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# Abiotic retention of nitrogen and dissolved organic matter by forest mineral soils

Naoko Watanabe University of New Hampshire, Durham

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## **ABIOTIC RETENTION OF NITROGEN AND DISSOLVED ORGANIC MATTER BY FOREST MINERAL SOILS**

**BY**

## **NAOKO WATANABE B.S.A., West Virginia University, 2003**

### **THESIS**

**Submitted to the University of New Hampshire in Partial Fulfillment of the Requirements for the Degree of**

**Master of Science**

**in**

**Natural Resources**

**September, 2006**

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#### **ABSTRACT**

## **ABIOTIC RETENTION OF NITROGEN AND DISSOLVED ORGANIC MATTER BY FOREST MINERAL SOILS**

**by**

## **Naoko Watanabe University of New Hampshire, September 2006**

The effect of  $NO_3$  deposition on  $NH_4$ <sup>+</sup>, DON, and DOC retention as well as **abiotic NO**<sup>3</sup> **' retention via the hypothesized "ferrous wheel" mechanism was examined in oxic and anoxic tropical and oxic temperate soils using sorption isotherm experiments. Adsorption of NH4+, DON, and DOC by mineral soils was examined in forest floor extracts with DOC levels of 0-50 mg/L. Experimental treatments included no added** NO<sub>3</sub>, 4 mg/L of added NO<sub>3</sub>, or 4 mg/L of NO<sub>3</sub> and 2 mg/L of  $Fe^{3+}$ . Ferric iron was **added since it would likely increase DOC retention in the context of podzolization, and it** might also influence N retention. Retention of NH<sub>4</sub><sup>+</sup> and DOC did not change upon **NO**<sup>3</sup> **' addition in any of the soils. Retention of DON increased upon NO**<sup>3</sup> **' addition in the temperate soil while no adsorption of DON could be demonstrated in the tropical soils.** With added Fe<sup>3+</sup>, NH<sub>4</sub><sup>+</sup> retention decreased in the anoxic tropical soil but remained **unchanged in the temperate and oxic tropical soils. Neither DOC nor DON retention in** any of the soils was affected by  $Fe^{3+}$  addition. The change in retention upon  $NO_3$  as well as  $Fe^{3+}$  addition seems to be related to the mineralogy of the soil and pH of the input **solution. As DON and DOC response to NO**<sup>3</sup> **' was different, N and C cycles may not be fully connected in the soil.**

For abiotic  $NO_3$ <sup>-</sup> retention, DOC,  $Fe^{3+}$ , and hydroquinone are likely to be involved according to the ferrous wheel hypothesis. To examine abiotic NO<sub>3</sub><sup>-</sup> retention, different levels of  $NO_3$ <sup> $\cdot$ </sup> (0-10 mg/L) with no DOC, 50 mg/L of DOC, 50 mg/L of DOC **and 2 mg/L of Fe3+, 10 mg/L of hydroquinone, or 10 mg/L of hydroquinone and 2 mg/L of Fe3+ was added to the soil and changes in** NO3" **retention were compared. No strong retention was observed in any of the soils despite the treatments. Although there are some experimental conditions that could be changed, the results indicate that the ferrous** wheel hypothesis does not explain the NO<sub>3</sub> retention by mineral soils that has been **observed in the field.**

#### INTRODUCTION

**Human activities have increased atmospheric nitrogen (N) deposition to temperate forests in the Northeastern U.S. as well as in other forest ecosystems in the world and have subsequently altered the nutrient cycling in these forests, particularly N. Anthropogenic atmospheric N deposition originates mainly from fossil fuel combustion and N fertilizer application. Fossil fuel combustion, which is a main source of nitrate (NO**<sup>3</sup> **') deposition, has increased due to the rise of automobiles and power plants. As NOx is released into the atmosphere from combustion, it reacts with water and produces** nitric acid (HNO<sub>3</sub>), which subsequently dissociates into hydrogen ions  $(H<sup>+</sup>)$  and NO<sub>3</sub><sup>-</sup> (Aber and Melillo, 2001). The amount of  $NO<sub>x</sub>$  emitted from the combustion sources **was 6.9 Tg, 6.5 Tg, and 3.3 Tg in the U.S., Asia, and in Europe, respectively, within 21 Tg of the total global NOx emission in 1998 (Howarth et al., 2002).**

**The use of N fertilizer, in the form of ammonium (NH**4**+), has increased due to greater demand for food production caused by the human population growth (Galloway and Cowling, 2002). Ammonia that is volatilized from the fertilizers applied on the** ground surface is washed off by rain and deposited as NH<sub>4</sub><sup>+</sup> to the earth's surface (Porter **et al., 2000). The use of N fertilizer in the U.S. in 1999 was 11.2 Tg yr'1, which largely** increased from 3.1 Tg  $yr^{-1}$  in 1961. Global use of N fertilizer in 1999 was 86 Tg, and **the N from fertilizer makes the largest source of anthropogenic N (Howarth et al., 2002).**

**The tendency of increasing N deposition has continued not only in the U.S. but** also worldwide. In the U.S.,  $NO_3$ <sup>-</sup> and  $NH_4$ <sup>+</sup> deposition has spread to larger areas **(NADP, 2004). The amount of N emission from developed countries may not increase**

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**much in the future; however, if maximum projected human population (~ 8.9 billion people) and the average N emission rate in North America in 1995 (~ 100 kg N person**' 1 **yr'1) were achieved worldwide, N emission is expected to increase significantly especially in South America, Asia and in Africa in the future (Galloway and Cowling,** 2002).

**Considering the expectation that the future atmospheric N deposition will increase even more, how ecosystems will respond to a greater amount of N input is an issue to consider.' Water quality is one of the most significant impacts related to increased atmospheric N deposition. Once N is deposited on the ground surface as rain, it percolates into the soil horizons. As N goes down the soil solum, it is taken up by plants and microbes or adsorbed to soil surfaces. Ammonium can be taken up by plants and microbes and tends to be retained by cation exchange sites. Nitrate, however, tends to leach out since its negative charge is not attracted to the negative charge of soil humus** and clays. Leached NO<sub>3</sub>, which increases as the input increases (Magill et al., 2004), **percolates to groundwater or to streams and impacts water quality. Ammonium can also leach out if the input is large (Magill et.al., 2004).**

**Leached N has large effects on aquatic ecosystems and humans. Stream water with high N concentration causes eutrophication and subsequently hypoxia/anoxia in lakes and ponds as well as in estuaries and coastal waters (EPA, 2002). Eutrophication also decreases biodiversity in the sea floor community, such as seaweeds, seagrasses, and corals, as well as planktonic organisms (Vitousek et al., 1997). High N in estuaries and coastal waters may promote toxic algal blooms, which kill fish and shellfish and make the water unsafe to swim (Vitousek et al., 1997; EPA, 2002). High concentrations of**

NO3" **in groundwater and streams can contaminate the drinking water, which may result in methemoglobinemia, or Blue Baby Syndrome, in human infants. High N concentration in streams also acidifies water, which mobilizes mercury (Hg) and aluminum (Al). Mercury tends to accumulate as the trophic level increases and humans can be indirectly affected by eating Hg-contaminated fish. Aluminum is directly toxic to fish due to its impacts on gill functions and osmoregulation, and results in a decrease in biodiversity (EPA, 2002; Driscoll et al., 2003).**

**Due to the adverse effects that atmospheric N deposition could have on ecosystems and our everyday lives, researchers have investigated how ecosystems react to increased inputs of N. Aber et al. (1998) examined the effects of long-term N deposition on temperate forests in the Northeastern U.S. In the context of N saturation** theory, which suggests that the availability of  $NH_4^+$  and  $NO_3^-$  exceeds the demand by **plants and microbes and can be detected by increased NH4+ and** NO3' **leaching from below rooting zone (Aber et al., 1989), they first hypothesized that high N deposition in the long term would eventually cause more N mineralization followed by nitrification and** subsequent dissolved inorganic N  $(DIN - NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub>)$  leaching (Aber et al., 1989). **However, the result after** 6 **years of N amendment showed that N mineralization generally declined, and DIN leaching was small relative to the input (Aber et al., 1998). This suggested that forest soils have an ability to retain N inputs and could be an excellent buffer that prevents N from leaching into aquatic ecosystems, such as streams, lakes, and estuaries. After 9 more years of N amendment, they found that most N retention appeared to occur in mineral soils rather than in forest floors (McDowell et al., 2004).**

