



**Potential Impacts of Anthropogenic Impervious
Surfaces on Alkalinization in Urban Watersheds**

Tom Doody

Geology 394H

April 28, 2014

Advisor: Dr. Sujay Kaushal

1. Abstract

Impervious surfaces are ubiquitous in urbanized settings. As population centers have grown around rivers and waterways that serve as important centers of commerce, the replacement of forested land by roads and sidewalks has significantly altered the natural landscape. The materials that compose these anthropogenic surfaces change the response of the environment by altering hydrologic flow and readily carrying both organic and inorganic particulate matter into surface waters. Additionally, as the private and public transportation industries have grown with urban sprawl, communities find ways to adjust to maintaining regular habits through seasonal weather changes; increased usage of de-icing salts maintains safe transportation. Salt applications can be regulated and well-managed, but they are often overused. Further, accumulation of chlorides on the surface of roadways and sidewalks can be damaging to the physical structures of the material, enhancing corrosion and exacerbating the effects of freeze-thaw cycles. The fate of chloride in the environment has become a topic of much interest in recent years.

Along with the creation of a new, impervious lithology in population centers, urbanization has for decades contributed to acidified precipitation. Direct deposition into streams can significantly reduce pH, affecting sensitive ecosystems. Acid rain has played a role in accelerating the chemical weathering of building materials. Damaged infrastructure has a significantly shorter life span that requires costly replacement or repair on a regular basis. But only recently has attention been drawn to alkalinization of streams in the Baltimore-Washington area, a region with minimal carbonate lithology. It is usually this presence of abundant carbonates that could cause an increase in stream pH in an area that continues to have major concerns about acid rain deposition.

In an effort to examine the role of increased salinization and acidification on the chemical weathering of impervious surfaces, I designed a series of small-scale laboratory experiments. Over varying time periods I simulated short interactions between the surface and water that may contact or saturate it during periods of precipitation. Primary water chemistry measures of interest were pH and concentration of dissolved inorganic carbon, both of which might indicate a significant interaction between the material and surface water. If the role of salt enhanced the alkalinization of surface waters through a chemical interaction with the anthropogenic material, it would create an additional reason to better manage its application in the area. If the role of acidity also increased the dissolution of inorganic carbon, the infrastructure itself could be considered a source of additional carbon into surface water.

Preliminary results indicate that salinization did not significantly increase pH and DIC concentrations over that which occurred in a non-salinized water-surface interaction. However, acidification, time of interaction, and freshness of material surface area each may have a role in alkalinization in urbanized settings. The data obtained from this project can be expanded to a larger, more complex study that may yield results that are useful for best management practices in urbanized watersheds.

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2. Introduction

Stream chemistry can be largely influenced by lithology, land use, and atmospheric deposition (Liu *et al.*, 2000). For example, underlying lithology can influence the pH and carbonate chemistry of streams and rivers (Lauerwald *et al.*, 2013). On a regional scale, if a lithologic gradient underlies a watershed, water chemistry can be heterogeneous due to changes in the weathering rates of local bedrock and overlying regolith (Meybeck, 2003). Composition and solute concentrations in surface waters are often used to characterize chemical weathering rates, and a linear correlation has been observed between increased runoff and increased solute fluxes (White, 2003). Increased wetting of mineral surface areas promotes increased chemical weathering rates and can contribute to changes in stream chemistry. Often times, weathering rates are difficult to characterize due to reaction times and differences between lab and field studies (White, 2003). In addition to chemical weathering, leaching can influence elemental speciation in the solution and solid phase, and contributes to general partitioning of chemical species between solid and aqueous phases via processes such as ion exchange/sorption, precipitation/dissolution and complexation (Engelsen *et al.*, 2010). The purpose of this project was to elucidate potential impacts of weathering and leaching of anthropogenic impervious surfaces on the acid/base chemistry of urban runoff.

In a natural lithologic setting, water infiltrates into the subsurface at varying rates based on, among other factors, the perviousness of the lithology. In natural rock surfaces with a well-developed network of pore spaces, infiltration rates are naturally higher. As that water moves through the rock, it may interact with the minerals, dissolving ions in solution as it advances, altering the water chemistry. Leaching of ions from minerals by dissolution and/or desorption into water can be particularly important for influencing stream chemistry and is partially a result of the volume, residence time and chemistry of the initial water source. These same underlying mechanisms and reactions related to natural water-rock interactions may also influence anthropogenic impervious surfaces in urban watersheds. However, relatively less is known regarding the weathering of anthropogenic impervious surfaces and potential impacts on water chemistry in the entire watershed.

2.1 Anthropogenic Surfaces

Human activities have created easily weathered impervious surfaces dominated by anthropogenic materials that can influence leaching and chemical weathering across broader geographic scales. A study by Elvidge *et al.* (2004) estimated that impervious surface area in the conterminous United States covers 112,610 km² ($\pm 12,725$ km²), an area roughly the size of the state of Ohio. Composition of anthropogenic surfaces may also be a significant factor in affecting urban water chemistry. Concrete materials used in roadways and drainage systems may provide an artificial source of calcium and bicarbonate to leach into urban waters. Generally, concrete is composed of cement filler, water and an aggregate material of crushed rock and sand. Aggregate mineralogy and grain size vary, but it is selected and tested for non-reactivity with the filler and its resistance to polishing by vehicular traffic (Maryland SHA, 2013). Common aggregates are typically silicates, limestone and non-pyritic rocks (Maryland SHA, 2013). Cement composition is also variable, but the most widely-used is Portland cement, a hydraulic cement that is a superheated blend of limestone and clay, which cures and hardens as

it dries. Properties of the concrete vary based on ratios of aggregate, cement and water, as well as compaction. Carbonation is a major factor in concrete degradation, resulting from chemical reactions between CO₂ and concrete hydrates and calcium silicate hydrates. The reaction produces calcium carbonate (CaCO₃) and water (Davies *et al.*, August 2010). Chemical weathering of concrete is affected by a number of additional factors including pH, chloride levels, sulfate levels and leaching (ACI, 1982). Weathering of concrete may also be impacted by acid deposition in urban areas, but this has been less studied (Kaushal *et al.* 2013).

In addition to concrete, asphalt pavement represents a larger and growing portion of anthropogenic surface coverage in more recently developed urban areas. Asphalt pavement is not only used in new roads, but can be layered atop a pre-existing concrete road. The development of asphalt pavement is conceptually similar to concrete but with a different filler material. The asphalt filler is a hydrocarbon-rich petroleum product. The surface of the layer is often coated with a coal-tar-based sealcoat. Asphalt pavement may also contain recycled concrete aggregate as a sub-base material. The sub-base can experience leaching of minerals and contaminants, dependent upon on temperature, pH, external loading from traffic and rates of infiltration of surface water (Engelsen *et al.*, 2012). Vehicular traffic, sunlight and freeze-thaw cycles regularly contribute to weathering rates of asphalt. Weathered asphalt and coal tar-sealcoated pavement contribute to runoff into urban streams and are significant sources of particulate carbonaceous material in the form of black carbon (Yang *et al.*, 2010). Although sealcoats are marketed to extend the usable life of the asphalt pavement, the most common sealcoat contains polycyclic aromatic hydrocarbons (PAHs). PAHs are detrimental to terrestrial and aquatic ecosystems and are potential human carcinogens. An abundance of particulate PAHs on roadways may be transported aerially or through storm runoff to surrounding soils and streams (Mahler *et al.*, 2012).

Although anthropogenic surfaces are now ubiquitous in urban watersheds, their direct effects on water chemistry have not been well studied until very recently. For example, previous work has focused on the hydrologic effects of impervious surfaces instead of their direct contribution to water chemistry (e.g., Paul and Meyer 2001). Recent works suggest that degradation of impervious surfaces and the evolution of urban ecosystems over time can influence stream chemistry directly and indirectly (Kaushal and Belt 2012). Similar factors that influence weathering of rocks naturally may impact weathering of anthropogenic surfaces such as concrete and asphalt, which have become part of the urban lithology. Interaction of road salts with anthropogenic surfaces and deposition of acidic precipitation may significantly increase weathering.

