IIIg/L) 41.1	(118/1)	(IIIg/L) 24.0	(118/1)	(IIIg/L)	(1164)
- 11	21	2014		220	14.5	0.1	41.1	4.0	24.9	4.0	13.7	1.0
/ 0	22 E	2014		220	14.3	0.1	41.1	3.4 2 E	20.9	3.3	12.2	1.5
0	21	2014		222 E90	14.7	0.0	41.0	3.5	100.0	5.5	12.0	1.5
	21	2014		505	10.2	0.1	105.0	0.8	109.9	4.5	10.1	5.5
5	18	2014	MW 6	521	6.1	0.1	143.4	0.0	79.7	2.3	10.1	6.5
6	24	2014	MW 6	515	0.4	0.1	1/12.4	1.5	78.5	2.3	10.5	5.9
8	5	2014	MW 6	5/18	11.2	0.1	1/9.6	0.2	79.1	2.6	11.7	6.1
7	10	2014	MW 6 2m	530	10.6	0.1	145.0	0.0	76.5	2.0	11.5	5.7
7	10	2014	MW 64m	520	9.7	0.1	141.2	0.0	77.0	2.7	11.2	6.0
7	10	2014	MW 67m	519	9.5	0.1	139.8	0.2	76.2	2.6	10.8	6.1
7	10	2014	MW 6 11m	520	9.5	0.1	140.5	0.0	76.7	2.7	10.8	6.2
11	21	2014	MW 7	447	16.9	0.1	127.3	0.2	83.3	3.3	10.5	6.9
5	6	2014	MW 7	437	9.6	0.1	133.1	0.2	69.6	1.5	5.3	11.5
5	20	2014	MW 7	491	9.1	0.1	140.0	0.3	77.9	2.0	6.4	10.5
6	18	2014	MW 7	543	7.8	0.1	156.9	0.1	85.2	1.9	7.1	10.5
7	17	2014	MW 7	606	8.9	0.1	173.5	0.1	94.3	3.0	10.3	8.0
8	5	2014	MW 7	645	8.1	0.0	184.4	0.6	97.2	3.9	13.5	6.3
11	21	2014	MW 8	510	25.7	0.1	150.4	0.6	97.2	4.5	14.9	5.7
5	6	2014	MW 8	482	10.0	0.0	139.4	0.4	74.6	1.8	6.5	10.0
5	20	2014	MW 8	513	8.2	0.0	143.0	1.1	81.1	2.1	6.8	10.3
7	17	2014	MW 8	549	10.0	0.0	151.8	1.2	85.1	2.6	9.9	7.5
8	5	2014	MW 8	587	10.8	0.1	163.8	0.3	89.1	3.4	12.7	6.1
11	21	2014	MW 9	404	15.8	0.0	113.0	1.5	75.5	3.1	11.6	5.7
5	6	2014	MW 9	523	11.0	0.0	148.2	1.3	79.5	2.5	9.1	7.6
5	20	2014	MW 9	522	9.5	0.0	143.3	0.5	79.6	2.7	9.9	7.0
6	18	2014	MW 9	571	7.4	0.0	160.6	0.2	85.3	2.3	10.8	6.9
7	17	2014	MW 9	501	8.9	0.0	135.6	0.5	75.3	2.5	11.2	5.8
8	5	2014	MW 9	665	4.6	0.0	184.9	0.6	95.2	4.7	17.4	4.8
				Spec.	Sulfate	FI	а	Nitrate	Na	Mø	Ca	Na/Ca
Month	Dav	Vear	Well Name	(uS/cm)	(mg/l)	(mg/I)	(mg/I)	(mg/L)	(mg/L)	(mg/I)	(mg/I)	ratio (meg)
WOITCH	Day	Tear	MW/3	284	11 7	0.1	50.2	0.0	26 1	57	16.0	1 2
	Ave	rages		547	11.7	0.1	150.6	0.9	20.1	3.7	10.9	1.5
	/	4900	N/W/5	347	13.0	0.1	130.0	0.0	20.0	3.0	12.0	1.5
			MW6	223 5/1	14.0	0.1	41.0	3.0 0.7	22.2 85 1	3.5 2 1	12.7	1.5 E.0
			MW7	578	10.7	0.1	152.9	0.7	84 6	3.1 2.6	2.5	0.0 א פ
			MW8	528	10.1	0.1	149 7	0.7	85.4	2.0	10.2	
			MW9	520	95	0.0	147.6	0.8	81.7	3.0	11.7	6.1
			MW10	482	9.9	0.1	134.3	1.7	73.5	2.6	99	6 5
			MW11	956	14 4	0.1	280.3	0.6	166.6	2.6	12.0	12.1
			98 series	73	9.3	0.1	10.1	1.7	6.3	0.7	2.7	2.0



Figure 23 - Spatial distribution of average water quality parameters in THB monitoring wells. MW3 and MW5 have the lowest Na/Ca ratio, lowest Cl⁻ concentration, and lowest Na⁺ concentration, but the highest average Ca^{2+} concentration. MW11 has the highest Na/Ca ratio and Na⁺ concentration.



Figure 24 - C^L concentration of THB monitoring well samples and THB surface water samples throughout the summer of 2014. Throughout sample collection, MW11 had the highest CL- concentration. Surface water samples and MW7 samples show increased CL⁻ concentration at the end of the summer after a long stretch with no rain.