**At this point, mechanisms of N retention are not fully understood. Nitrogen**

**uptake by vegetation does occur, but the amount of uptake does not seem sufficient to account for a large fraction of inputs despite the increased amount of atmospheric CO**<sup>2</sup> **. Using a collection of 15N tracer studies, Nadelhoffer et al. (1999) reported that only 20% of N deposition was recovered in plant biomass while 70% of N was recovered in soil (another 10% was lost as leachate and gas). Microbial immobilization is another possible mechanism of N retention; however, Micks et al. (2004) reported that microbial respiration did not increase as N was added. But at the same time, a large amount of N that was applied to the plots disappeared in the soils. They referred to this discrepancy as an abiotic N immobilization rather than microbial immobilization (Micks et al., 2004).**

**Abiotic immobilization of N, especially NO**<sup>3</sup> **', is a topic that is getting increasing** attention recently. Studying  $NO_3$  immobilization in zero and high N (15 g N m<sup>-2</sup>) input **plots at the Harvard Forest, Bemtson and Aber (2000) reported that fast abiotic NO**<sup>3</sup> **' immobilization seemed to be a major pathway to retain NO**3**" in soils in pine plots regardless of the amount of N input as well as in the high N input hardwood plots. These plots seemed to lose the slow microbial N immobilization pathway. Dail et al.** (2001) documented that a large amount of  ${}^{15}N-NO_3$  added to soils disappeared within 15 **minutes and was recovered in dissolved organic nitrogen (DON). Davidson et al., (2003) suggested a "ferrous wheel hypothesis", which is a hypothesized mechanism of** abiotic NO<sub>3</sub> immobilization to dissolved organic matter (DOM) in the forest floor that is **mediated by iron (Fe).**

**If such a mechanism occurs widely in soils, then N retention by mineral soils, which often contain large amounts of Fe, receive large DOM inputs from the overlying forest floor, and show net N retention in long-term experiments (McDowell et al., 2004)**

**might be an important pathway for N conservation in forest ecosystems. The forest** floor is the main source of DOC,  $NO_3$ , and  $NH_4$ <sup>+</sup> in forest soils (Solinger et al., 2001) **and they are all transferred to mineral soils and typically lost from solution by a wide variety of biotic and abiotic pathways before reaching deeper groundwater or Surface runoff (Qualls and Haines, 1992; Solinger et al., 2001). Considering these reports, I** chose to examine the retention of  $NO<sub>3</sub>$ ,  $NH<sub>4</sub>$ <sup>+</sup>, and organic matter (DOC and DON) in **several forest soils. Mechanisms of abiotic retention are not well studied in mineral** soils, although tropical soils are known to be most likely to retain NO<sub>3</sub> abiotically (Cahn **et al., 1992; Rasiah et al., 2003). Ammonium can be fixed by 2:1 clays (Sparks, 2003).** There is a report that the retention of NH<sub>4</sub><sup>+</sup> in mineral soil is related to base saturation and **cation exchange capacity (CEC) (Matschonat and Matzner, 1996), but, in general, studies on abiotic NH4+ in mineral soils are scarce.**

**In addition to its importance in potential regulations of N flux, examining the dynamics of DOC in mineral soils will provide perspective in terms of C sequestration. Soils, especially mineral soil horizons, are considered to be large C sink (McDowell and Likens, 1988). Carbon can be sequestered in the soil as DOC is adsorbed; for example, McDowell and Wood (1984) reported an adsorption of DOC to the B horizon soils in temperate forest in the Northeastern U.S. They suggested that DOC would quickly precipitate with Fe on the B horizon soil in the podzolization process, which is a soil forming process in which Fe and Al are leached from the E horizon and are deposited in the B horizon. Tropical soil, which tends to contain a high amount of Fe and Al oxides, is reported to retain DOC as well (McDowell, 1998; Schwendenmann and Veldkamp, 2005). This ability of C sequestration in soils, however, may change in the situation of** **high N deposition due to competition and interaction between DOC and** NO3', **which are both negatively charged. Since N deposition is speculated to increase, its effect on DOC retention is worth examining.**

**The presence of Fe does seem to play an important role in DOC retention in soils. For example, in their podzolization experiment, McDowell and Wood (1984) reported** that more DOC was adsorbed to the B horizon when ferric iron (Fe<sup>3+</sup>) was added to the **soil solution. Dissolve organic carbon retention may be changed by N deposition; however, addition of Fe to soil solution, which would simulate the leaching of Fe from the upper soil horizon, would further alter DOC adsorption in an enhanced N condition. Adding Fe may affect DON and DIN dynamics as well.**

**Addition of Fe may indirectly influence N retention, especially NO**3**", in mineral soils, too. As DOC percolates through the soil horizons, it is possible that DOC gets involved not only in the retention but also in some interactions with other chemical components. In the studies by Davidson et al. (2003) and McDowell and Wood (1984), DOC (DOM) and Fe seem to be common factors.**

**In the ferrous wheel hypothesis, Davidson et al. (2003) suggested that reduced C** in the soil, such as hydroquinone, phenol, DOC, and humic substances can reduce  $Fe<sup>3+</sup>$  in soil minerals. Subsequently reduced  $\text{Fe}^{3+}$  becomes  $\text{Fe}^{2+}$  and  $\text{Fe}^{2+}$  reduces NO<sub>3</sub> to NO<sub>2</sub><sup>-</sup>. **Nitrite is highly reactive and is known to react with phenolic compounds to produce nitrophenols. Phenolic compounds are components of DOM and they hypothesized that NO**<sup>2</sup> **' reacts with DOM (DOC) to produce DON, although they only suggested possible fates (e.g. microbial uptake, adsorption, leaching) of DON. In the podzolization process, DOC precipitates with Fe in the B horizon (McDowell and Wood, 1984). Combining**

these 2 studies, it may be possible that  $NO_3$  would react with DOC and the  $NO_3$ -DOC **component precipitates onto the mineral soils in the presence of Fe, which is abundant in the mineral soils. Hydroquinone could be used to examine if the combination of the ferrous wheel hypothesis and the podzolization process would increase NO**<sup>3</sup> **' adsorption. Hydroquinone is contained in the hydrophobic portion of DOC and is abundant in the soil (Cory and McKnight, 2005). Hydroquinone is a reduced form and as it is oxidized, it** can reduce  $Fe^{3+}$  to ferrous iron  $(Fe^{2+})$ , which may further drive the ferrous wheel hypothesis and increase NO<sub>3</sub> adsorption.