My thesis project examined the effect of water-surface interactions on water chemistry, specifically pH and dissolved inorganic carbon (DIC). As land around a stream becomes more urbanized, inorganic carbon contributions may, to some extent, come from impervious surfaces via runoff. My project explored the degree to which these surfaces influence water chemistry variables through the following hypotheses:

- i. **Increased salinization significantly increases the weathering of dissolved inorganic carbon from impervious surfaces and increases pH of urban surface waters.**
- ii. **Increased acidification significantly increases the weathering of dissolved inorganic carbon from impervious surfaces and increases pH of urban surface waters.**

2.2 Background: Potential Impacts of Salinization on Weathering

Urban areas naturally experience more vehicular traffic on their roads. During the winter months, cities experiencing snowfall and freezing rain will often apply de-icing salt or a saline brine to roads. The application of salt lowers the freezing point of water. Chemicals used for de-icing salt vary, but the most common, due to their solubility, are sodium chloride (NaCl), calcium chloride (CaCl₂) and magnesium chloride (MgCl₂). NaCl remains the industry standard due to its availability, lower cost, and effectiveness at pavement temperatures of 20°F and above (Maryland SHA, 2013). Total de-icing salt usage varies based on snowfall rates, but approximately 8-12 million tons of de-icing salt is applied annually by United States municipalities (Cunningham *et al.*, 2008). In addition to road salt, de-icers purchased by individual consumers spread in unregulated quantities on driveways and sidewalks and contribute to the total salt application in the watershed.

The transport of de-icing salts to nearby soils and streams can have significant ecological effects. Long-term de-icing salt application changes soil structure due to leaching and reduces the flushing of organic matter (Green *et al.*, 2008). A buildup of de-icing salts impacts biogeochemical cycling, redox changes and microbial community structure in freshwater wetlands (Kim and Koretsky, 2012). High salt and chloride concentrations in urban lakes can affect annual spring turnover of the water, limiting the transport of oxygen to benthic sediments (Novotny *et al.*, 2008). Increased soil salinization induces ion exchange, potentially increasing the mobility of H⁺ ions and trace metals, resulting in increased trace metal concentrations in streams (Lofgren, S., 2001). Infiltration of de-icing salts contaminates groundwater, impacting drinking water supplies and future urban growth potential (Howard and Maier, 2007).

Effects of de-icing salt application have also been studied as they relate to problems with corrosion of concrete and asphalt infrastructure. Specifically, dissolved salts that infiltrate concrete and asphalt surfaces in highway overpasses can interact with rebar support structures, causing oxidation. Through iron oxidation, expansion and corrosion of the rebar material results in fractures in the surrounding concrete or asphalt material. This initiation of fracture can spread further in the material through contraction and expansion during freeze-thaw cycles. Vegetation and freeze-thaw can also further exploit surface fractures, leading to spalling, or significant disintegration of joint/crack edges. Finally, the salts in solution that infiltrate through pore spaces in the materials may, over longer periods of time (months to years), effloresce. This salt recrystallization increases internal pressure in the material, further weakening the structure and creating additional fractures that are subject to future propagation. Evidence of significant secondary efflorescence can be found in chloride “stalactites” hanging below overpasses that have degraded through this process. However, beyond some of the many mechanical weathering processes through which de-icing salts erode the infrastructure, the question of the role of salt in chemical interactions with the surface material is less studied.

2.3 Background: Potential Impacts of Acidification on Weathering

In addition to salinization, acidification from atmospheric deposition can contribute to human-accelerated chemical weathering (Kaushal *et al.*, 2013). Bicarbonate alkalinity (dissolved inorganic carbon) is often a by-product of these chemical weathering reactions. It is expected that watersheds underlain by carbonate lithology can increase stream and river alkalization. Interestingly, stream alkalization has occurred in streams of the Baltimore-Washington metropolitan area with minimal natural carbonate lithology (Kaushal *et al.*, 2013). This stimulates the question – what is the source of increasing alkalinity in the streams and

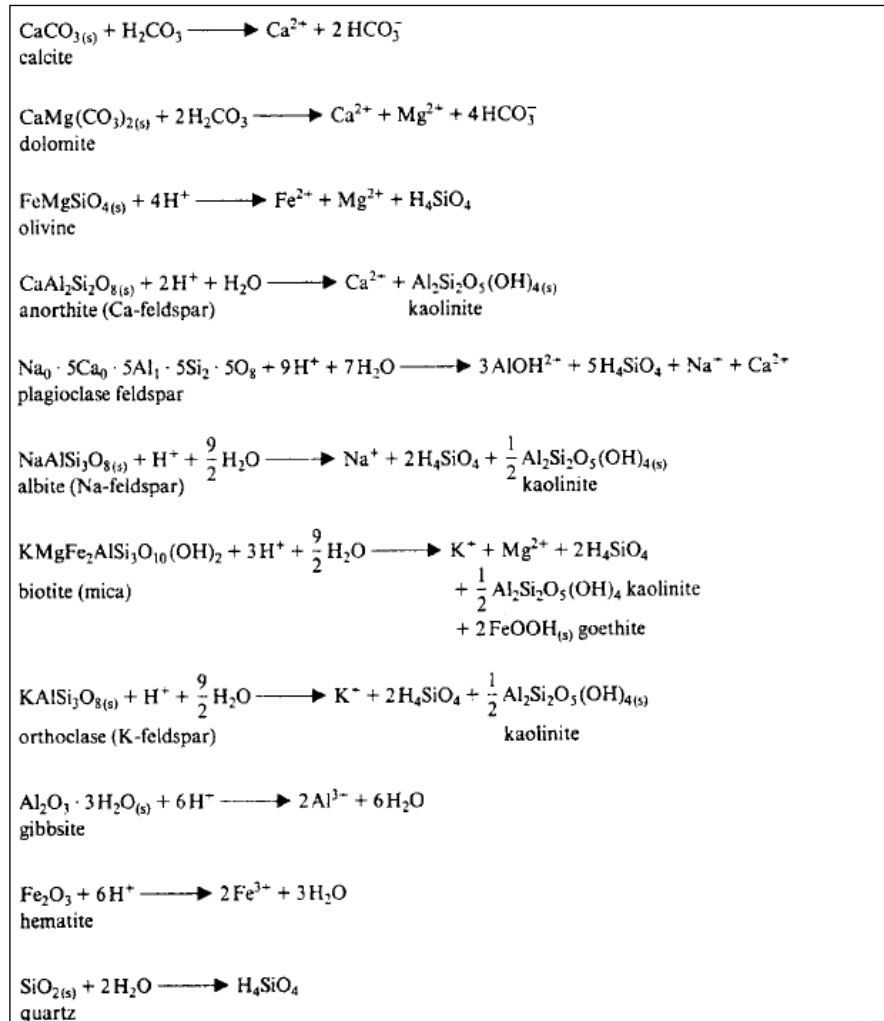


Figure 1 from Schnoor and Stumm (1986) demonstrating common weathering reactions of natural lithology from most susceptible (top) to least susceptible (bottom) and potential for generation of alkalinity.

could it be related to human-accelerated weathering of impervious surfaces?

The minerals present in the anthropogenic surface material are derived from natural sources and are prone to the same weathering processes experienced by the natural lithology. As previously mentioned, the aggregate material used in varying proportions in concrete and asphalt may include quartz, feldspar, mica and sometimes carbonates. Figure 1 displays some of the common weathering reactions that can occur in the natural lithology and, potentially, the aggregate materials as they are exposed to surface air and acidified water in the form of precipitation. The most susceptible at the top are carbonates that may be considered as proxies for some of the filler material in concrete.

2.4 Increasing Regional Importance of Salinization and Acidification

In the northeastern U.S., urban areas have been heavily impacted by both salinization and acid rain. Salinization has been documented for decades in fresh water ecosystems (e.g.,

Kaushal *et al.*, 2005, Kelly *et al.*, 2008). Current questions exist as to whether de-icing salt should be managed due to ecological effects (Findlay *et al.*, 2011). Additionally, trends in acid rain are studied as a part of understanding stream chemistry, protecting aquatic ecosystems, and managing restoration practices (Likens, 2012).

Maryland primarily uses a NaCl de-icing salt in its road and highway applications (Maryland SHA, 2013). From 2008-2012, the annual statewide average for de-icing salt application was 877 pounds of salt used per lane mile per inch of frozen precipitation. Because centers of population expect higher road usage, salt application is significantly greater in urban



Photo from chesapeakestormwater.net

areas. During the same time period, the average annual usage in Baltimore County was reported at 1545 pounds of salt per lane mile per inch of frozen precipitation (Maryland SHA, 2013). Although best management practices are followed for application of de-icers, the inevitable transport of de-icing salts by surface runoff has significantly increased chloride levels in Baltimore streams and storm water management ponds. High specific conductance, a measure of chloride salt loading, alters the ecosystem structure in storm water ponds, reducing their effectiveness as a management strategy (Van Meter *et al.*, 2011). Baseline salt

concentrations in rural streams in the Baltimore area have increased, even in areas with a low concentration of roadways. Across a broader land use gradient in Baltimore, chloride concentrations in many urban and suburban streams has exceeded the maximum limit of 250 mg/L recommended for protection of freshwater life (Kaushal *et al.*, 2005). Peak chloride concentrations by land use in select Baltimore streams also indicate significant spikes in winter months in urban and suburban areas (Kaushal *et al.*, 2005).