Month	Day	Year	Sample Site	Spec. Conductance (uS/cm)	Sulfate (mg/L)	Fl (mg/L)	Cl (mg/L)	Nitrate (mg/L)	Na (mg/L)	Mg (mg/L)	Ca (mg/L)	Na/Ca ratio (meq)
5	6	2014	Cinema	484	9.8	0.0	132.1	0.9	74.2	1.9	8.7	7.5
5	20	2014	Cinema	506	8.8	0.1	138.3	0.9	79.0	2.3	9.8	7.0
5	29	2014	Cinema	457	7.4	0.0	124.7	0.9	71.1	2.2	9.2	6.7
6	3	2014	Cinema	426	7.4	0.1	114.9	0.7	65.2	2.4	9.4	6.1
6	18	2014	Cinema	561	7.5	0.1	150.4	1.9	85.7	2.8	12.4	6.0
6	24	2014	Cinema	792	25.0	0.1	210.6	3.0	116.7	5.0	21.8	4.7
7	10	2014	Cinema	581	7.3	0.0	157.2	2.0	86.6	3.3	13.7	5.5
7	17	2014	Cinema	536	7.6	0.1	149.0	1.1	84.8	2.4	11.6	6.4
7	22	2014	Cinema	678	8.2	0.1	191.9	2.6	104.5	4.1	16.7	5.5
8	5	2014	Cinema	846	9.9	0.1	234.1	3.2	121.7	6.0	22.7	4.7
5	6	2014	Mill Pond	684	8.8	0.1	189.8	3.0	93.8	3.3	15.1	5.4
5	20	2014	Mill Pond	532	9.0	0.1	145.1	1.3	80.9	2.8	10.9	6.5
5	29	2014	Mill Pond	480	7.6	0.1	130.2	1.0	73.3	2.4	9.9	6.5
6	3	2014	Mill Pond	452	7.7	0.1	121.7	0.8	68.0	2.6	10.3	5.8
7	10	2014	Mill Pond	602	7.3	0.1	160.9	2.0	86.0	4.1	14.8	5.1
7	17	2014	Mill Pond	586	9.0	0.1	161.4	1.3	89.6	2.7	12.8	6.1
7	22	2014	Mill Pond	691	8.4	0.0	193.5	2.7	101.4	4.7	18.3	4.8
8	5	2014	Mill Pond	868	11.6	0.1	246.2	3.8	126.4	6.2	23.5	4.7
5	20	2014	Mill St	521	8.8	0.1	142.9	1.1	80.4	2.7	10.7	6.5
5	29	2014	Mill St	468	7.4	0.1	128.3	1.0	72.4	2.4	9.6	6.6
6	3	2014	Mill St	436	7.3	0.1	117.8	0.9	66.0	2.5	9.9	5.8
6	10	2014	Mill St	722	8.2	0.1	203.5	2.2	102.5	3.6	15.5	5.8
6	18	2014	Mill St	554	6.8	0.1	153.5	1.5	85.6	3.1	12.9	5.8
6	24	2014	Mill St	844	18.8	0.0	231.9	3.1	118.9	6.6	25.6	4.0
7	10	2014	Mill St	587	6.5	0.0	156.9	1.6	84.3	3.6	14.7	5.0
7	17	2014	Mill St	567	8.1	0.1	157.0	1.1	86.8	2.6	12.5	6.1
7	22	2014	Mill St	667	7.0	0.1	189.4	2.1	99.3	4.6	18.0	4.8
5	20	2014	South St	528	11.7	0.1	142.1	1.2	79.3	2.9	11.2	6.2
8	5	2014	South St	870	14.5	0.1	245.5	0.2	124.6	6.3	24.7	4.4
5	20	2014	near Well 10	546	9.3	0.1	149.0	1.1	83.1	2.9	11.6	6.2
5	29	2014	near Well 10	487	7.9	0.1	133.9	1.9	75.3	2.4	10.1	6.5
6	3	2014	near Well 10	457	7.8	0.1	123.1	0.9	68.8	2.6	10.4	5.8
6	10	2014	near Well 10	663	8.9	0.0	186.2	2.4	90.5	3.6	15.9	4.9
6	18	2014	near Well 10	583	7.9	0.0	160.1	2.2	84.3	2.7	12.1	6.1
6	24	2014	near Well 10	756	13.9	0.1	208.9	0.4	108.2	5.6	21.4	4.4
7	10	2014	near Well 10	608	7.9	0.1	162.7	2.4	86.6	3.8	15.4	4.9
7	17	2014	near Well 10	594	9.6	0.1	166.0	1.4	91.5	2.8	13.3	6.0
7	22	2014	near Well 10	696	9.7	0.1	194.8	0.3	102.4	4.6	18.9	4.7
8	5	2014	near Well 10	869	14.1	0.1	245.0	0.3	125.1	6.2	24.6	4.4
5	20	2014	YMCA	529	9.3	0.2	143.2	4.5	79.8	2.7	10.8	6.4
5	29	2014	YMCA	472	7.5	0.0	129.0	0.8	72.6	2.4	9.8	6.5
6	3	2014	YMCA	444	7.6	0.1	119.5	0.8	66.5	2.6	10.1	5.7
6	10	2014	YIMCA	663	8.4	0.1	187.3	2.6	94.6	3.8	15.5	5.3
6	18	2014	YMCA	558	7.2	0.1	154.8	1.3	81.4	2.6	11.8	6.0
6	24	2014	YMCA	810	15.4	0.1	208.8	2.3	100.4	4.9	20.9	4.2
7	10	2014	YMCA	595	7.2	0.0	159.6	2.0	84.8	3.8	15.1	4.9
7	17	2014	YMCA	581	8.7	0.1	158.1	1.4	88.0	2.6	12.6	6.1
7	22	2014	YIMCA	674	8.0	0.1	189.7	2.5	98.6	4.8	18.5	4.7
8	5	2014	YIMCA	851	11.2	0.1	243.6	3.5	122.2	6.5	24.2	4.4
				Conductance	Sulfate	FI	CI	Nitrate	Na	Mg	Ca	ratio
Month	Day	Year	Well Name	(uS/cm)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(meq)
			Cinema	587	9.9	0.1	160.3	1.7	89.0	3.2	13.6	6.0
	Ave	rages	Mill Pond	612	8.7	0.1	168.6	2.0	89.9	3.6	14.5	5.6
		-	Mill St	596	8.8	0.1	164.6	1.6	88.5	3.5	14.4	5.6
			near Well 10	626	9.7	0.1	173.0	1.3	91.6	3.7	15.4	5.4
			YMCA	618	9.0	0.1	169.4	2.2	88.9	3.7	14.9	5.4

-

Table 10 - Complete ion chromatography analysis of all surface water samples.