**For this study, I conducted a series of adsorption experiments to examine retentions of** NO3', NH4+, DOC, **and** DON **by mineral soils. I added forest floor extract** with and without added  $NO_3$  to the mineral soils and compared the sorption of  $NH_4^+$ , DON, **and** DOC **in the presence of high and low** NO3' **concentrations. I also examined** NO3' **sorption with and without added** DOC, DOC **and Fe3+, hydroquinone, or** hydroquinone and  $Fe^{3+}$ , as these are all potentially important in  $NO_3$ <sup>-</sup> retention according to the ferrous wheel hypothesis. Adding  $Fe^{3+}$  would increase reducing power to drive NO3' **retention as well as** DOC **adsorption.**

**Three contrasting soils were chosen for this study. One soil is from the Northeastern U.S., where large-scale N retention has been repeatedly observed, and 2 soils are from Puerto Rico. Soil properties, such as Al, Fe and organic matter (total CN) contents, soil texture, and pH were measured. Using tropical soils is important since studies on N retention and dynamics in tropical soils are scarce even though the tropical regions are expected to have increased atmospheric N emission (Galloway and Cowling, 2002) and possibly deposition in the future. Also, tropical soils tend to contain high Fe,**

and some are known to adsorb NO<sub>3</sub>. Iron is a part of the ferrous wheel hypothesis, and **as it is reduced, reduced Fe will further reduce** NO3' **to drive the mechanism. For this reason,** NO3' **retention via the ferrous wheel hypothesis could be easily observed in tropical soils. Due to the different soil properties, C and N retention and susceptibility to** NO3' **deposition may be different in these 3 soils. Examining the difference would be useful to predict each ecosystem's response to increased atmospheric N deposition as well as provide a wide range of conditions under which N and DOM retention can be examined.**

## CHAPTER I

## **OBJECTIVES OF STUDY**



H1 The order of N retention in mineral soil will be  $NH_4^+$ >DON>NO<sub>3</sub><sup>2</sup>, and is unaffected by NO<sub>3</sub>' levels.

H2 Adding  $Fe^{3+}$  and NO<sub>3</sub> will change NH<sub>4</sub><sup>+</sup> and DON retention in soils.



**H2 Adding Fe3+ and** NO3' **will increase DOC adsorption in soils.**



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## CHAPTER II

## **MATERIALS AND METHODS**

#### **Study sites**

**Among 3 soils that I used' for my experiments, 2 soils were sampled from the Luquillo Experimental Forest in Puerto Rico. The Luquillo Experimental Forest has been used for tropical ecosystem study for about 100 years (Long Term Ecological Research Network, 2004). Within the experimental forest, soils were sampled from the Sonadora and the Icacos watersheds. In the Sonadora watershed, the dominant soil is Los Guineos clay (Ultisols) and the bedrock is andesite, mudstone origin. Main vegetation types are palms (***Prestoea montana***), and tabunuco (***Dacryodes excelsa***). In the Icacos watershed, the dominant soil is Utuado clay (Inceptisols) and the bedrock is quartz diorite. Vegetation types are dominated by Colorado (***Cyrilla racemiflora)* **and palms** *{Prestoea montana***) (McDowell et al., 1992; McDowell and Asbury, 1994). In the Sonadora watershed, the soil was oxic and bright orange in color. In the Icacos watershed, a riparian soil was sampled, which was highly anoxic and pale grayish in color.**

**Another soil was sampled from a temperate region in the northeastern United States. College Woods is a study facility that is a part of the University of New Hampshire campus in Durham, NH. The site is located in the Oyster River watershed in the seacoast region of NH. The soil series of the sampling site is the Hollis-Charlton complex (Spodosols). The bedrock type of the Hollis series is quartzite, but the**

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**Charlton series contains calcareous schist materials (Soil Survey, 1973); therefore, the soil is expected to have weathered materials from these 2 components. The dominant vegetation at the sampling site is eastern hemlock** *(Tsuga canadensis***). The soil was oxic and the color was yellowish brown.**

#### **Soil sampling, processing, and DOC preparation**

**Sonadora and Icacos soils were collected by William H. McDowell in December 2005. The E horizon soils were chosen since Fe is abundant due to laterization, which is a soil forming process that silicon (Si) is leached from the E horizon and Fe and Al are left in the E horizon (Aber and Melillo, 2001).**

**College Woods soil was collected by the author and Jacqueline A.** Aitkenhead-Peterson in March 2006. Forest floor was removed and the ground was dug **using a shovel to the depth of 40 to 60 cm and the soil from the Bs horizon was collected using a scoop. The Bs horizon was chosen for its high iron and low organic matter contents.**

**All the soils were taken back to the soil laboratory at the University of New Hampshire for processing. For drying, the soil was spread on a clean aluminum tray and left with a paper towel cover on at room temperature in the laboratory until it dried** ( 1 **to 2 weeks). Upon drying, large clumps were cut or broken into small pieces as necessary to make the subsequent processing easier. Dried soil was sieved at 2 mm and pieces of organic matter were removed from the soil during the processing. A mortar and a pestle were used to break hard clumps and make them go through the sieve. Even though I was measuring abiotic processes, the soils were not sterilized since sterilization methods (e.g. UV radiation, autoclave, HgCh) can change soil properties (Dail et al.,**

**2001; Barrett et al., 2002). The sieved soil was\* stored in a plastic bag at room temperature until the time of the experiment.**

**The forest floor solution that was used in the experiment was extracted from the corresponding forest floor collected in College Woods and the Luquillo Mountains. College Woods forest floor was collected in July 2005, and the tropical forest floor was collected in 2004 from the Icacos watershed. To extract the solution, 20 g of forest floor material and 1 L of deionized distilled water (DDW) were placed in a plastic bottle and** shaken for 24 hours. The solution was first filtered with a Whatman GF/C (1.2  $\mu$ m) and then with a GF/F  $(0.7 \mu m)$  glass-fiber filters under vacuum. Twenty grams of the filtrate **was transferred into a 60 mL HDPE bottle and diluted with 40 g of DDW to be used for DOC analysis (measured as the non-purgeable organic carbon with a Shimadzu TOC-V total carbon analyzer). The concentration of the original (stock) solution was back-calculated from the concentration of the diluted sample using the following equation.**

 $[stock solution] = [diluted sample] \times (mass_{sample} + mass_{DDW}) / (mass_{sample})$ 

**The rest of the filtrate was stored in 500 mL plastic bottles and kept frozen until the time of experiment.**

### **Experimental procedures**

To examine changes in retention of  $NH_4^+$ , DON, and DOC in the soil upon  $NO_3^$ **addition, I conducted sorption isotherm experiments (Nodvin et al., 1986) using various dilutions of forest floor extract with and without added NO**<sup>3</sup> **' (4 mg/L). Input solutions in each treatment were made in 100 mL flasks. For the treatment with no NO**3**" added, 0,** 10, 20, 30, 40, and 50 mg/L of DOC solutions and associated concentrations of NH<sub>4</sub><sup>+</sup> and DON (0-1.25 and 0-1.57 mg/L, respectively) were prepared. Concentration of NO<sub>3</sub> in **the solution was negligible. A mass of forest floor stock solution was calculated to achieve a desired concentration of DOC in each flask by using the equation, required** mass of stock solution = ([DOC desired]  $\times$  V of flask) / [stock solution], and was diluted with DDW. For the treatment with added  $NO<sub>3</sub>$ , a mass to achieve 4 mg/L of  $NO<sub>3</sub>$ <sup>-</sup> was **added to each flask.**

To examine the Fe effect on DOC, DON, and NH<sub>4</sub><sup>+</sup> adsorption, I conducted **sorption isotherm experiments that contained 0-50 mg/L of DOC in forest floor extract, 4**  $mg/L$  of added NO<sub>3</sub><sup>-</sup>, and 2 mg/L of added Fe<sup>3+</sup>. Dissolved organic carbon and NO<sub>3</sub><sup>-</sup> **were calculated and prepared as described earlier and a required mass to achieve 2 mg/L of Fe3+ was added to each flask.**

**To test the ferrous wheel hypothesis, I conducted NO**<sup>3</sup> **' sorption isotherm (0-10 mg/L NO**<sup>3</sup> **') on a stock NO**<sup>3</sup> **' solution with and without DOC added at 50 mg/L. I also** examined the effects of added  $Fe<sup>3+</sup>$  as well as hydroquinone on  $NO<sub>3</sub>$  sorption by conducting experiments with 1) 50 mg/L DOC and 2 mg/L  $Fe^{3+}$ , 2) 10 mg/L hydroquinone, and 3) 10 mg/L hydroquinone and 2 mg/L  $Fe<sup>3+</sup>$ .