In addition to salinization, acid rain presents an important regional water quality problem. Acid rain has been recognized as a serious regional environmental problem since the early 1970s (Likens *et al.*, 1972). Despite Phase II of the Clean Air Act in which sulfur dioxide was regulated, acid deposition continues to be a problem (although it is improving). Acid rain leads to increased deposition of nitrates and sulfates in the Chesapeake Bay Watershed, which can threaten the health of aquatic ecosystems. Acidic precipitation on impervious surfaces in urban areas leads to direct runoff into streams.

The National Atmospheric Deposition Program (NADP) collects data regularly for a group of precipitation chemistry variables. The closest NADP site to Baltimore, MD-99 in Beltsville, MD, has collected weekly precipitation data since 2004. Over the last decade, the weighted annual mean pH of precipitation events has ranged from 4.38 in 2004 to 4.99 in 2012, the final year of available data. Over the course of that period, data from individual precipitation events list a range of pH 3.57 to pH 6.44 (NADP, 2014).

3. Study Area and Methods

3.1 Site Descriptions and Geologic Setting

The four sites below represent lithologic and land use gradients along the Gwynns Falls watershed, the main focal watershed of the Baltimore LTER site (www.beslter.org). Watersheds and streams have been extensively described in Groffman *et al.* 2004, Kaushal *et al.* 2005, and Kaushal *et al.* 2008.

- Pond Branch is the smallest watershed and is a completely forested site with no urbanization. Pond Branch drains a 0.12 square mile area and is located in Oregon Ridge State Park, just west of Cockeysville, MD.
- Baisman Run also flows through Oregon Ridge State Park and an adjacent suburban area. The small watershed drains an area of 1.47 square miles and receives input from Pond Branch. The area around Baisman Run has 1% impervious surface coverage in the form of roads, driveways, sidewalks and rooftops.
- Villa Nova drains an urbanized area of 32.5 square miles in the Gwynns Falls system. The land is 70 percent developed. At the sampling site the channel is deeply incised and is bordered by 4-6 lane roads, local businesses and homes.
- Carroll Park is the furthest downstream site in the Gwynns Falls system and the most heavily urbanized. The drainage area of 69.5 square miles is 79 percent developed. The channel at the sampling site is confined and relatively straight. Multiple highway overpasses and entrance ramps cross the stream channel.

In the Pond Branch and Baisman Run watersheds, the underlying bedrock is medium- to coarse-grained biotite-oligoclase-muscovite-quartz schist with garnet, staurolite, and kyanite. This Upper Cambrian to Lower Ordovician pelitic schist is the lower member of the Glenarm Supergroup of the Piedmont-Blue Ridge province. Further south and west along the Gwynns Falls stream, toward Villa Nova, lithology transitions from a pelitic schist to the Cambrian/Ordovician Cockeysville Marble and Precambrian Baltimore Gneiss. In the Cockeysville Marble, metadolomite, calc-schist, and calcite marble are predominant. The Baltimore Gneiss is a biotite-quartz-feldspar gneiss and biotite-hornblende gneiss. Furthest downstream in the older, Carroll Park area, natural lithology is dominated by the late Precambrian Baltimore Gabbro Complex, a hypersthene gabbro containing olivine gabbro, norite, anorthositic gabbro, and pyroxenite (Maryland Geological Survey, 1968). Overall, the amount of naturally-occurring carbonate lithology in the area is minor.

3.2 Collection of Water Samples

I collected stream water samples from the Pond Branch forested stream on four occasions between October 2013 and April 2014. The pH of Pond Branch water is relatively neutral, with seasonal ranges from pH 6.8 to pH 7.1. During each sampling event, water was collected in 500 mL, high-density polyethylene (HDPE) Nalgene bottles that were rinsed five times in the stream on site prior to sample collection. Full sample bottles were capped below the water surface to minimize head space. Samples were kept cold in an Igloo cooler containing reusable freezer packs and transported to the lab for storage at 4.0°C until they were used for leaching

experiments. Due to the sensitivity of carbon sources measured in the water chemistry, storage time was minimal and samples were collected either the day before or day of the lab experiments.

3.3 Collection of Geologic Materials and Anthropogenic Impervious Surface Materials

Samples of the pelitic schist were collected in early October. Using a rock hammer, three small pieces of rock were removed from an outcrop near the entry point of the Pond Branch tributary into Baisman Run. Samples were collected from outcrop areas that were not moss-covered and were immediately placed in quart-sized Ziploc bags. The schist was heavily weathered, and was observed in hand sample to be composed of predominantly biotite, muscovite, quartz and plagioclase, with a few small garnet porphyroblasts.

Initial asphalt samples were collected from a roadside in a residential neighborhood in Glyndon, MD. Concrete samples were collected in two areas: residential area along Owings Mills Blvd. in Owings Mills, MD and near the USGS gaging station at Carroll Park, west of downtown Baltimore. These were discarded concrete cores from the overpass above the stream at Carroll Park. All anthropogenic surface materials were collected from loose samples without the destruction of public or private property. As the project progressed, a connection was made with Eric Dougherty of the Maryland State Highway Administration (SHA). Mr. Dougherty and members of his team supplied a variety of concrete and asphalt cores that represented samples of surfaces throughout the highway system.



Photo by Tom Doody

3.4 Sample Preparation

For salinization and acidification experiments, pieces of source materials were separated from the larger samples collected in the field and through Maryland SHA. Equal surface area was not considered in sample preparation for the first experiment, but in all subsequent experiments, samples were measured for surface area. Initial surface area measurements were attempted using a combination of ImageJ software. The software proved to be cumbersome due to the number of photos needed to image all sides of each sample, rather than just one surface. Therefore calipers were used for all measurements. The mean surface area of the combined population of 70 asphalt and 71 concrete samples used throughout my experiments was $65.8 \pm 8.1 \text{ cm}^2$ (2σ). Samples of the pelitic schist were not prepared due to the degradation and low integrity of the material and were therefore not used in further experiments. Additionally, the primary area of interest was the response of the impervious anthropogenic surface material to salinization and acidification.

3.5 Salinization Experiments

Salinization experiments were performed in multiple phases over the course of the project to examine the potential effect of salt on pH and leaching of inorganic carbon from the various surface materials in the Gwynns Falls watershed. In a laboratory setting, samples were introduced to water in mason jars for specific periods of time. Water was reserved for measurement of dissolved inorganic carbon (DIC) prior to the interaction with any of the materials in order to obtain baseline readings. pH was measured before and after each leaching period for every sample. At the end of the prescribed time interval for each sample, the source material was removed from the water to stop further reaction. Water was immediately poured off, filtered and prepared for DIC analysis.

The first experiment consisted of separately wetting source materials in either stream water or in salinized stream water for a period of 24 hours. 100 mL of water was used in all jars. For the salinized water, a solution had a concentration of 100 mg/L of NaCl. A total of 12 source material samples were used. Water from each mason jar was then vacuum filtered, poured into 24 mL clear glass vials and capped to prepare for DIC analysis.

As the project progressed and data were reviewed, shorter time increments were utilized to investigate whether or not an initial wetting phase on the scale of minutes or seconds was a key in the interaction. Additionally, samples with measured surface areas were used in order to eliminate or better identify some of the potential variability from sample to sample. De-icing salt was acquired from the Maryland SHA and used in place of laboratory grade NaCl. It is worth noting that the de-icing salt is stored outdoors in covered bins and silos, but is nevertheless exposed to dust and some levels of other particulate matter. Among the salt was sand, small gravel and fragments of glass.

For the remaining salinization experiments, the volumes of untreated and salinized water remained unchanged at 100 mL, and the concentration of the salinized water was 100 mg/L NaCl. A second round of experiments was completed utilizing minute-scale time increments: 1, 15, 30, 60, 120 and 240 minutes, respectively. A total of 48 material samples (24 concrete and 24 asphalt) were used in order to test a pair of each material type at each level of salinization at each time period.

A third and final round of experiments in early spring explored pH and DIC change in experiments on the time scale of seconds: 15, 30, 45 and 60 seconds, respectively. The same protocol was followed, with paired samples of each material type tested at each level of salinization and time interval. 32 material samples (16 asphalt and 16 concrete) were used in this round of experiments. A slight revision was made to conditions of the experiment. In order to perhaps simulate colder weather conditions during which de-icers would interact with roadways, both the surface materials and water were stored at 4°C until immediately before the experiment. This also addressed the potential issue of temperature sensitivity of pH measurements. However, the room was not refrigerated, due to the need to use a lab with access to vacuum lines and filtering equipment. Mason jars were not chilled. Over the course of the short experiments, water temperatures rose as much as 6.8°C, with a mean change in temperature of $4.2 \pm 1.3^\circ\text{C}$ (2σ) due to interaction with the ambient air.