Section 6. Discussion

6.1 Differential Deicer Pathways

The stratigraphy of well cores taken at MW1, MW2, MW3, and MW5 can put in context of the area's glacial geologic history. These data suggest that these wetland areas are likely former kettle depressions that are now filled in with fine sand and fine silt sediments at the bottom, with compacted peat covering the top 5 meters. Based on low estimated K values of these sediments (Table 3, Fig. 12, Fig. 15), the photographs of gray coloration indicative of a reducing environment with little movement of oxygenated water (Fig. 11), and pump tests in the wetlands near MW5 (Table 4, Fig. 16), it can be deduced that these kettle wetlands are areas of reduced flow of groundwater and dissolved contaminants migrating along pathways toward pumping well NOR-1 and NOR-6.

Conversely, in the riparian areas surrounding the kettle depressions at MW7, MW8, MW9, and MW10, we see a very different lithology. These regions have thick horizons of course sand and pebbles (Fig. 13) that represent a more dynamic depositional environment when contrasted to the regions of peat and silt described previously. High-energy streams of glacial meltwater carried and deposited coarse sand and pebbles around stationary blocks of ice that had broken from the retreating glacier. Later, as the glacier continued to retreat north, the deposited ice blocks melted and developed ponds through which small streams were flowing. These smaller streams, being more distal from the glacier than the original high-energy streams, were carrying only fine sediments. This fine sand and silt was deposited into the kettle depressions and accounts for the bottom 6 meters of sedimentation seen in the well cores. After deposition of these sediments,

organic material has built on top to produce the 4 meters of compacted peat observed at the top of the well cores.

Surrounding areas of glacial outwash are composed of larger grain sizes than the wetland regions (Fig. 14), higher estimated K values (Table 4, Fig. 15) and dark red / rust colored horizons indicative of an oxidizing environment and the presence of new, oxygenated water (Fig. 13), and thus suggest the potential for greater groundwater flow through these areas relative to the peat deposits. Figure 26 shows the sediment cores aligned south to north. This representation makes clear the wetland region of low conductivity adjacent to the outwash region of course sand and pebbles that acts as the preferential pathway. When such different deposits (with differing K values) are juxtaposed like we see in this area, it is assumed that groundwater will follow the path through the highly conductive horizons of sand and not through the peat deposits of low conductivity.

In addition to sediment core analysis, pump tests were done using NOR-1 and the monitoring well array along THB (Fig. 14). Estimated hydraulic conductivity (K) between NOR-1 and these wells was calculated using the Thiem equilibrium method for an unconfined aquifer (Equation 2). The estimated K value between MW5 (in the wetlands) and NOR-1 is less than half of the estimated K between NOR-1 and the other monitoring wells (MW7 through MW10) that lie outside of the wetland areas (Table 4). This further indicates reduced groundwater flow through the wetlands. Figure 25 shows the wetland areas south and west of the pumping wells. Pathways of groundwater entering into the pumping wells are most likely from the northern and eastern regions of the aquifer.

46



Figure 25 - Wetland regions adjacent to public supply wells and Third Herring Brook. NOR-1 lies closer to Third Herring Brook, while NOR-6 is 400m east of NOR-1. Blue shaded areas represent regions of known wetlands where sediment cores revealed fine sediments with very low estimated hydraulic conductivity. Red shaded areas represent other wetland regions that could potentially have similar kettle depressions with low conductivity. These red regions were designated by shrublike wetland groundcover and are covered by water 9 months out of the year. Groundwater flowing to pumps NOR-1 and NOR-6 cannot move through these wetland regions, and thus is likely to originate from the northern or eastern regions of the aquifer.



Figure 26 - Nine sediment cores alligned South to North (left to right). MW 1, 2, 3, and 5, are in wetlands that originated as kettle depressions. These regions are made of peat and fine sediments with low hydraulic conductivity. Monitoring wells 4, 7, 8, 9, and 10 are in glacial outwash outside of these kettle depressions. These regions of course sand and pebbles are the preferential pathways of groundwater moving toward pumping well NOR-1.

It is commonplace for water contour maps, like that made by Reed (1995) (Fig. 10), to be made using hydraulic head measurements. These typical groundwater maps show simple, smooth water contours that do not account for subsurface complexities; they represent groundwater as laminar flow through a homogeneous substrate. More accurate would be groundwater maps of contours that are not always so simple, but instead that represent complex three dimensional systems that consider flow around these former kettles; contouring and contorting pathways that results in more complex groundwater flow. To obtain the understanding of the subsurface needed to represent pathways in this way, sediment cores must be taken and analyzed. This data can then be interpreted in

conjunction with traditional groundwater maps to evaluate preferential pathways of water and contaminants from sources to points of discharge.

The Old Pond Meadow aquifer is a shallow glacial basin with hydrologic characteristics typical to the north and northeastern United States. The subsurface heterogeneity, and subsequent impacts this complex geology has on groundwater conductivity and pathways, is prevalent all throughout these areas of glacial sedimentation.