Each treatment had 2 replicates and the weight of NO<sub>3</sub>, FeCl<sub>3</sub>, and DOC added **to each flask was recorded to calculate exact concentrations. The stock solutions of** NO<sub>3</sub>, FeCl<sub>3</sub>, and hydroquinone were made from NaNO<sub>3</sub>, anhydrous FeCl<sub>3</sub>, and **granulated hydroquinone (HOC**6**H**4**OH), respectively. For the soil, 3.5 g was weighed in a 50 mL plastic centrifuge tube. Exact weight of the soil was also recorded.**

**All the treatments were done with each of the 3 different soils. Thirty five grams of the input solution was added to the soil and the exact weight was recorded.**

**After solutions were added to all the tubes, they were placed in a refrigerator to suppress microbial activities. To ensure a good contact between the soil and the solution, the mixture was gently inverted 5 times every 15 minutes for 2 hours. About 30 minutes before the end of the** 2 **hours, a centrifuge was run for** 2 0 **minutes to refrigerate the inside of the machine to 5 °C. After 2 hours, tubes were centrifuged at 46,000G for 20 minutes. Supernatant liquid was taken carefully not to disturb the soil at the bottom using a plastic syringe. The liquid was first transferred to a glass vial for pH measurement. After that,** the liquid was filtered through a Whatman GF/F  $(0.7 \mu m)$  glass-fiber filter and 20 g of the **liquid was transferred into a 60 mL HDPE bottle. The sample was diluted with 40 g of DDW. Both the liquid and DDW weight were recorded. The input solution was also transferred into the same type of bottle in the same manner but without filtering. The diluted samples as well as the input solution were kept frozen until the time of analyses.**

#### **Soil property analyses**

**Soil CN, exchangeable and organically bound Al and Fe, exchangeable magnesium (Mg) and manganese (Mn), soil pH, and soil texture were measured on each soil. For the soil CN, the soil was first ground to a flour-like texture and analyzed by combustion using a Perkin Elmer 2400 Series II CHNS/O Analyzer. Exchangeable and organically bound Al and Fe and exchangeable Mg and Mn in the soil were extracted using KC1 and sodium pyrophosphate extraction methods, respectively, and the samples were sent to the Department of Plant and Soil Science at the University of Vermont for the analysis. For soil pH, 10 g of soil and 20 g of DDW were placed in a glass beaker and stirred manually for 15 minutes. After the soil settled down, pH was measured.**

**Soil texture was measured using the hydrometer method. Thirty grams of soil**

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**was weighed in a plastic jar and 100 mL of 5 % sodium hexametaphosphate solution was added. The lid of the jar was tightly closed and the mixture was agitated on a shaker for 24 hours. After 24 hours, the mixture was transferred into a 1000 mL cylinder and DDW was added to fill the cylinder to 1000 mL. A control was also prepared by putting 100 mL of 5 % sodium hexametaphosphate solution and DDW in another 1000 mL cylinder. The cylinders were inverted several times to homogenize the mixture. Temperature and hydrometer readings were taken about 20 seconds after they were put into the mixture. After the first reading, the cylinders were covered and left for 2 hours until the second reading. Percent sand and clay were calculated based on the first and second readings, respectively, and % silt was obtained by subtracting % sand and clay from 100%. All the soil properties are described in Table 1.**

## **Chemical analyses and data presentation**

**Nitrate, NH**4**+, DOC, TDN, and soil CN analyses were done at the Water Resources Research Center at the University of New Hampshire. Nitrate and NH**4**+ were analyzed colorimetrically, using the USEPA 353.3 method (reduction by Cd-Cu) and the USEPA 350.1 method (reaction with phenol and then hypochlorite), respectively, with a WestCo SmartChem Discrete Wet Chemistry Analyzer. Dissolved organic carbon and TDN were analyzed by high temperature Pt-catalyzed combustion using a Shimadzu TOC-V Total Carbon Analyzer. Since all the samples were diluted, the concentrations obtained by the analyses were back-calculated in the same manner as stated for the DOC stock solution above. Dissolved organic nitrogen concentration was calculated by the equation,**  $[DOM] = [TDN] - [NO_3^-] - [NH_4^+]$ **.** 

**The retention of** NO3', **NH4+,** DON, **and** DOC **were analyzed using the initial**

**mass isotherm approach (Nodvin et al., 1986). In the initial mass isotherms, the mass of a component in the input solution (Xi) and the mass of component retained or released (RE) are plotted on the x-axis and the y-axis, respectively, and both are presented as mass** per unit soil mass  $(\mu g/g)$ . The mass retained by or released from the soil is obtained by **subtracting the mass of a component in the output solution from the input solution. The Xi and RE values were based on the average of 2 replicates. The relationship between**  $Xi$  and RE is explained by the equation,  $RE = mXi - b$ . The partition coefficient (slope, **or m) represents the fraction of the Xi retained in the soil. The larger the value, the greater the affinity of the component for the soil. The release term (b) represents the** amount of component that is released when  $Xi = 0$ .

**Throughout this study, I used the m and b values as well as the equilibrium,** which is the x intercept, to describe the isotherm regression. The equilibrium is the **point where no release or retention of a component occurs in the soil-solution system and the value was obtained by calculating for Xi when RE is zero. The m value ranges between 0 and 1 when sorption has occurred (Nodvin et al., 1986), and when an m value is negative, it indicates that no retention of a chemical component has occurred. The b value is supposed to be negative (Nodvin et al., 1986) and the equilibrium should be positive. When values of those parameters were not in the appropriate range, they were not reported on the tables.**

#### **Statistical analyses**

**When the regression describing the sorption experiment was not statistically significant, it was not used in the statistical analyses. Treatment effect on the retention of chemical components was analyzed using Analysis of Covariance to test the**

**homogeneity of slopes. Throughout the statistical analyses, a result was considered significant when p<0.05.**

### CHAPTER III

### **RESULTS**

#### N retention in systems that did not receive  $NO<sub>3</sub>$ <sup>-</sup> addition

**The order of N retention was different in each soil, which did not agree with my original hypothesis. In the College Woods soil, NH4+ and DON retention were not** significantly different (Figure 1a, Table 2). In the Sonadora soil, NH<sub>4</sub><sup>+</sup> showed higher **retention than that of DON (Figure lb, Table 2). In the Icacos soil, since the regression of DON retention was not significant, the difference between NH4+ and DON retention was not analyzed (Figure lc, Table 2). The pH of the input solution decreased as DOC concentration increased for all the soils (Table 3).**

The concentration of NO<sub>3</sub><sup>-</sup> that was originally present in the forest floor extract was small, and the concentration of NO<sub>3</sub><sup>-</sup> in the input solution for the temperate and tropical soils was  $0-90 \mu g/L$ . At this concentration level, it was difficult to be confident **about the analyzed values for the input solution as well as the output solution, and thus I** have not reported  $NO_3$ <sup>-</sup> sorption with no added  $NO_3$ <sup>-</sup>.

Effect of NO<sub>3</sub><sup> $\cdot$ </sup> on DON and NH<sub>4</sub><sup> $+$ </sup> retention and their changes by Fe<sup>3+</sup> addition

**Upon** NO3' **addition,** DON **retention significantly increased in the College Woods soil (Figure 2a, Table 4). For the Sonadora and Icacos soils, the difference in** DON **retention was not analyzed due to the lack of significance in the regression of one of the treatments (Figure 2b, 2c, Table 4). Dissolved organic N retention did not** significantly change compared to  $NO_3$ <sup>-</sup> addition alone when both  $NO_3$ <sup>-</sup> and  $Fe^{3+}$  were

**added to College Woods (Figure 2a, Table 4). In the Sonadora and Icacos soils, the** effect of  $Fe^{3+}$  on DON retention was not analyzed because of the lack of significance in **one or both of the treatment isotherms (Figure 2b, 2c, Table 4).**

**Ammonium retention did not change significantly upon NO**3**" addition in any of the soils (Figure 3, Table 5). Ammonium retention was lower in the Icacos soil** compared to the College Woods and Sonadora soils. As Fe<sup>3+</sup> was added, the retention still did not change significantly in the College Woods and Sonadora soils (Figure 3a, 3b, Table 5). In the Icacos soil,  $NH_4$ <sup>+</sup> retention significantly decreased with  $Fe^{3+}$  addition **(Figure 3c, Table 5).**

**The pH of the input solution increased upon NO**<sup>3</sup> **' addition in the College Woods** and Icacos soils, while it decreased in the Sonadora soil (Table 6). Upon Fe<sup>3+</sup> addition. **pH of the input solution largely decreased in all the soils (Table 7).**

Effect of NO<sub>3</sub> on DOC retention and its change by  $Fe<sup>3+</sup>$  addition

The addition of NO<sub>3</sub><sup>-</sup> did not affect DOC retention in any of the soils (Figure 4, Table 8). Addition of Fe<sup>3+</sup> and NO<sub>3</sub><sup>-</sup> also had no effect on DOC retention in any of the soils (Figure 4, Table 8).