3.6 Acidification Experiments

I tested the effects of acidity on weathering to impact concentrations of DIC and alkalization at three different starting pH levels. I used the stream water from Pond Branch as my water source, which at the time of collection in early April had a field pH of 6.84. In the lab, pH varied slightly, with a mean pH of 6.86 ± 0.02 (2σ). This natural stream pH was used as the least acidic for the experiments. Volumes of water were acidified in the lab under the fume hood with microliter volumes of 15.7 M nitric acid to reach two separate levels of acidity. 3 liters of water were acidified to $\text{pH } 2.99 \pm 0.04$ (2σ) and 3 additional liters to $\text{pH } 4.49 \pm 0.04$ (2σ). The rationale for acidifying to pH 3 is based simulation of driving rainfall in a study of acid attack on concrete (Chen *et al.*, 2012); as previously cited, mean pH of precipitation in the Baltimore-Washington metropolitan area has ranged from 4.38 to 4.99 over the last decade, with a weekly mean average of pH 4.52 (NADP, 2014). A small volume of water at each level of acidity was reserved and prepared for analysis for DIC without any surface material interaction.

Remaining source materials were divided among experiments at the different pH levels. Due to inavailability of some equipment in the lab and a shortage of usable samples, tests at the desired number of time intervals, with replication, was not possible. Further, because my previous experiments used stream water pH levels, I focused most of my efforts on the two levels of higher acidity. 30 asphalt samples and 31 concrete samples were used altogether in the experiment, divided between the different acidity levels and different time intervals of 30 seconds, 60 seconds and 180 seconds. Finally, for individual samples in the 180-second time interval, pH was monitored throughout to better understand a pH path over the course of that timeframe.

3.7 Water Chemistry Analyses

DIC was analyzed on a Shimadzu TOC-L (total organic carbon) Analyzer in Dr. Kaushal's biogeochemistry lab. The TOC-L has high detection sensitivity, with a detection limit of $4 \mu\text{g/L}$. The Shimadzu utilizes a 680°C combustion catalytic oxidation method in an oxygen-rich environment. The sample is delivered to the combustion furnace, which is supplied with purified air. It then undergoes combustion through heating to 680°C with a platinum catalyst. Upon decomposition and conversion to carbon dioxide, the sample is cooled and dehumidified, and then detected by the infrared gas analyzer (NDIR). Concentration of total carbon is obtained through comparison with a calibration curve formula. By subjecting the oxidized sample to a sparging process, the inorganic carbon in the sample is converted to carbon dioxide, and the concentration is detected by the NDIR (Shimadzu Analytical and Measuring Instruments, <http://www.shimadzu.com>). Concentration of total organic carbon is then calculated by subtracting the inorganic carbon concentration from the obtained total carbon concentration. A simplified schematic of the process may be referenced in Figure 9 in Appendix B at the end of the paper.

pH measurements were made with a multipurpose, all-weather meter made by Hanna Instruments. I used a traditional three-point method with buffering solutions of pH 4, 7 and 10 to calibrate the meter. Instrument sensors were thoroughly rinsed with deionized water and dried between measurements. As a general practice, I recalibrated the pH meter every 10 measurements, and on occasion more frequently as needed if readings were significantly inconsistent within the same water sample.

4. Results

4.1 Salinization experiments

Preliminary salinization experiments demonstrated in all cases that pH and DIC changed with increased time, but the impact of the salt was difficult to determine. In the experiment that focused on a scale of minutes-to-hours, changes in an initial wetting phase in the first few minutes appeared to be significant for both pH and DIC, which directed an additional round of experiments toward shorter time periods.

pH

Although pH increased in all treatments with a salt addition, the same held true in treatments without salt, regardless of the surface material. The alkalinization of samples corresponded more to time of interaction and surface material, but a salt effect was not clear. These patterns can be seen in Figures 2 and 3, in which the water interacting with the concrete samples resulted in higher levels of alkalinity, but not consistently in those with a salt addition. Water that interacted with asphalt samples also became more alkaline, but the effect was less distinct relative to the concrete. A divergence occurs very quickly after an initial period of interaction, on the scale of seconds as displayed in Figure 3.

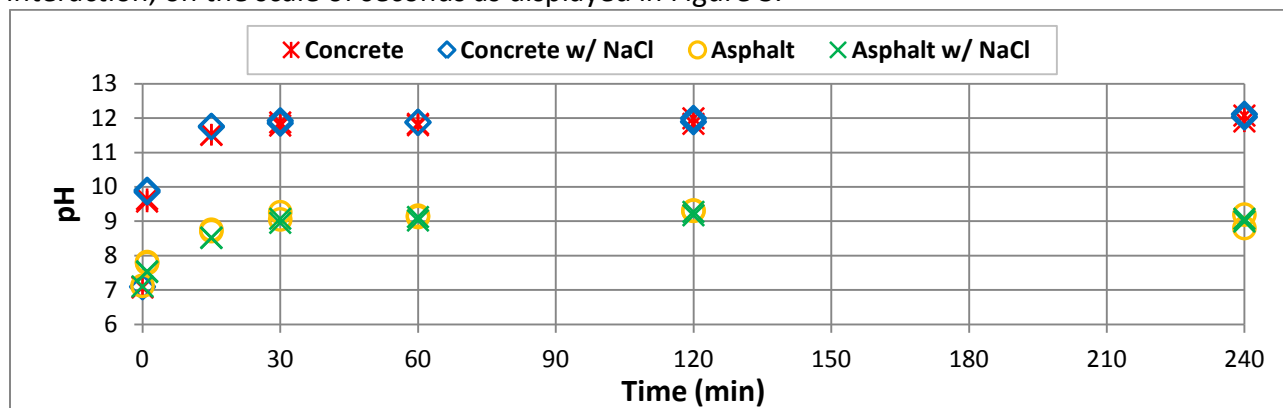


Figure 2: Alkalinization of water during minute- to hour-scale salinization treatments

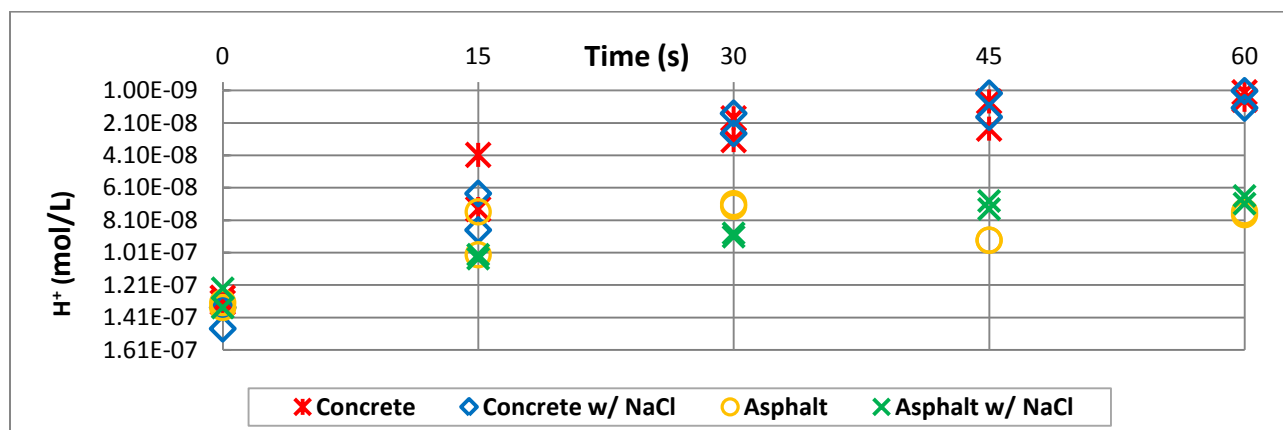


Figure 3: Alkalinization observed during salinization experiments. Note the vertical axis values are reversed. As time increases, concentration of H⁺ decreases, indicating increased alkalinity.

Dissolved Inorganic Carbon (DIC)

Changes in DIC also displayed variability across time increments and sample materials without a clear effect from a salt treatment. Data displayed in Figure 4A actually show lower DIC values in water samples in which concrete interacted with salinized water. However, the sample size is limited and additional replication is needed to establish a stronger case that a salt treatment consistently has an effect on DIC concentrations in either direction.