6.2 Water chemistry as an indicator of different deicers and source

Monitoring well 11, the furthest north of the THB monitoring wells, has unique water chemistry when compared to the other monitoring wells along THB. MW11 has the highest Na/Ca ratio (11.8 - 12.9) and highest chloride concentration (241 - 306 mg/L). Meanwhile, samples from MW6, MW7, MW8, MW9, and MW10 have chloride levels between 118 and 184 mg/L and Na/Ca ratio range of 5.1 - 8.3 (Table 7, Fig. 27).

To achieve the Na/Ca ratio of the MW 11 water, the samples must contain a mix of 87% NaCl and 13% CaCl₂. Using this same analysis, the average water from MW6, MW7, MW8, MW9, and MW10 (average Na/Ca ratio 6.57) is created by a mix of 80% NaCl, 20% CaCl₂. Conversion of chloride to moles of salt was done using the molar mass of sodium chloride (58.44 grams per mole) and calcium chloride (110.98 grams per mole). Chloride ion makes up 60.7% and 63.8% of these salts (by mass), respectively. The higher salinity and Na/Ca ratio of MW 11 tell us there is a preferential pathway toward MW11 from a concentrated NaCl source such as the state owned salt storage shed.



Figure 27 - Na/Ca ratio v Chloride Concentration of water samples taken from THB monitoring wells. The linear relationship between Na/Ca ratio and chloride is indicative that MW6 though MW10 are a mix of the extreme water sources.

The salt storage shed 1000 meters northwest of NOR-1 has two large covered barns that hold the rock salt on a concrete slab and protect it from the elements. To the east of the barns there is a large pile of additional rock salt that is not protected from rain and snow (Fig. 28). This salt dissolves during precipitation events, runs off the pavement and infiltrates into the subsurface. Once this brine reaches the water table, it likely travels directly down gradient through the preferential pathways described earlier in section 6.1. The water chemistry data supports the theory that a point source such as this storage shed could be contributing to the high Na/Ca ratio and high Cl⁻ levels seen in MW11.



Figure 28 - A large pile of rock salt exposed to the elements at the salt storage shed on the corner of highway 53 and Mill St. in Norwell, Massachusetts (May 21, 2015).

Monitoring wells 6 through 10 show evidence of pathways with more influence from CaCl₂ sources like Hanover Mall and other commercial and residential sources (Fig. 29). Figure 21 and Table 6 show Cl⁻ levels and Na/Ca ratios for THB surface water samples taken in August of 2014. These samples were taken during times of extremely low flows – the lowest flows of the year – and therefore represent near surface groundwater discharging into the stream as baseflow. The Cl⁻ levels in the surface water samples almost double as the water passes underneath the four lane highway Massachusetts Route 3. As THB and near surface groundwater passes by Hanover Mall, the Na/Ca ratio drops from 5.7 at Jacob's pond to 4.4 by the time it reaches Mill Pond 300 meters to the south. The lower Na/Ca ratio at sites close to Route 3 (Cinema and Mill St.) signify infiltration of the CaCl₂ from Hanover Mall and short, shallow pathways through the subsurface to these proximal discharge points in THB.



Figure 29 - An empty bag of Peladow deicer found in a snow bank on the edge of the Hanover Mall. Peladow is a 90% CaCl₂ deicer. Since Hanover Mall and other commercial parking lots are salted with CaCl₂, we can use Na/Ca ratio as a means to identify preferential pathways from different sources.

MW3 and MW5 have very different water chemistry than the rest of the monitoring wells around NOR-1 and THB. These two wells are in the middle of the wetland region described in section 6.1 – about 30 meters west of NOR-1 and 10 meters from THB (Fig. 30). These monitoring wells have a much lower Na/Ca ratio (below 2), signifying more influence from CaCl₂ sources and less influence from NaCl sources. The peat deposits could retard the movement of the salt plume and rainfall directly on these areas could cause the dilution we see in the water chemistry relative to surrounding samples.



Figure 30 - Na/Ca ratio of monitoring wells along Third Herring Brook.MW3 and MW5 are in the wetland region and have the lowest Cl⁻ and lowest Na/Ca ratios. MW11 is the farthest north and has the highest Cl⁻ and Na/Ca ration. MW6 through MW10 represent mixing of these two waters.

Water chemistry analysis can also be used to rule out ocean water intrusion as the potential source of salinity in OPM. Ocean water has a high Na/Ca and low Ca/Mg ratio (Table 11).

Table 11 – Average major ions of ocean water (Pinet, 2013).

	Na⁺ (mg/L)	Ca ²⁺ (mg/L)	Mg ²⁺ (mg/L)	Cl ⁻ (mg/L)	Na/Ca ratio (meq)	Ca/Mg ratio (meq)
Average Ocean						
Value	10,800	441	1,290	19,400	21.36	0.21

While some samples from the NAWQA study also show an elevated Na/Ca ratio, none come close to approaching the ratio seen in ocean water. Ocean water has much higher Mg²⁺ levels than Massachusetts groundwater, so the Ca/Mg ratio of ocean water is far below 1 (Table 11). Every sample collected throughout this study had a Ca/Mg ratio above 1.8. If sea water intrusion were to blame for these high salinity readings in Massachusetts groundwater, it would be expected that the Na/Ca and Ca/Mg ratios of the groundwater samples match that of the ocean – even if the overall concentration of the water had been diluted. Dilution would affect concentrations of Na⁺, Ca²⁺, and Mg²⁺ ions equally, and therefore would not affect the ratio. Through comparison of seawater ratios (Table 11) to the ratios seen throughout OPM (Tables 9, 10, 11 and 12), we conclude that ocean water intrusion is not the culprit of the salt being found in OPM groundwater.