#### NO<sub>3</sub> adsorption and the ferrous wheel hypothesis

**In the College Woods soil, the regression for NO**<sup>3</sup> **' retention was not significant in most of the treatments; therefore, the effect of the treatments could not be analyzed, as adsorption did not occur (Figure 5, Table 9). In the Sonadora soil, NO**<sup>3</sup> **' sorption only occurred in 3 of the treatments, and there was no difference in NO**<sup>3</sup> **' sorption among those treatments (Figure 5, Table 9). Although the treatment effect was not significant, some NO**3**" retention does seem to occur in this soil. For the Icacos soil, the regression of**

NO3' **retention was not significant in any of the treatments. There is no "m" when the regression is not statistically significant.**

#### CHAPTER IV

### **DISCUSSION**

#### N retention in systems that did not receive NO<sub>3</sub> addition

**The order of retention in N species was different in each soil, and thus I am forced to reject my original hypothesis. In the College Woods soil, retention of NH**4**+ and DON was not different. As quartzite and schist weather, quartz sandstone, feldspar, and mica (biotite and/or muscovite) would be produced (Fichter, 2000). The point of zero charge (pzc) is the point at which surface charge is zero and the surface gives negative charge when pH is higher than the pzc. The pzc is low in quartz and feldspars (2.0-2.4) (Sparks, 2003). Ammonium retention would be attributed to the presence of these minerals since pH of the input solution was higher than the pzc of quartz and feldspar. Iron is present in the soil; however, since the clay fraction is small in the College Woods soil, Fe would be present as Fe coatings on the minerals, not as Fe oxides. In the study by McCracken et al. (2002), which they studied interactions between DOC and several minerals soils from New Hampshire, they suggested that coatings on the soil partially consist of organic carbon and Fe. For DON adsorption, Kaiser and Zech (2000) reported a linear relationship between DON adsorption and Fe and Al oxides content in the soil. As I stated above, the clay fraction is low in the soil, so Al and Fe oxides are less likely to be related to DON adsorption. It may be the Fe coatings that contribute to DON adsorption.**

In the Sonadora soil, NH<sub>4</sub><sup>+</sup> showed higher retention than DON. Ammonium

**could have been fixed by clays, which accounts for a large portion in the soil texture. The bedrock of the Sonadora soil is andesite, which could be weathered into allophane**  $[(A1<sub>2</sub>O<sub>3</sub>)(SiO<sub>2</sub>)<sub>1.3</sub>$ <sup>\*</sup>2.5(H<sub>2</sub>O)], which has high CEC as well as high specific surface area **(Sparks, 2003). Although tropical soils tend to contain high kaolinite, which has low CEC and low expandability, allophane content would have enhanced NH4+ retention in the Sonadora soil. There is another report that Puerto Rican Ultisols also contains smectite up to 19% (Appel et al., 2003). Smectite has relatively high CEC as well as** high expandability (Sparks, 2003). This may also have contributed to NH<sub>4</sub><sup>+</sup> retention.

**Dissolved organic N retention was the second most readily adsorbed form of N in the Sonadora soil. Although the soil has high clay content, clay is not as effective as Fe and Al oxides in DON retention (Kaiser and Zech, 2000). Since Al and Fe content, especially organically bound Fe, is low in the Sonadora soil, the soil may not contain high** Al and Fe oxides, which could be related to the lower DON retention than that of  $NH_4^+$ . **However, allophane could possibly be responsible for DON retention. Lilienfein et al. (2004) suggested an importance of allophane in DOC and DON retention.**

**In the Icacos soil, the regression of DON retention was not significant, and therefore it was not included in the analysis. Ammonium adsorption was low in the Icacos soil. This result seems to correspond to the finding by McDowell et al. (1992),** who found that NH<sub>4</sub><sup>+</sup> is the dominant N form in groundwater in the Icacos watershed. As the retention of  $NH_4^+$  is low and the equilibrium amount of  $NH_4^+$  for this soil is quite high, NH<sub>4</sub><sup>+</sup> would leach out to groundwater. The low retention of NH<sub>4</sub><sup>+</sup> could be related **to the composition of clay minerals in the soil. The bedrock of the Icacos soil is quartz diorite. Turner et al. (2003) reported that the weathering of the granitic rock into**

kaolinite, quartz, biotite, and Fe<sup>3+</sup> oxides in the Icacos watershed. Cation exchange **capacity as well as specific surface area of kaolinite and biotite is small (Sparks, 2003),** and this can be related to the low retention of  $NH_4^+$ .

## Effect of NO<sub>3</sub> on DON and NH<sub>4</sub><sup>+</sup> retention and their changes by  $Fe<sup>3+</sup>$  addition

Effect of NO<sub>3</sub> on DON and NH<sub>4</sub><sup>+</sup> retention was different among the soils, and **therefore my hypotheses were rejected. In the College Woods soil, DON retention** significantly increased upon  $NO<sub>3</sub>$  addition. Change in  $NH<sub>4</sub>$ <sup>+</sup> retention was not **significant. The difference that would be related to NO**<sup>3</sup> **' addition in the input solution would be pH. Comparing the pH of the input solution of the 2 treatments, pH was slightly higher with NO**<sup>3</sup> **' addition. Since pH upon NO**3**" addition was still above the pzc** of quartz and feldspar, NH<sub>4</sub><sup>+</sup> retention was probably not affected. For DON retention, **functional groups in DON could have been affected by the pH change, which may be related to the change in the retention, although the change in pH seems to be too small.**

Addition of  $Fe<sup>3+</sup>$  did not change DON and  $NH<sub>4</sub>^+$  retention compared to the treatment that NO<sub>3</sub> was added. As pH largely decreased upon Fe<sup>3+</sup> addition, some **changes in charges in DON as well as in the soil would have occurred, but the retention did not reflect it. One possibility is a reaction between Fe3+ and DON. Dissolved organic N is reported to have a pattern of adsorption to Fe oxides as similar as DOC** (Kaiser and Zech, 2000). Also, DOC is known to precipitate with Fe<sup>3+</sup> (Nierop et al., **2002). Although conditions that are related to DON adsorption or desorption are still** not clear (Kalbitz et al., 2000), it is possible that DON may also precipitate with Fe<sup>3+</sup>. Precipitation of DOC with Fe<sup>3+</sup> seemed to happen in my experiment since DOC **concentration of the input solution was lower than that of I aimed at whenever I added** **Fe3+. Dissolved organic N concentration is much lower than that of DOC and it makes** it difficult to tell if the precipitation of DON and Fe<sup>3+</sup> actually occurred. If this really happened, DON retention would be higher than the reported value. No change in NH<sub>4</sub><sup>+</sup> **retention could be because the pzc of quartz and feldspars is still lower than the pH of the input solution.**