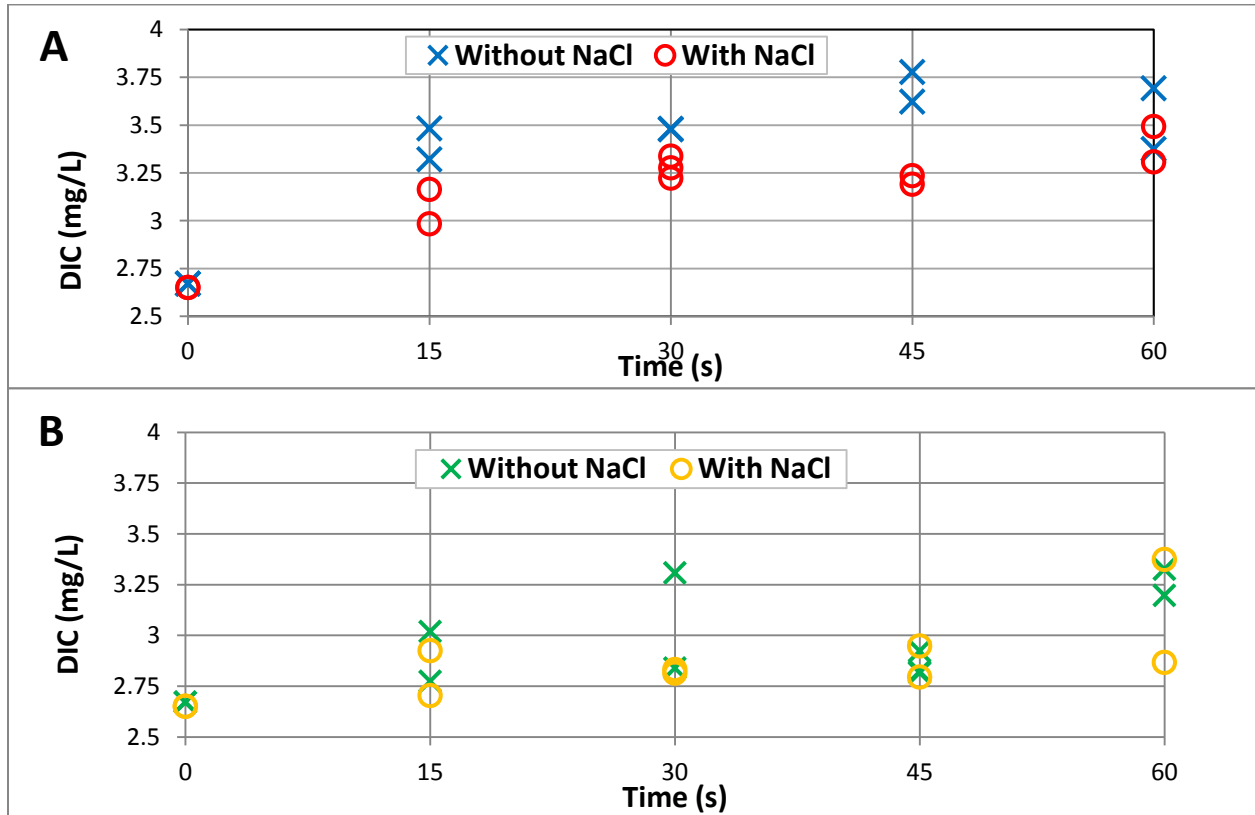


Figure 4: Concentrations of DIC from salinization experiments on short time scales with (A) concrete and (B) asphalt samples.

The degree to which DIC concentrations increase in the water-concrete interactions appear significantly greater than those of the asphalt interactions. This is consistent with the variation in increased levels of alkalization displayed in Figure 3 over shorter time scales. Changes in DIC concentrations over longer increments trended similarly overall, but the rapid reaction to an initial wetting phase was actually the opposite (see Appendix B, Figure B1).

4.2 Acidification experiments

As referenced in the methods portion of the paper, the rationale behind acidification experiments is to simulate contact between impervious anthropogenic surfaces and acid precipitation or runoff. Weathering, especially of carbonate material, is sensitive to pH. Alkalinization and DIC concentration data due to acidification complement the data from salinization experiments to gather information about impacts of human-influenced changes to the surface.

pH

Figure 5 displays a complete summary of all pH measurements made during all acidification experiments. The most notable trend is an increase in alkalinity among all samples regardless of starting pH, especially in a concrete interaction. At the stream pH level, this is consistent with the trend measured in salinization experiments. Some variability is apparent, but the trend toward greater alkalinization remained consistent with replication at various time steps.

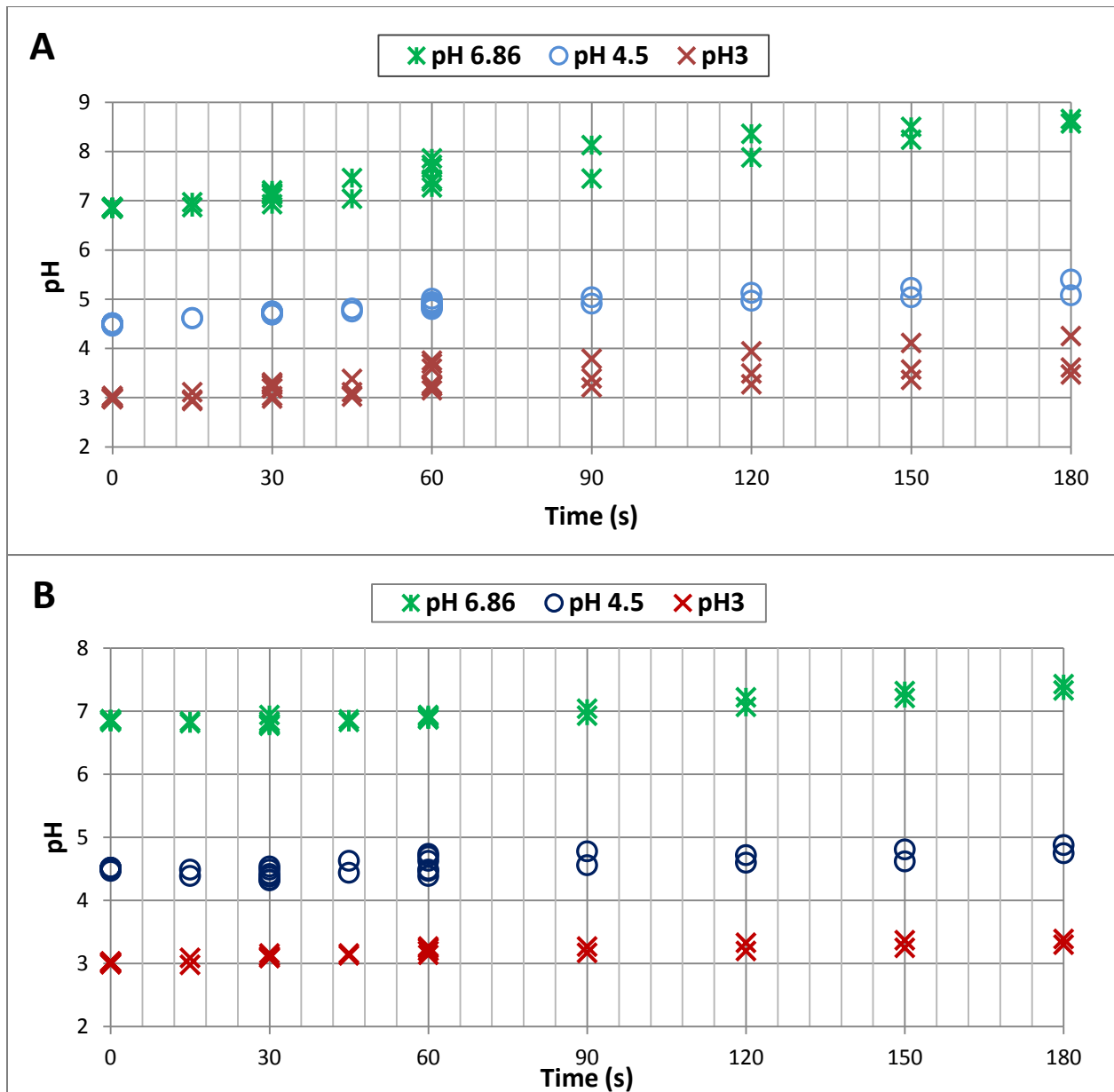


Figure 5: Summary of pH measurements during acidification experiments using (A) concrete and (B) asphalt surface materials.

In concrete interactions, the amount of alkalization was greater in shorter time scales relative to asphalt. Figure 5B displays a small, but interesting initial trend during the first 30-45 seconds of interaction between water and asphalt. Several of the water samples became temporarily more acidic, possibly due to some weathering of the petroleum-based asphalt filler material, which can be a source of organic carbon. It may also be due to a reaction with organic material on the surface of the samples, but this phenomenon was observed in more than one case.

Dissolved Inorganic Carbon

Upon acidification, DIC concentrations of just the stream water (not introduced to any surface material) decreased. This may be indicative of no bicarbonate at lower pH levels, at which point I would expect less/little DIC. At a higher pH, bicarbonate is the predominant carbonate species and, if enough alkalization occurs, a solution may be saturated with respect to calcium in the case of an interaction between a solution and CaCO_3 .