6.3 Road density regions above the Old Pond Meadow aquifer

There is a large difference (150 mg/L) between the Cl⁻ concentration levels of groundwater samples taken from the THB monitoring wells on the western side of OPM and the 1998 series of monitoring wells on the eastern side of OPM (Table 7). Figures 17 and 18 show land use for the THB watershed and demonstrate how much the salted impervious roadway and parking surface is upgradient and in closer proximity to NOR-1. Furthermore, Figure 19 shows development of the area between Hanover Mall and NOR- 1 from 2001 to 2013. In this time span, 19.6 acres of additional impervious surface parking has been added between Hanover Mall and NOR-1 – directly upgradient from NOR-1 and along the banks of Third Herring Brook. The western half of the aquifer near NOR-1 contains 25 lane miles of highway and city roads per square mile and a total of 61 acres of commercial parking and other salted impervious surfaces; the eastern side of the aquifer by NOR-6 contains 17.45 lane miles of highway and city roads per square mile and no additional salted impervious parking surface (Fig. 31).



Figure 31 - Roadways and impervious surfaces above the OPM. Roads and impervious surfaces on the western (NOR-1) side of the aquifer are in blue and roads on the eastern (NOR-6) side of the aquifer are in green.

This heterogeneity in water quality throughout OPM tells us that the aquifer is not well mixed. The majority of the expressway, highway, and impervious parking surface are at the junction of Route 3 and highway 53 or just south of the highway near Hanover Mall - therefore we assume the majority of salt loading occurs at these locations (Figs.6 & 31). All of these are directly upgradient of NOR-1 and the THB monitoring well array that show year-round high (150+ mg/L) Cl⁻ levels (Tables 6 & 7). The strong influence of local, proximal, salt sources on water quality in these monitoring wells and NOR-1 indicate the presence of short, shallow pathways (Fig. 32). Road salt deicers are introduced around the intersection of highway 53 and Massachusetts Route 3; some of the dissolved salts then infiltrate the subsurface and travel directly down gradient toward NOR-1 – reaching their discharge point in THB or NOR-1 without infiltrating to the deeper regions of the aquifer. If all dissolved deicers were penetrating to the bottom of the basin, we would not see such a strong relationship between intense local loading and high Cl⁻ in NOR-1. If the deicers traveled by only deep pathways, these pathways would carry the contamination much further south without discharge into THB or the monitoring wells, and the salt contamination would be held in the subsurface for decades or centuries before discharge.



Figure 32 - When infiltration and discharge are close in proximity, the groundwater pathways are shallow and short. More distal sources follow deeper pathways and that water can remain in the subsurface for decades or centuries before discharge (taken from Newport, 2015.)

Knowledge of these shallow deicer pathways is relevant for water quality concerns with respect to both human consumption of water abstracted at NOR-1, and for the health of wildlife in the extensive wetland regions along THB south of Jacob's pond. Many surface water samples from THB and adjoining wetlands showed Cl⁻ levels above the EPA standard for prolonged wildlife exposure (230 mg/L) (Table 6).

6.4 Year-round elevated Cl⁻ levels in Third Herring Brook

High Cl⁻ concentrations (150+ mg/L) are seen in THB monitoring wells and streamflow (baseflow) samples taken in the late summer and early fall, not only during times of salt application in the winter (Table 13). Samples taken in May show the same or lower ion concentrations than samples taken in August (Table 12). Evapotranspiration and subsequent concentration of groundwater is the suspected reason that both surface water and groundwater see elevated chloride values in August. Clearly, not all of the salt that is applied throughout the winter months is removed from the watershed surface during the spring melt. In the late winter and spring, some dissolved salts are removed from the basin with overland flow. The remaining salts infiltrate the subsurface and remain in solution in groundwater for an extended period of time. Over the summer and fall months, another fraction of these deicers in groundwater discharge through THB baseflow or as public drinking water abstracted through NOR-1.

As discussed in section 6.3, there are shallow, direct pathways of concentrated deicers in groundwater that are seen proximal to loading sources. However, the year round presence of such high levels of salt in the OPM near THB indicates deeper pathways for groundwater and dissolved deicer contamination in addition to these shallow pathways discussed earlier (Fig. 32). These deeper pathways represent influence from either more distal sources, or more concentrated brines that infiltrate more rapidly and to greater depths than those previously discussed. The presence of shallow pathways and of deeper pathways is an indication that the intense salt loading in winter months is saturating the western region of the small OPM aquifer.

Natural, "pristine", New England waters from HBW6 have major ion concentrations below 1 mg/L. All groundwater and surface water samples taken from OPM over the course of this study have ion concentrations higher than these background levels – some over 400x greater than natural levels. This data, coupled with the extremely high summertime ion concentrations, are evidence that the OPM aquifer is acting as storage of road salt deicers. The road salt deicers that are not washed away as direct flow or discharged as baseflow appear to remain in the aquifer and build up winter after winter. Each winter snowfall since road salting began in the 1940's has added additional deicer to the aquifer that builds upon those salts retained from years past. This is consistent

58

with the studies on retention discussed earlier (Anderson 2013, Howard and Haynes

1997, Bester 2006, Godwin 2003, Novotny 2010), and current work being done on

surface water chemistry in OPM (Bello, 2015).

Table 12 – Major ion chemistry of groundwater and surface water samples taken on May 20, 2014. These samples were taken at the end of the spring snow melting season. MW3, MW4, and MW5 are inaccessible in the spring months due to flooding of the wetlands. The ion levels in these spring samples are similar or slightly lower than those taken at the end of the summer, despite these samples being taken shortly after the winter salt applications ended.