In the Sonadora soil, a change in DON retention upon  $NO_3$ <sup>-</sup> as well as  $NO_3$ <sup>-</sup> and **Fe3+ addition was not analyzed due to a lack of significance in the regression describing** the sorption isotherm. Ammonium retention did not change upon  $NO_3$ <sup>-</sup> as well as  $Fe^{3+}$ **addition. The pH of the input solution decreased upon** NO3' **addition and decreased** even more as  $Fe^{3+}$  was added. No change in  $NH_4^+$  retention in the both treatments could **be attributed to the presence of smectite, which has minor variable charges.**

For the Icacos soil, a change in DON retention upon  $NO_3$ <sup>-</sup> as well as  $Fe^{3+}$ **addition was not analyzed because the regression describing the sorption isotherm was not significant. Ammonium retention did not change upon** NO3" **addition but decreased** upon  $Fe^{3+}$  addition. The pH of the input solution increased a bit when  $NO_3$ <sup>-</sup> was added, **but decreased as Fe3+ was added. Cation exchange capacity of the soil could be low in the first place since kaolinite and biotite would be the dominant minerals in the soil. The pzc of kaolinite is about 4.6 to 4.8 (Sparks, 2003). Since the pH in the input solution upon** NO3' **addition was still above the pzc of kaolinite, it would not affect CEC. But as pH decreased upon Fe3+ addition, CEC could have decreased as pH got in the range of the pzc of kaolinite.**

## Effect of NO<sub>3</sub> on DOC retention and its change by  $Fe^{3+}$  addition

With and without addition of NO<sub>3</sub><sup>-</sup>, DOC retention in the College Woods soil

**was high. The soil has a substantial fraction of sand; however, Al and Fe contents are high. As I mentioned earlier, the clay fraction is small, and Al and Fe oxides could not have contributed much to DOC retention. Iron in the soil might exist as Fe coatings (McCracken et al., 2002) rather than as Fe oxides. Dissolved organic C would be adsorbed to the Fe coatings and it could result in high DOC retention.**

**Dissolved organic C retention was not changed by NO**<sup>3</sup> **' addition in the College Woods soil. Nitrate addition to the input solution did not seem to affect DOC retention at all, which is a little different from DON retention. Kaiser and Zech (2000) reported a similar pattern of retention of DOC and DON to mineral soils, but they did not examine how the retention of DOC and DON would be altered by adding NO**<sup>3</sup> **'. A change in the retention could be related to different functional groups that are expected to be present in DOC and DON, which would respond differently to a change in pH that might be related to the addition of a chemical component. Or, in the case of my experiment, in which the change in pH was not large, NO**3**" might have an influence on DON but not the DOC retention mechanism. In the Harvard Forest chronic N amendment study, no change in DOC flux and a large increase in DON flux have been reported (McDowell et al., 2004). This could also suggest that DOC and DON behave differently and their cycles may not be fully connected. As NO**<sup>3</sup> **' was added at only one concentration in my experiment, a range of NO**<sup>3</sup> **' concentration additions may be useful to obtain a more detailed view of DOC and DON dynamics and their differences.**

**With only DOC addition, DOC retention was high in the Sonadora soil, and it is probably due to its high clay content. Although the Sonadora soil has low Fe content, clay is reported to compensate for low Fe in retaining DOC (Fiedler and Kalbitz, 2003).**

**Also, allophane could contribute to DOC retention. Lilienfein et al. (2004) observed that DOC and DON retention are linearly related to allophane concentration.**

**Dissolved organic C retention isotherms also did not change upon NO**3**" addition** in the Sonadora soil. The pH of the input solution decreased upon NO<sub>3</sub> addition; **however, it did not seem to affect DOC retention. Functional groups on DOC might not have been affected by the pH, which may be related to the insignificant change in DOC retention.**

**Dissolved organic C retention in the Icacos soil was lower than other 2 soils when only DOC was added and it could be because of high sand content although the soil has high Fe content. High Fe content despite the anoxic condition is puzzling as mentioned earlier. But another contradictory thing is the low DOC retention although Fe oxides have been reported to retain DOC (Jardine et al., 1989; McDowell and Wood, 1984). One possible explanation is that Fe might exist as surface coating of minerals and not necessarily as weathered minerals, which I also suggested for the College Woods soil. If most of the Fe exists as a surface coating, then it would be mostly on the sand fraction. The surface area of the sand fraction is small compared to that of clay minerals. Dissolved organic C would be retained to the Fe coatings, but the amount would be small.**

**However, this idea may not make sense since the College Woods soil also has a substantial sand fraction and showed much higher DOC retention. Another explanation could attribute to the nature of the bedrock. As I mentioned, the bedrock of the Icacos watershed is quartz diorite and it is reported that the weathering of the granitic rock into** kaolinite, quartz, biotite, and Fe<sup>3+</sup> oxides (Turner et al., 2003). Although Fe<sup>3+</sup> oxides would be left after weathering, biotite  $[KMg_{2.5}Fe^{2+}{}_{0.5}AlSi<sub>3</sub>O<sub>10</sub>(OH)<sub>1.75</sub>F<sub>0.25</sub>]$  could have
contributed a lot to the Fe content. Iron analysis could not differentiate  $Fe^{3+}$  and  $Fe^{2+}$ . **If biotite dominated the Fe content, it might not have contributed a lot to DOC retention.** Nierop et al. (2002) observed a weak precipitation between Fe<sup>2+</sup> and DOC. The soil pH, **which is higher than other soils, would decrease positive charge in the soil as well. As the soil pH is larger than the pzc of the mineral components in this soil, such as kaolinite and quartz, the minerals would exert negative charge (Sparks, 2003). As DOC exerts negative charge in general, DOC retention would have been small in this soil.**

**As** NO3' **was added, DOC retention in the Icacos soil did not change. There was a small change in pH in the input solution upon** NO3' **addition, but it does not seem to affect the retention of DOC. Since the change in pH was small, functional groups of DOC might not have been affected.**

When Fe<sup>3+</sup> was added in the presence of NO<sub>3</sub><sup>-</sup>, DOC retention did not change in **the College Woods and Sonadora soils, and the Icacos soils. However, the result from** my experiment on DOC retention with  $Fe<sup>3+</sup>$  addition could be misleading since  $Fe<sup>3+</sup>$  could **have precipitated out with DOC in the input solution. To measure the retention of N species and DOC, I analyzed for their concentrations in the input and output solutions and subtracted the output concentration from that of the input. During the analyses, I noticed that the DOC concentration in the input solution was lower than the target** concentration when I added  $Fe<sup>3+</sup>$  to the input solution. Nierop et al. (2002) observed a strong quick precipitation when they added Fe<sup>3+</sup> to DOM at molar metal/carbon was more **than 0.014. It was not related to pH. Considering the fact that the concentration of Fe3+ that I added to the input solution was high, and some flocculates were observed in** the input solution, it is possible that the precipitation of DOC with  $Fe<sup>3+</sup>$  occurred in my

**experiment.**

**Since I could not confirm the exact DOC concentration before precipitation occurred, I used the concentration that was measured in the input solution. Therefore, if the amount of the precipitated DOC in the input solution is considered, DOC retention** would be much higher in all the soils in the presence of  $Fe^{3+}$ . As Jansen et al. (2004) **suggested that organic matter mostly adsorbed to freshly created Fe in the lower B horizon in addition to the precipitation as organo-Fe complexes, it would have been** closer to the real podzolization situation if I have added  $Fe<sup>3+</sup>$  to the soil, not to the input **solution. Another thing to consider regarding the legitimacy of the experiment is the experimental condition for the Icacos soil. The Icacos soil is originally an anoxic soil and it might not have been appropriate to dry it. Moreover, the experiment was done** under oxic conditions. If  $Fe<sup>3+</sup>$  was added to an anoxic environment, it would be reduced to Fe<sup>2+</sup>, subsequently dissolved, and leached out. In that case, even if Fe<sup>3+</sup> comes into **an anoxic environment, it is less likely to contribute to DOC retention. In that sense, my experiment was not simulating the field conditions. In the field, however, a reduction in DOC concentration in the course of riparian zone to the stream has been observed in the Icacos watershed (Chestnut and McDowell, 2000). As Fe would not be accounted for much of DOC retention, there could be other factors that are related to the removal of DOC in a course of riparian zone. There was a small DOC retention when only DOC was added in my experiment. As Fe that would contribute to DOC retention would be small in the first place in the soil, this DOC retention would be corresponding to the decrease in DOC concentration in the course of riparian zone to the stream in the field.**