The panels in Figures 6 and 7 offer a good representation of this relationship between alkalization and DIC. Figure 6 details the change in DIC at the three different starting pH levels, up to periods of 180 seconds. In a comparison of Figures 6A and 6B, the amount of alkalization (decrease in H^+ concentration) that can occur in the limited time frame is noticeably different. The buffering capacity of the water varies from one pH level to another. The concentration of DIC increases by a greater amount in the pH 4.5 and concrete interaction relative to the pH 3 interaction. Whether this relative difference is statistically significant is to be determined, but it is interesting and makes sense if a portion of the carbonate material in the concrete, and potentially some of the aggregate material, is being weathered that quickly and dissolved in solution.

By comparison, Figure 7 details the alkalization and DIC paths for asphalt-water interactions. Absolute increases in DIC and levels of alkalization are very different than those observed in the concrete samples. As previously discussed, the nature of the carbon in the asphalt filler is much different than the cement that binds concrete. However, a measurable increase in DIC is still detected in some of the asphalt-water interactions, indicating that a reaction is either occurring between the acidified water and particulate matter stuck to the surface, or with some part of the asphalt filler and/or aggregate material.

Finally, it is worth noting that any interaction between water and surface material (concrete or asphalt) resulted in a change in DIC, regardless of acidity level.

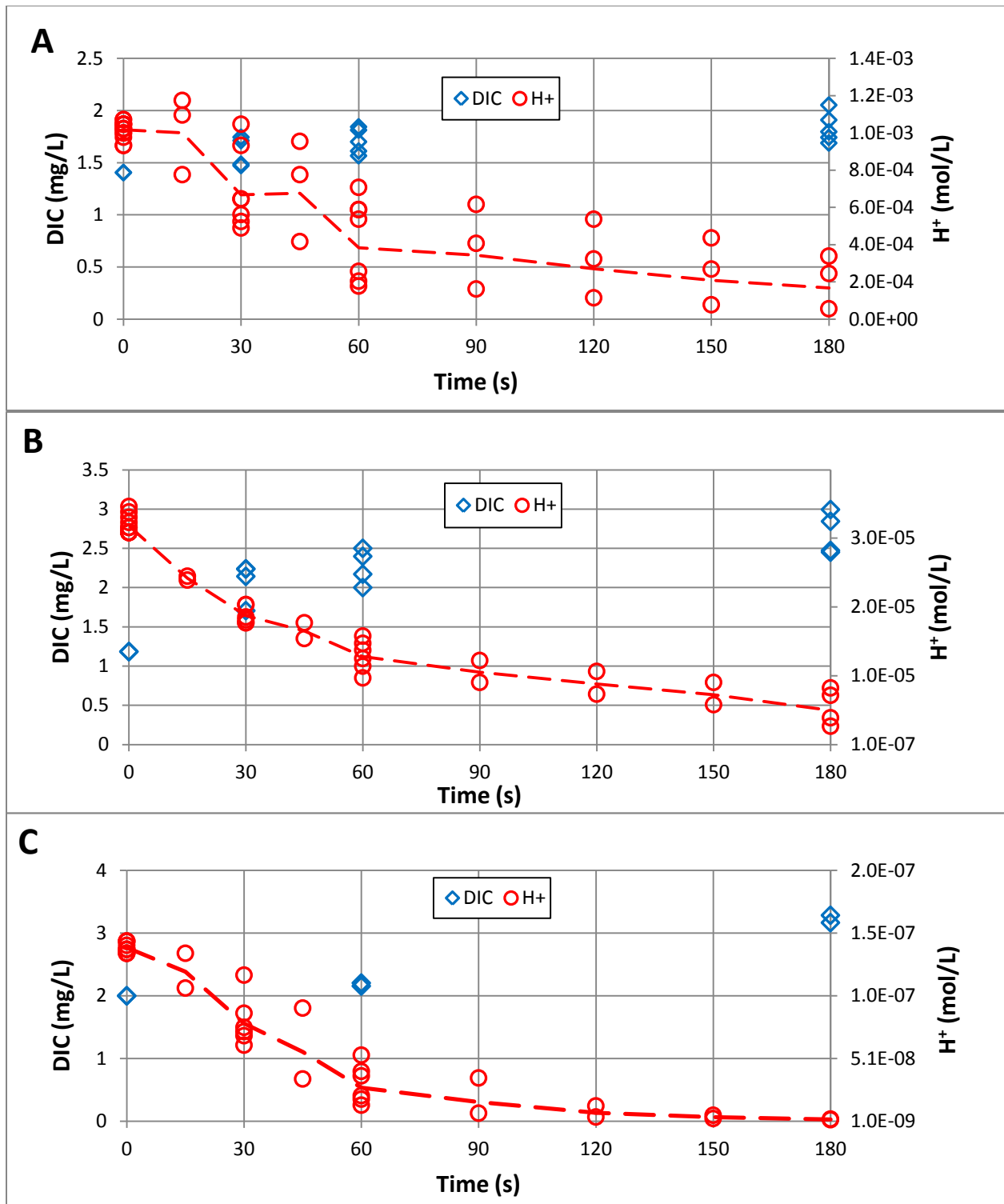


Figure 6: In concrete samples, DIC increases with time as alkalinization occurs. Starting acidity levels were pH 3 (panel A), pH 4.5 (B) and pH 6.86 (C). Note that the dotted red lines are drawn through mean H⁺ concentrations at each time step and are not trend lines.

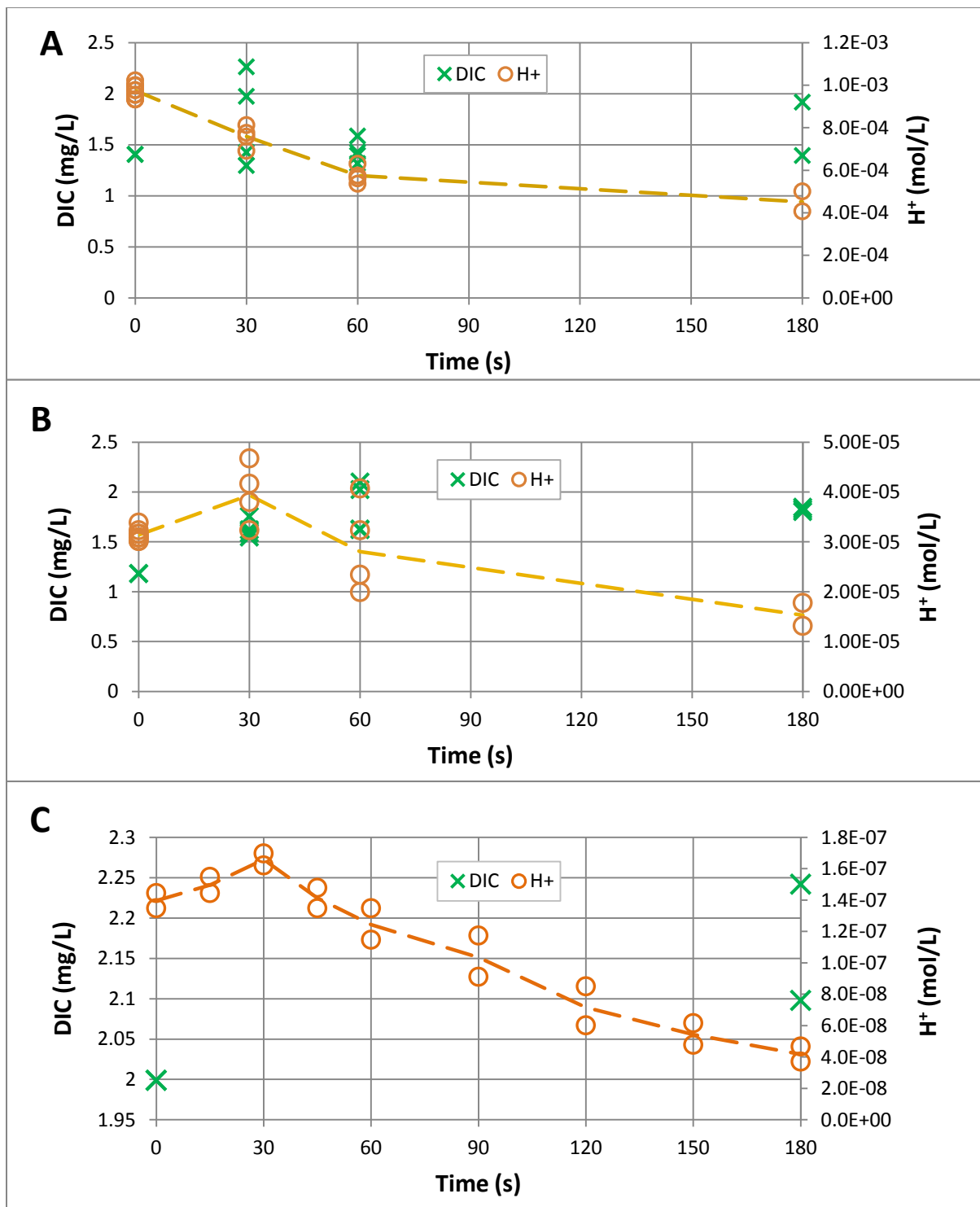


Figure 7: In asphalt samples, DIC increases with time and increased alkalinization. Starting acidity levels were pH 3 (panel A), pH 4.5 (B) and pH 6.86 (C). Note that the dotted orange lines are drawn through mean H⁺ concentrations at each time step and are not trend lines.