	Na⁺	Ca ²⁺	Cl	Na/Ca	Ca/Mg
Sample Location	(mg/L)	(mg/L)	(mg/L)	(meq)	(meq)
MW 6	79.68	10.10	145.38	6.88	2.48
MW 7	77.87	6.44	139.95	10.54	1.99
MW 8	81.08	6.84	142.99	10.34	1.98
MW 9	79.58	9.89	143.32	7.01	2.22
MW 10	45.45	4.99	79.26	7.93	1.45
MW 11	165.45	12.14	291.45	11.88	2.67
THB Cinema	79.03	9.83	138.32	7.01	2.60
THB MPS1	80.94	10.91	145.10	6.46	2.38
THB Mill St.	80.37	10.71	142.87	6.54	2.44
THB S. St Bridge	79.31	11.21	142.07	6.16	2.32
THB well 10	83.10	11.65	148.97	6.22	2.45
THB YMCA	79.82	10.80	143.25	6.44	2.44

Table 13 – Major ion chemistry of groundwater and surface water (baseflow) samples taken on August 5, 2014. During this summer time sample collection, the CI- levels were some of the highest seen during the 2014 calendar year. All samples from OPM show major ion levels extremely elevated as compared to pristine New England water samples from the Hubbard Brook Experimental Forrest (HBW6).

	Na [⁺]	Ca ²⁺	Cl	Na/Ca	Ca/Mg
Sample Location	(mg/L)	(mg/L)	(mg/L)	(meq)	(meq)
MW 3	24.24	15.92	59.98	1.33	1.88
MW 4	79.67	13.10	141.63	5.30	2.26
MW 5	20.96	12.01	40.96	1.52	2.18
MW 6	79.93	11.34	149.57	6.15	2.61
MW 7	97.25	13.49	184.39	6.29	2.08
MW 8	89.09	12.69	163.80	6.12	2.29
MW 9	95.21	17.39	184.88	4.77	2.26
MW 10	53.14	8.08	116.48	5.73	2.44
MW 11	166.41	12.01	282.04	12.08	3.04
THB Cinema	121.74	22.73	234.13	4.67	2.29
THB MPS1	126.40	23.53	246.15	4.68	2.31
THB MSD	124.50	23.76	242.96	4.57	2.33
THB S. St. Bridge	124.60	24.70	245.49	4.40	2.39
THB Well 10	125.14	24.56	245.01	4.44	2.41
THB YMCA	122.22	24.15	243.62	4.41	2.24
HBW6	0.84	0.97	0.46	0.75	2.04

6.5 Water quality differences between NOR-1 and NOR-6

Norwell Water Department pumping well NOR-1 lies 350 meters west of pumping well NOR-6. Despite their close proximity, NOR-1 produces water with 50-60 mg/L higher Cl⁻ (Fig. 20). In addition to higher Cl⁻ concentration⁻ NOR-1 also has a higher ratio of sodium ion to calcium ion (Na/Ca) than NOR-6. In August of 2014, NOR-1 produced water with a Na/Ca ratio of 5.6 (meq/meq), while NOR-6 water had a Na/Ca ratio of 4.6 (meq/meq) (Table 7). Both of these ratios are significantly elevated with respect to pristine New England water from the Hubbard Brook Experimental Forrest, which has a Na/Ca ratio of 0.75 (meq/meq) (Table 1). This deviation from natural waters is indicative of 70 years of road salt deicer application onto roads of the Third Herring Brook watershed above the Old Pond Meadow aquifer.

The pumping wells NOR-1 and NOR-6 are situated east of THB, while most of the loading into the aquifer comes from west of the stream. (Fig. 31). Subsurface analysis done in section 6.1 shows wetland regions directly west of NOR-1 that likely restrict groundwater flow. The preferential pathways of groundwater were in outwash areas north and east of these wetlands. Water and dissolved contaminants must first flow east through these preferential pathways of coarse sand and pebbles, and then migrate south toward NOR-1, passing the THB monitoring well array.

Groundwater samples collected from the OPM show that three unique types (or sources) of water are present in the aquifer (Table 8). Figure 33 shows an endmember mixing model for pumping wells NOR-1 and NOR-6 with respect to these three water sources, similar to analysis done by Musgrove and Banner (1993). The specific conductivity of the three endmembers was plotted against their unique Na/Ca ratio. When NOR-1 and NOR-6 were also plotted, they both fell within the triangle of

60

influence of the three endmembers. Pumping well NOR-1 water consists of 40% water from the eastern side of OPM (endmember 1), 35% water from the north of the aquifer by MW11 (endmember 2), and 25% surface water coming from THB (endmember 3). This surface water from THB is flowing into NOR-1 via pathways created by the outwash sedimentation at MW7. NOR-6 does not pull any surface water from THB. The water from NOR-6 is 65% endmember 1, 35% endmember 2 (Fig. 33).



Figure 33 - Three water sources within the Old Pond Meadow aquifer that represent 3 endmember mixing in the South St. water treatment plant. NOR-1 consists of a mix of 40% endmember 1, 35% endmember 2, and 25% endmember 3. NOR-6 consists of 64% endmember 1 and 36% endmember

Figure 34 models the pathways of water into the public supply wells using the subsurface geology from section 6.1 and water quality analysis described in sections 6.3 and 6.4. Endmember 1 consists of waters with low Cl⁻ concentration and low Na/Ca ratio from the eastern side of OPM. This water originates from outside the THB watershed

and outside the influence from the heavy salt loading sources such as Route 3, highway 53, Hanover Mall, and the storage shed. This water flows from the east into NOR-6 and from the southeast into NOR-1. Endmember 2 is high salinity, high Na/Ca ratio water that shows contribution from a NaCl point source such as the state owned salt storage shed (Fig. 6.). This water is north of the treatment plant and flows down gradient (south) into both NOR-1 and NOR-6. Endmember 3 is THB surface water. This water has a much lower Na/Ca ratio (4 meq/meq) than endmember 2, but still quite high conductivity (over 800 uS/cm). This surface water shows greater influence from CaCl₂ sources, as shown by the lower Na/Ca ratio. CaCl₂ applied to Hanover Mall and other parking surfaces north of the OPM infiltrates into the groundwater in the region around the mall. This water discharges into THB as baseflow and is pulled into NOR-1 as it passes by the outwash sediments just south of the well by MW7.