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## NO<sub>3</sub> adsorption and the ferrous wheel hypothesis

When only  $NO_3$ <sup>-</sup> was added,  $NO_3$ <sup>-</sup> retention was much lower than that of DON, **NH4+, and DOC. Retention was observed in the College Woods and Sonadora soils, but not in the Icacos soil. Sonadora soil showed generally higher retention than the College Woods soil, and this could be because of the presence of allophane. Ryan et al. (2001) reported that Al-rich allophane, which is less weathered, adsorbed more NO**<sup>3</sup> **' compared to Si-rich allophane, which is highly weathered. Aluminum content is actually low in the Sonadora soil, which may indicate the soil contains less Al-rich allophane; however, retention of NO**3**" would be related to the presence of allophane.**

The treatment did not have an influence on NO<sub>3</sub>' retention in any of the soils. **Mostly, the regression of** NO3" **retention was not significant or** NO3' **retention did not occur. Even if the regression was significant, the treatment did not have any effect on** NO3' **retention. Among the soils, however, the Sonadora soil seems to show a small amount of** NO3' **retention, although it is not related to the treatment. There are some factors that should have been scrutinized before the experiment. The possible** precipitation of DOC with Fe<sup>3+</sup> in the input solution, which is mentioned earlier, is one of them. Although I added  $Fe^{3+}$  to increase the opportunity for  $Fe^{2+}$  production through reduction by DOC,  $Fe^{3+}$  did not behave as I expected. Adding  $Fe^{2+}$  might give a **different result as it would not precipitate with DOC.**

**Another thing to consider is the quality of DOC. Since I did not further analyze the components of DOC, I do not know it contained constituents that have reducing power.** It is possible that those components were not high enough to reduce  $Fe^{3+}$ . It would have been useful to analyze DOC for  $Fe^{3+}$ ,  $Fe^{2+}$ , and reductants before the

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**experiment. Also, if I wanted to simulate the situation in the B horizon as closely as possible, I should have used soil solution from the upper B horizon, not forest floor extract, since the composition and component that has reducing power in DOC would be different. Ussiri and Johnson (2004) actually reported that characteristics of DOM that was extracted from the O horizon and Bh horizon was different; high alkyl-C and** *i* **carboxyl C in the Bh horizon and high O-alkyl C in the O horizon.**

**Use of hydroquinone, with strong reducing power, did not result in enhanced NO**<sup>3</sup> **' retention. The reason why I used hydroquinone is to increase reducing power in the input solution to enhance the "ferrous wheel" reaction. Nitrate retention did not** increase when only hydroquinone was added as well as when it was added with  $Fe<sup>3+</sup>$ . Davidson et al. (2003) suggested that  $NO<sub>3</sub>$ <sup>-</sup> can be reduced to  $NO<sub>2</sub>$ <sup>-</sup> in anaerobic **microsites. Since I dried and sieved the soil at 2 mm, anaerobic microsites could have been decreased. For the Icacos soil, I should have done the experiment under anaerobic conditions. It would have been better if I used field moist, unseived soil.**

## **Conclusion**

**The results of my experiments would indicate immediate responses in N and DOC retention upon** NO3' **deposition. Nitrogen and C dynamics can be affected by** NO3' **addition although the magnitude and tendency of the change would be different in each soil, which could be related to soil properties as well as pH. More detailed analyses on soils properties, such as clay mineralogy, would be useful to examine further retention mechanisms. Although not all the changes were significant,** DON **retention** seems to be more influenced by  $NO_3$ <sup>-</sup> addition than  $NH_4$ <sup>+</sup> retention. Effects of  $NO_3$ <sup>-</sup> **addition on DOC retention were generally smaller than on N species retention and a**

**decrease in retention was not observed in any of the soils. This may suggest that DOC dynamics are less susceptible to a change caused by** NO3' **deposition. As DON** responses to NO<sub>3</sub><sup>-</sup> addition were different from that of DOC, C and N cycles could be **different in the soil.**

For NO<sub>3</sub>' retention, strong retention was not observed in any of the soils, which supports previous studies (Nodvin et al., 1986; Kaiser and Zech, 1996). Adding Fe<sup>3+</sup> or **hydroquinone did not influence NO**<sup>3</sup> **' retention, either. Although there are some experimental conditions that can be changed, my results suggest that the ferrous wheel hypothesis does not explain the net retention of N by mineral soils that has been inferred from the results of field manipulations.**

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**Table 1. Chemical and physical properties of the soils**

**+ Exchangeable**

*\** **Organically bound**

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**Table 2. Partition coefficient (m), release term (b), equilibrium amount, and r**2 **value of a** regression line describing NH<sub>4</sub><sup>+</sup> and DON adsorption when 0-50 mg/L of DOC, 0-1.25 mg/L of NH<sub>4</sub><sup>+</sup>, and 0-1.57 mg/L of DON were added to the soil. Small **case letter beside the m value represents the significance of differences in slope** between NH<sub>4</sub><sup>+</sup> and DON for a given soil.

Soil	N species	m	$\mathbf b$ $(\mu g/g)$	Equilibrium $(\mu g/g)$	$r^2$
College Woods	$\text{NH}_4$ <sup>+</sup>	$0.342$ <sup>a</sup>	$\cdot$ t	$\overline{\phantom{0}}$	0.906
	<b>DON</b>	0.613 <sup>a</sup>	$-1.448$	2.362	0.978
Sonadora	$NH4+$	$0.791$ <sup>a</sup>	$-0.885$	1.119	0.996
	<b>DON</b>	0.907 h	$-2.662$	2.935	0.931
Icacos	$NH4+$	0.387 <sup>a</sup>	$-4.390$	11.343	0.968
	<b>DON</b>	0.274 <sup>b</sup>	$-0.693$	2.531	N.S

**t The value was more than zero.**

**\* The value was negative.**

**N.S = not significant**

	College Woods		Sonadora		Icacos	
Target DOC concentration	$pH_i$	$pH_f$	$pH_i$	$pH_f$	$pH_i$	$pH_f$
$\boldsymbol{0}$	5.85	5.17	6.98	6.14	6.55	6.14
10	5.41	5.30	6.28	5.94	6.00	6.16
20 <sup>°</sup>	5.29	5.37	6.11	5.97	5.88	6.10
30	5.24	5.40	5.94	5.91	5.81	6.08
40	5.23	5.45	5.85	5.86	5.75	6.07
50	5.18	5.49	5.81	5.82	5.70	6.06

Table 3. pH of the input and output solution when a target concentration of 0-50 mg/L of DOC was added to the soil.