5. Statistical Analyses

Two-Factor Analysis of Variance (ANOVA) was used for significance testing. In a Two-Factor ANOVA, variance is partitioned into multiple components based on the factors in the experiment. This type of ANOVA does not specify where the variance lies, but rather an indication of a significant variance. The four components of variation are an among group variation from Factor 1 + error, Factor 2 + error, interaction between Factors 1 and 2 + error, and total error (McKillup and Dyar, 2010). Because experimental design progressed over the course of the project, sets of experiments was analyzed separately. The two factors in each analysis changed slightly based on differing time periods, salinization and acidification. In all ANOVA tests, a confidence interval of $\alpha=0.05$ was used.

Tables 1 and 2 detail variations in concentrations of dissolved inorganic carbon due to salinization. In both cases, the calculated F statistic is smaller than a critical F value; an F statistic larger than the critical value would indicate a significant difference due to a salt addition. As anticipated, variance due to the time each material interacted with water was significant, as DIC concentrations increased consistently at each time step. Degrees of freedom are very small due to the small number of samples tested (a pair of each surface material at each level of salinization), and a definitive conclusion cannot be reached without further replication.

<i>Source of Variance</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Salinization	0.481	1	0.481	0.782	0.391	4.600
Elapsed Time	20.160	6	3.360	5.463	0.004	2.848
Interaction	1.434	6	0.239	0.389	0.874	2.848
Within	8.611	14	0.615			
Total	30.686	27				

Table 1: Variance in DIC--Concrete and Salinization--1-240 minutes elapsed time

<i>Source of Variance</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Salinization	0.014	1	0.014	0.433	0.521	4.600
Elapsed Time	31.356	6	5.226	163.652	0.000	2.848
Interaction	0.152	6	0.025	0.792	0.591	2.848
Within	0.447	14	0.032			
Total	31.969	27				

Table 2: Variance in DIC--Asphalt and Salinization--1-240 minutes elapsed time

Contrarily, from the same experiment, Tables 3 displays a significant difference in pH due to salinization in concrete samples. Sample data indicate that pH values were lower at some time steps and higher at others. The source of variance may again be due to composition

variability rather than a salt effect leading to increased alkalization, but this is inconclusive without further replication.

<i>Source of Variance</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Salinization	0.08	1	0.08	22.49	0.00	4.60
Elapsed Time	81.76	6	13.63	4080.69	0.00	2.85
Interaction	0.07	6	0.01	3.46	0.03	2.85
Within	0.05	14	0.00			
Total	81.95	27				

Table 3: Variance in pH--Concrete and Salinization--1-240 minutes elapsed time

Two-Factor ANOVA for data acquired during acidification experiments were run slightly differently. An analysis was run for each of the three pH levels, with the two factors set as elapsed time and type of source material. Tables 4 and 5 display examples of variance in DIC at the higher levels of acidity used in the experiments, pH3 and pH4.5.

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Surface Material	0.573	7	0.082	2.339	0.062	2.488
Elapsed Time	0.453	3	0.151	4.318	0.016	3.072
Error	0.735	21	0.035			
Total	1.761	31				

Table 4: Variance in DIC--Acidification at pH 3

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Surface Material	1.659	7	0.237	3.660	0.010	2.488
Elapsed time	5.243	3	1.748	26.996	0.000	3.072
Error	1.359	21	0.065			
Total	8.260	31				

Table 5: Variance in DIC--Acidification at pH 4.5

Variance in DIC due to surface materials at the most acidic level is close to a level of statistical significance, but not quite. At pH 4.5, however, the elapsed time and type of surface material are each independently a significant source of variation. This is in agreement with previous figures that display a significantly higher concentration of DIC among water samples with concrete interaction.

Despite some preliminary confirmation of significant variance, *a posteriori* analyses are necessary to examine the normality of the distribution of my data and perhaps other means of significance testing.

6. Discussion

Given the great extent of impervious surface coverage in the United States, the potential for water quality impacts is considerable. Experimental results demonstrate that interactions between water and impervious surfaces consistently increased the pH and DIC concentration of water, contributing to alkalinization in urban watersheds. Concrete showed the greater rates of increase compared to asphalt.

The results of this study suggest that weathering of impervious surfaces may be one potential factor contributing to increased DIC and pH changes in urban watersheds. Previous work has found that dissolved inorganic carbon concentrations and fluxes are higher in urban watersheds. Other studies have demonstrated that DIC concentrations are elevated in urban portions of the Chesapeake Bay watershed (Prasad, Kaushal and Murtugudde, 2013) and that trends in bicarbonate alkalinity in these areas cannot be accounted for by natural, lithological carbonate sources. Other potential factors influencing DIC and alkalinization in urban watersheds may be sewage inputs and liming materials. However, more work is needed to explore the potential impacts of human-accelerated weathering of anthropogenic impervious surfaces.

Results suggest that acidification can accelerate weathering of anthropogenic impervious surfaces through the production of DIC and reduction in acidity, supporting one of my hypotheses. Previous work has pointed to the importance of lithology on neutralizing acidity along hydrologic flowpaths in forested watersheds (Johnson *et al.*, 2010). Relatively less work has focused on acid neutralization in urban environments. However, a growing body of research suggests that atmospheric deposition of acid anions can be concentrated near roadways (Bettez and Groffman, 2013).

The role of salinization is less clear regarding its impact on alkalinization and contributions of DIC to surface waters. Based on the data I collected and analyzed, my hypothesis stating that increased salinization increases DIC concentrations and alkalinization is rejected. However, I do find value in continuing to study the impacts of de-icing salt in urbanized areas through other methods of experimentation. Ample research on the role of salt on mechanical weathering processes has been limited in large part to engineering and materials science disciplines. But if mechanical weathering caused by salt application creates fresh material surfaces for surface water interaction during storm events, the potential for chemical weathering may increase. Better management of de-icing salt application must continue to be a goal.

Finally, the type of impervious surface cover tested is significant as it relates to DIC and alkalinization. Concrete clearly is more reactive to weathering, but a great deal of variability may exist due to age of infrastructure and composition within the material. Over the past two decades, new materials have been developed to protect the metal infrastructure that is otherwise susceptible to corrosion from salt. New forms of filler material in both asphalt and concrete have been developed to extend the life of roadways and reduce impact on the environment. However, we know that hydrologic changes that occur due to impervious surface

coverage significantly alter the geochemistry in urban rivers and streams. Even the simple interaction between neutral water and impervious surface materials is relevant to urban stream water chemistry.

7. Conclusion and Broader Implications

Human-accelerated weathering of impervious surfaces may need to be further considered a factor influencing urban water quality. As aging urban infrastructure continues to degrade, it must be monitored for its persistent effects at small and large watershed scales. In small-scale experiments, it may be possible to establish reasonable rates of weathering and alkalization of impervious surfaces based on area and water interaction. If, through repeated testing and data collection, rates are determined with confidence, they may be useful in scaling exercises. Models of sustainability and land use management on watershed scales incorporate fluxes of nutrients, chloride, trace metals, and many contaminants. If the degradation of concrete and asphalt surfaces are significant contributors to fluxes of inorganic carbon into surface waters, it should be considered in creating better management practices. Reducing impervious surface coverage by installing pervious concrete or re-establishing green spaces may do more than work toward improved hydrologic function in urban areas. It may lead to a better understanding of additional point and non-point sources of increased alkalinity and inorganic carbon in our watersheds.

8. Acknowledgements

I gratefully thank my wife, Betsy Lawrence, for her unflagging support as I work my way through school. I thank my advisor, Dr. Sujay Kaushal, for his generosity with time and guidance. Thanks to all of the other members of our lab group, especially Rose Smith and Julia Gorman, for assistance in the field, help with stats, and for teaching me great habits in the lab. Thank you to Eric Dougherty and Barry Catterton of the Maryland State Highway Administration for meeting with me and supplying asphalt, cores, concrete samples and de-icing salt for my experiments. Finally, thank you to all faculty members who offered guidance and constructive comments during this senior thesis project.

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10. Appendices

Appendix A. Honor Code:

“I pledge on my honor that I have not given or received any unauthorized assistance or plagiarized on this assignment.”