Figure 34 - Modeled pathways of groundwater into NOR-1 and NOR-6 from three difference source waters. Public supply well NOR-1 pumps 40% water from the eastern pathway, 35% from the northern pathway, and 25% from Third Herring Brook. NOR-6 pumps 65% of its water from the eastern side of the aquifer, with the remainder coming from the northern pathway.

Section 7. Conclusion

The use of road salt deicers in the northern United States is necessary to keep roads clear of ice and snow during winter months. However, it has been well documented that excess Na⁺ and Cl⁻ in surface and groundwater has negative impacts on wildlife, infrastructure, and human health. It was the goal of this project to evaluate the pathways that deicing chemicals take after application – establishing their migration routes from the sources to points of discharge.

Observational and sieve analysis of sediment cores reveal drastic changes in subsurface lithology over very short distances, with equally dramatic differences in hydraulic conductivity. This extreme heterogeneity in the subsurface adds previously unknown complexity to groundwater flow models.

Surface water and groundwater water chemistry reveal short, direct, shallow subsurface pathways directly from deicer sources to points of discharge as baseflow or through a public supply well field. But Cl⁻ levels were year high year-round, not only during the winter salting season. This is indicative of deeper, longer pathways that lead to salt retention in the aquifer. Like with the subsurface analysis, we see complexity and diversity with the pathways that groundwater and dissolved contaminants take as they migrate through the aquifer.

Water chemistry can also be used to reveal the impact of different sources on varying regions of the aquifer. From this, pathways of influence from each potential source can be extrapolated. Pathways carrying contaminants from predominantly residential and commercial salt application were revealed by a lower Na/Ca ratio, while pathways from NaCl sources such as a state owned salt storage shed were revealed by much higher Na/Ca ratios.

64
Protection of wildlife and public drinking water from high Na⁺ and Cl⁻ is an increasingly difficult task as road salt application in the northern United States enters its eighth decade. A complete understanding of where salt goes after application to the roads and parking surfaces will help with protection plans for wetlands and streams, and with design of new public water supplies. Subsurface analysis and major ion chemistry are well established and readily available techniques that can reveal major migration routes of salt through the subsurface and provide valuable information in the planning of groundwater use.

Section 8. References

- American Heart Association. (2014). High Blood Pressure or Hypertension. http://www.heart.org/HEARTORG/Conditions/HighBloodPressure/High-Blood-Pressure-or-Hypertension_UCM_002020_SubHomePage.jsp. Last accessed October 21, 2014.
- Anderson, J. (2013). Geochemical Tracers of Surface Water and Groundwater Contamination from Road Salt. (Master's Thesis). Boston College, Chestnut Hill, Massachusetts.
- Anning, D. W., and Flynn, M., E. (2014). Dissolved-Solids Sources, Loads, Yields, and Concentrations in Streams of the Conterminous United States. SIR 2014 5012.
- Bello, B. (2015). A High Frequency Specific Conductance Study of Dissolved Road Salt Transport in an Unconfined Massachusetts Aquifer. (Master's Thesis). Boston College, Chestnut Hill, Massachusetts.
- Bester, M. L., Frind, E. O., Molson, J. W., & Rudolph, D. L. (2006). Numerical investigation of road salt impact on an urban wellfield. *Ground Water*, 44(2), 165-175.
- Blott, S. J., & Pye, K. (2001). GRADISTAT: A grain size distribution and statistics package for the analysis of unconsolidated sediments. *Earth Surface Processes and Landforms*, *26*(11), 1237-1248. doi:10.1002/esp.261
- CBL & Associates Properties, Inc. (2014). The Hanover Mall Fact Sheet. http://www.cblproperties.com/pag.nsf/CorpSiteByAlphaWeb/Hanover+Mall?opendo cument. Last accessed April 21, 2015.
- Fay, L., & Shi, X. (2012). Environmental impacts of chemicals for snow and ice control: State of the knowledge. *Water Air and Soil Pollution*, 223(5), 2751-2770. doi:10.1007/s11270-011-1064-6
- Godwin, K. S., Hafner, S. D., & Buff, M. F. (2003). Long-term trends in sodium and chloride in the mohawk river, new york: The effect of fifty years of road-salt application. *Environmental Pollution*, *124*(2), 273-281.
- Granato, G. E., and Smith, K. P. (1999). "Estimating concentrations of road salt constituents in highway runoff from measurements of specific conductance." Water Resources Investigation Rep. No. 99-4077,USGS, Northborough, Mass.
- Harte, P. T., & Trowbridge, P. R. (2010). Mapping of road-salt-contaminated groundwater discharge and estimation of chloride load to a small stream in southern New Hampshire, USA. *Hydrological Processes*, 24(17), 2349-2368. doi:10.1002/hyp.7645