Table 4. Effects of added  $NO<sub>3</sub>$  and  $Fe<sup>3+</sup>$  on DON retention. Partition coefficient (m), **release term (b), equilibrium amount, and r**2 **value refer to regression lines describing DON retention, using the initial mass isotherm approach. Small case letter beside the m value represents the significance of differences in slope between treatments for a given soil.**

Soil	Treatment	${\bf m}$	$\mathbf b$ $(\mu g/g)$	Equilibrium $(\mu g/g)$	$r^2$
College Woods	Control	0.613 <sup>a</sup>	$-1.448$	2.362	0.978
	With NO <sub>3</sub>	0.768 <sup>b</sup>	$-0.082$	0.107	0.989
	With $NO3 + Fe3+$	$0.912^{b}$	$-0.384$	0.428	0.995
Sonadora	Control	$0.908$ <sup>†</sup>	$-2.662$	2.935	0.931
	With $NO3$	$0.733 \;$ $^{\dagger}$	$-3.667$	5.012	N.S
	With $NO3 + Fe3+$	$0.122^{\text{t}}$	$-4.450$	36.389	N.S
Icacos	Control	$0.274$ <sup>†</sup>	$-0.693$	2.531	N.S
	With $NO3$	$0.465$ <sup>t</sup>	$-5.246$	11.275	0.841
	With $NO_3$ + $Fe^{3+}$	11	$-1.397$	1.012	N.S

**t Statistical analysis was not performed due to insignificance of the regression.**

**\* The value was more than 1.**

**N.S = not significant**

Table 5. Effects of added  $NO_3$ <sup>-</sup> and  $Fe^{3+}$  on  $NH_4$ <sup>+</sup> retention. Partition coefficient (m), **release term (b), equilibrium amount, and r**2 **value refer to regression lines describing NH**4**+ retention, using the initial mass isotherm approach. Small case letter beside the m value represents the significance of differences in slope between treatments for a given soil.**

Soil	Treatment	${\bf m}$	$\mathbf b$ $(\mu g/g)$	Equilibrium $(\mu g/g)$	$r^2$
College <b>Woods</b>	Control	$0.342$ <sup>a</sup>	$\_$ † $\_$	$\overline{1}$	0.906
	With $NO3$	0.290 <sup>a</sup>	$-0.078$	0.279	0.900
	With $NO3+ + Fe3+$	0.290 <sup>a</sup>	$-0.112$	0.386	0.972
Sonadora	Control	$0.791$ <sup>a</sup>	$-0.885$	1.119	0.996
	With $NO3$	$0.720$ <sup>a</sup>	$-0.986$	1.372	0.998
	With $NO3- + Fe3+$	0.720 <sup>a</sup>	$-1.190$	1.653	0.988
Icacos	Control	$0.387$ <sup>a</sup>	$-4.390$	11.343	0.968
	With $NO3$	0.420 <sup>a</sup>	$-4.640$	11.050	0.969
	With $NO3- + Fe3+$	0.262 <sup>b</sup>	$-5.533$	21.126	0.907

**\* The value was more than zero.**

**\* The value was negative.**

		College Woods		Sonadora	Icacos	
Target DOC concentration	$pH_i$	$pH_f$	$pH_i$	$pH_f$	$pH_i$	$pH_f$
$\theta$	6.19	5.22	5.68	5.25	6.25	6.01
10	5.52	5.41	5.71	5.20	6.09	6.01
20	5.36	5.43	5.60	5.15	5.99	5.90
30	5.28	5.48	5.58	5.12	5.89	5.93
40	5.26	5.52	5.54	5.11	5.92	5.91
50	5.21	5.54	5.52	5.12	5.85	5.96

Table **6** . pH of the input and output solution when a target concentration of 0-50 mg/L of DOC and 4 mg/L of NO**3**' were added to the soil.

**Table 7. pH of the input and output solution when** DOC,  $4 \text{ mg/L of NO}_3$ , and  $2 \text{mg/L of Fe}^{3+}$ **a target concentration of 0-50 mg/L of were added to the soil.**

	College Woods		Sonadora		Icacos	
Target DOC concentration	pH <sub>i</sub>	$pH_f$	$pH_i$	$pH_f$	$pH_i$	$pH_f$
$\boldsymbol{0}$	4.02	4.78	4.18	5.32	4.20	5.74
$\mathbf{1}$	4.41	4.98	4.42	5.40	4.41	5.71
$\overline{2}$	4.60	5.08	4.56	5.35	4.57	5.71
3	4.71	5.18	4.62	5.32	4.63	5.67
$\overline{4}$	4.76	5.26	4.68	5.35	4.70	5.63
5	4.80	5.29	4.73	5.35	4.75	5.61

**Table** 8. **Effects of added** NO3' **and Fe3+ on DOC retention. Partition coefficient (m), release term (b), equilibrium amount, and r**2 **value refer to regression lines describing DOC retention, using the initial mass isotherm approach. Small case letter beside the m value represents the significance of differences in slope between treatments for a given soil.**



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Table 9. Effects of added DOC,  $Fe^{34}$  and hydroquinone  $(HQ)$  on  $NO_3$  retention. **Partition coefficient (m), release term (b), equilibrium amount, and r<sup>2</sup> value refer to regression lines describing NO**3**" retention, using the initial mass isotherm approach. Small case letters beside the values represents significance of differences between treatments for a given soil.**

Soil	Treatment	${\bf m}$	$\mathbf b$ $(\mu g/g)$	Equilibrium $(\mu g/g)$	$r^2$
College Woods	$NO3$ alone	0.036	$-0.484$	13.444	0.742
	$DOC + NO3$	$0.024$ <sup>t</sup>	$-0.538$	$\overline{\phantom{0}}$	$_{\rm N.S}$
	$DOC + NO_3 + Fe^{3+}$	$0.070^{\dagger}$	$-1.009$	1.449	N.S
	$HQ + NO_3$	$0.031$ <sup>t</sup>	$-0.155$	0.478	N.S
	$HQ + NO_3 + Fe^{3+}$	$0.043$ <sup>†</sup>		$\cdot$	N.S
Sonadora	$NO3$ alone	$0.103$ <sup>a</sup>	$-0.931$	0.897	0.838
	$DOC + NO_3$ <sup>-</sup>	$0.042^{\dagger}$	$-2.163$	5.116	N.S
	$DOC + NO_3 + Fe^{3+}$	$0.080$ $^{\rm a}$	$-1.610$	1.996	0.848
	$HQ + NO_3$	$0.106^{\text{ t}}$	$-2.692$	2.518	N.S
	$HQ + NO_3 + Fe^{3+}$	$0.065$ <sup>a</sup>	$-2.469$	3.802	0.820
Icacos	$NO3$ alone	$\overline{\phantom{1}}^{\ddag}$		6.333	N.S
	$DOC + NO3$ <sup>-</sup>	$\overline{\phantom{1}}$		0.485	N.S
	$DOC + NO3 + Fe3+$	0.023	$-0.165$	$-1$	N.S
	$HQ + NO_3$	$-1$	$-0.596$	$-1$	N.S
	$HO + NO3- + Fe3+$	$\overline{\phantom{0}}$		9.225	N.S

**+ Statistical analysis was not performed due to insignificance of the regression.**

**\* Value was negative.**

**Value was more than zero.**

**N.S = not significant**

a) College Woods



**N species Xi (ug/g)**

**Figurel. Retention of N species in the soil, which are naturally occurring in 0-50 mg/L of DOC. The line indicates that the regression is significant. Scale of the y-axis changes in different soils.**

a) College Woods



**b) Sonadora**





Figure 2. Effects of NO<sub>3</sub><sup>-</sup> (4 mg/L), and NO<sub>3</sub><sup>-</sup> and Fe<sup>3+</sup> (2 mg/L) on adsorption of DON from a **forest floor extract by mineral soils. The line indicates that the regression significant.**





Figure 3. Effects of NO<sub>3</sub><sup>'</sup> (4 mg/L), and NO<sub>3</sub><sup>'</sup> and Fe<sup>3+</sup> (2 mg/L) on adsorption of NH<sub>4</sub><sup>+</sup> from a **forest floor extract by mineral soils. The line indicates that the regression significant. Scale of the y-axis changes in different soils.**

a) College Woods



Figure 4. Effects of NO<sub>3</sub><sup>(4 mg/L), and NO<sub>3</sub> and Fe<sup>3+</sup> (2 mg/L) on adsorption of DOC from a</sup> **forest floor extract by mineral soils. The line indicates that the regression is significant.**

## a) College Woods



Figure 5. Effects of DOC (50 mg/L), DOC and Fe<sup>3+</sup> (2 mg/L), hydroquinone (10 mg/L), and **hydroquinone and Fe3+ on adsorption of N03' in mineral soils. The line indicates that the regression is significant.**

**APPENDIX: ADSORPTION EXPERIMENT RAW DATA**















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