**Thomas R. Doody
April 28, 2014**

Appendix B. Supplemental Figures

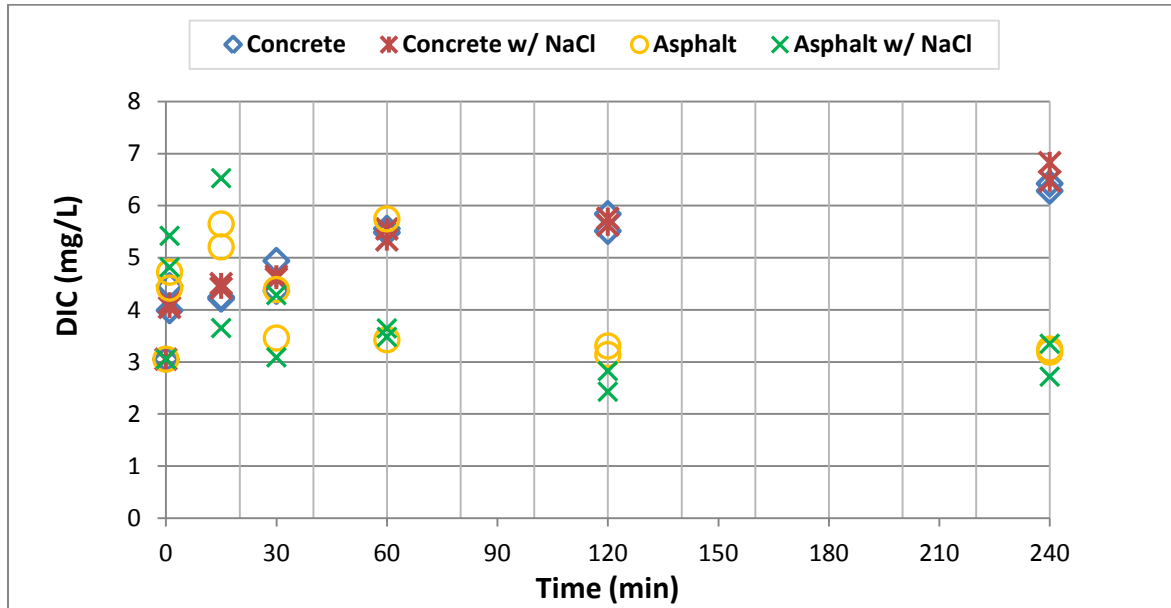


Figure B1: DIC concentrations from salinization experiments over longer time scales. Note the initial response in asphalt treatments to increased concentrations of DIC before dropping to original levels. I have not identified a mechanism that can account for this interaction at near-neutral pH levels. The water samples that interacted with concrete behaved consistently with similar treatments in other experiments. The salt addition did not appear to alter DIC concentrations.

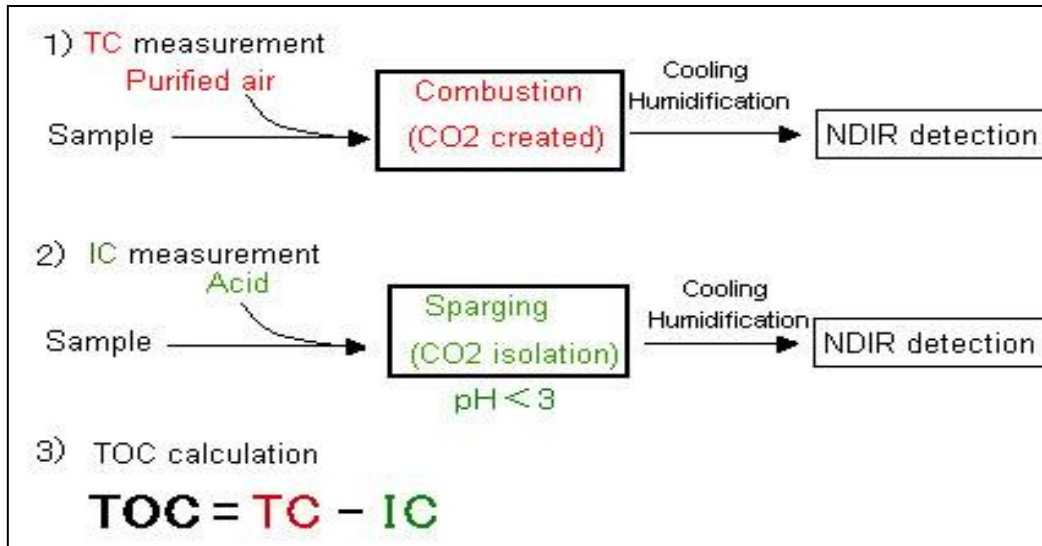


Figure B2: Simplified schematic of carbon analysis
(from <http://www.shimadzu.com/an/toc/lab/toc-l4.html>)

Appendix C: Supplemental Tables

ID	Area cm ²	ID	Area cm ²	ID	Area cm ²	ID	Area cm ²	ID	Area cm ²	ID	Area cm ²	ID	Area cm ²
a120a	65.2	a30b	60.5	an30-3b	66.5	ao60-45a	60.3	c120bs	66	c30ns	67.8	cn30-45b	72.2
a120as	71.3	a30bs	67.1	an30-45a	66.9	ao60-45b	64.3	c15a	60.7	c30o	66.8	cn30-7a	60.7
a120b	68.7	a30n	70.1	an30-45b	74.1	an60-7a	68.7	c15as	60.3	c30os	66.4	cn30-7b	61.5
a120bs	68.4	a30ns	69.8	an30-7a	66.5	an60-7b	74.9	c15b	61.3	c45n	67.7	cn60-3a	67.1
a15a	62.7	a30o	65.7	an30-7b	67.9	ao180-3a	65.3	c15bs	64.3	c45ns	63.9	cn60-3b	61.9
a15as	68.5	a30os	66.9	an60-3a	71.6	ao180-45a	61.9	c15n	66.4	c45o	65.6	cn60-45a	71.7
a15b	61	a45n	68.9	an60-3b	72.3	ao180-7a	66	c15ns	59.9	c45os	64.9	cn60-45b	62.3
a15bs	71.3	a45ns	70.2	an60-45a	63.8	ao30-3a	59.7	c15o	63.4	c60a	59.4	cn60-7a	62.4
a15n	72.3	a45o	66.8	an60-45b	58.9	ao30-3b	67.5	c15os	63.6	c60as	60.2	cn60-7b	61.8
a15ns	71.9	a45os	66.7	an60-7a	68.7	ao30-45a	69.7	c1a	62.3	c60b	59.7	co180-3a	72.6
a15o	70.8	a60a	71.4	an60-7b	74.9	ao30-45b	61.8	c1as	64.6	c60bs	61.7	co180-45a	66.5
a15os	69.4	a60as	65.2	ao180-3a	65.3	ao30-7a	63.8	c1b	59.8	c60n	67.3	co180-7a	68.5
a1a	67.3	a60b	61.3	ao180-45a	61.9	ao30-7b	60.2	c1bs	61.8	c60ns	68.5	co30-3a	64.3
a1as	64.5	a60bs	63	ao180-7a	66	ao60-3a	68	c240a**	65.5	c60o	66	co30-3b	63.2
a1b	63.2	a60n	64.7	ao30-3a	59.7	ao60-3b	65.5	c240as	68.2	c60os	65.8	co30-45a	60.5
a1bs	66.3	a60ns	63.4	ao30-3b	67.5	ao60-45a	60.3	c240b	65.3	cn180-3a	63	co30-45b	71.4
a240a	74.1	a60o	68.7	ao30-45a	69.7	ao60-45b	64.3	c240bs	66.5	cn180-3b	71	co30-7a	68.9
a240as	72.2	a60os	66.9	ao30-45b	61.8	ao60-7a	61.7	c30a	62.4	cn180-45a	59.8	co30-7b	70.2
a240b	70.2	an180-3a	75.2	ao30-7a	63.8	ao60-7b	65.2	c30as	58.9	cn180-7a	59.4	co60-3a	64
a240bs	75.1	an180-45a	63.2	ao30-7b	60.2	c120a	67.5	c30b	61.8	cn30-3a	61.3	co60-3b	61
a30a	70.7	an180-7a	62.4	ao60-3a	68	c120as	65.2	c30bs	63.2	cn30-3b	71.1	co60-45a	61.3
a30as	70.1	an30-3a	68.2	ao60-3b	65.5	c120b	68	c30n	64.7	cn30-45a	65.4	co60-45b	63.7
				co60-7b	66.3			co60-7a	59.5				

Table C1: Summary of surface areas of concrete and asphalt samples used in all salinization and acidification experiments. The mean sample surface area for all materials is 65.8±8.1 cm² (2σ).