- Heath, D., & Morse, D. (2013). Road salt transport at two municipal wellfields in Wilmington, Massachusetts. *New England Water Works Association*, *127*(1), 1-23.
- Howard, K. W. F., & Haynes, J. (1997). Contamination of urban ground water by road de-icing chemicals. *GEOtext*, (*St.John's*), *3*, 145-152.
- Hon, R., Dillon P., Besancon J., Beutel D., Bello B. (2014). "A Focused Study on Road Salt Contamination of Drinking Water Supply Aquifer, SE Massachusetts." Presentation at: 2014 Annual Conference of the Geological Society of America – Northeastern Section; March 23-25; Lancaster, PA
- Huling, E. E., & Hollocher, T. C. (1972). Groundwater contamination by road salt: Steady-state concentrations in east central Massachusetts. *Science*, 176(4032), 288-290.
- Kayama, M., Quoreshi, A. M., Kitaoka, S., Kitahashi, Y., Sakamoto, Y., Maruyama, Y., Koike, T. (2003). Effects of deicing salt on the vitality and health of two spruce species, picea abies karst., and picea glehnii masters planted along roadsides in northern japan. *Environmental Pollution*, 124(1), 127-137.
- Kelly, V. R., Lovett, G. M., Weathers, K. C., Findlay, S. E. G., Strayer, D. L., Burns, D. J., & Likens, G. E. (2008). Long-term sodium chloride retention in a rural watershed: Legacy effects of road salt on stream water concentration. *Environmental Science & Technology*, 42(2), 410-415. doi:10.1021/es0713911
- Kelly, W. R., Panno, S. V., Hackley, K. C., Sharp, J. M., Jr, & Hibbs, B. J. (2012). Impacts of road salt runoff on water quality of the Chicago, Illinois region. *Environmental & Engineering Geoscience*, 18(1), 65-81.
- Kelting, D., Laxon, C.L., 2010. Review of Effects and Costs of Road De-Icing with Recommendations for Winter Road Management in the Adirondack Park. www.adkaction.org Last accessed October 23, 2014.
- Kostick, D.S., (2007). Salt USGS Mineral Resources Program. http://minerals.usgs.gov/minerals/pubs/commodity/salt/saltmyb01.pdf. Last accessed July 21, 2014.
- Likens, G.E. (2015). *Chemistry of Stream water at the Hubbard Brook Experimental Forest, Watershed 6, 1963 – present.* Hubbard Brook Data Archive. http://hubbardbrook.org/data/dataset.php?id=81. January 10, 2015.

MassDEP. (2014). Standards and Guidelines for Contaminants in Massachusetts Drinking Water.

http://www.mass.gov/eea/agencies/massdep/water/drinking/standards/standards-and-guidelines-for-drinking-water-contaminants.html#Guidelines. Last accessed March 5, 2015.

- MassDOT. (2015). Frequently Asked Questions Snow & Ice Highway Division. https://www.massdot.state.ma.us/highway/Departments/SnowIce/FAQs.aspx. Last accessed April 22, 2015.
- Miller, R., Bradford, W., Peters, N. (1988). Specific Conductance: Theoretical Considerations and Application to Analytical Quality Control. U.S. Geological Survey Water-Supply Paper 2311.
- Musgrove, M., & Banner, J.L. (1993). Regional Ground-Water and the Origin of Saline Fluids: Midcontinent United States. *Science*, 259(5103), 1877-1882.
- Newport, B. (2015). Road Salt and Water Quality What's the Big Deal? An EPA Perspective. Presentation at: 14th Annual Road Salt Symposium; February 5; Minneapolis, MN. http://freshwater.org/wp-content/uploads/2012/07/Road-Salt-Symposium-Bob-Newport-2-5-15.pdf
- NOAA. (2001). Normals, Means, and Extremes. Boston, Ma. http://www.erh.noaa.gov/er/box/climate/BOSTON_MA____.html. Last accessed April 21, 2015.
- Novotny, E. V., & Stefan, H. G. (2010). Projections of chloride concentrations in urban lakes receiving road de-icing salt. *Water Air and Soil Pollution*, 211(1-4), 261-271.
- Pinet, P. R. (2013). Invitation to Oceanography, 6th Edition. Burlington, MA. Jones & Bartlett Publishing.
- Reed, D. (1995). Zone II Delineation Old Pond Meadows Aquifer Towns of Hanover and Norwell (unpublished). *Internal Report to the Board of Public Works*. Hanover, Ma.
- Sun, H., Lucarino, K., Huffine., M., and Husch, J.M. (2010). Retention of Sodium in a Watershed due to the Application of Winter Deicing Salt. Proceedings of the 10th International Symposium on Stochastic Hydraulics and 5th Conference on Water Resources and Environmental Research.
- Transportation Research Board. (1991). Highway Deicing, comparing salt and calcium magnesium acetate, Special Report 235. Transportation Research Board, National Research Council, Washington, DC.
- USEPA. (1988). Ambient Water Quality Criteria for Chloride. 440/5-88-001. February, 1988.
- USEPA. (2006). Secondary drinking water regulations: guidance for nuisance chemicals. U.S. Environmental Protection Agency. http://www.epa.gov/safewater/consumer /2ndstandards.html. Last accessed March 7, 2015.

- USGS. (1999). New England Coastal Basins NAWQA Program: Groundwater Studies Land Use Study. http://nh.water.usgs.gov/project/nawqa/gw_lus.htm. Last Accessed February 11, 2015.
- Wheeler, D., Thompson, J., & Bell, J. (1999). Laboratory comparison of soil redox conditions between red soils and brown soils in Minnesota, USA. *Wetlands*, 19(3), 607-616.
- Wilcox, D. A. (1984). The effects of NaCl deicing salts on sphagnum recurvum P. beauv. *Environmental and Experimental Botany*, 24(4), 295-304.
- Wilcox, Douglas A. (1986). The Effects of Deicing Salts on Water Chemistry in Pinhook Bog, Indiana. Water Resources Bulletin 22.1: 57-65.
- Windsor, C. (2011). White paper: Verifying the use of specific conductance as a surrogate for chloride in seawater matrices. In-Situ Inc. Accessed December 10, 2013.