# Nitrate Removal from Water Using Conifer Tissues

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**ABSTRACT**

The state of Washington has ongoing nitrate contamination problems in the mid-Colombia Basin and estuarine ecosystems, such as the Hood Canal. Forest Service researchers have found that Eastern juniper wood fibers show promise in contaminant removal from water and became more effective after prior use at acid mine sites. The purpose of this study was to select tree species from the Northwest region and determine portions of these trees (wood, bark) that might make effective filters for nitrate removal from water.

Six species of trees in the Cedar and Bald Cypress families were selected. Samples of heartwood, sapwood and bark were obtained. The wood samples were pretreated with a weak acid solution (pH 3) and distilled water (control). The following data were recorded: liquid absorbed during pretreatment, tannin leaching, tissue density and sorption of nitrate from solution. Samples that proved most effective at nitrate removal were also evaluated for re-release of sorbed nitrate back into water.

Nitrate removal from water solution was most effective with incense cedar bark (22% removal/water pre-treatment, 28% removal/acid pre-treatment) and Port-Orford cedar bark (33% removal/water pre-treatment, 30% removal/acid pre-treatment).

**KEYWORDS:** nitrate, sapwood, tannins, nitrate contamination, heartwood, acid mine drainage, bark, sorption/absorption, leaching.

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## 1. INTRODUCTION

Nitrate ($NO_3^-$) is a naturally-occurring form of nitrogen that is an integral part of the biogeochemical cycle of nitrogen. Nitrate is found in air, soil, water and food (Barrett *et al*, 1986).

The state of Washington has ongoing nitrate contamination problems. Nitrate concentrations in groundwater are elevated in the mid-Columbia basin as the result of various poor land-use practices, especially over-fertilization of crops (Dept of Ecology, 2002). Both state and federal governments have established a maximum contaminate level of 10 mg/L nitrate-nitrogen for drinking water. Contamination of drinking water with nitrate has associated health risks, including changes in the dynamics of some human diseases such as cancers and methylglobanemia, or blue baby disease (CDC, 1995). The eutrophication of estuarine ecosystems is another result of high nitrate levels in water. The Hood Canal is a 60-mile long fjord branching from Puget Sound. In 2003, the Pew Oceans Commission listed the lower Hood Canal as a 'dead zone' due to oxygen depletion (Chasan 2008). Elevated nitrate levels in water can favor the growth of algal species which bloom and deplete dissolved oxygen, killing other oxygen requiring aquatic species.

Human sources that contribute nitrate to groundwater and waterways include faulty septic systems and fertilizer run-off. New technologies to remove nitrate from drinking water have been developed (ion exchange, reverse osmosis, chemical systems, enzyme/microbial immobilization). Such technologies are not cost effective for temporary treatment of surface water point-source contamination of environments from common sources such as failing septic systems.

Researchers from the USDA Forest Service Forest Products Laboratory in Madison, WI developed a novel water filter, made from wood fibers, which has shown promise in removing nitrate from surface waters. These wood fibers of eastern juniper trees were used to clean heavy metals from former mine sites. The mine site water 'acidified' the wood filters. When the acidified wood filters were reused at other sites, they were efficient at removing nutrient pollutants from water (Newsline. 2002). The purpose of the study was to identify tree species from the Pacific Northwest region which might effectively remove nitrate from water and determine which portion of the tree (bark, heartwood, sapwood) was the most effective.

## 2. METHODS

Six species of trees from the Pacific Northwest were selected for study. Selection was based upon similarity of their wood and bark to that of the previously used Eastern juniper. Five species were in the Cedar family (Cupressacea) and one was in the Bald Cypress family (Taxodiacea). All have bark with a similar morphology (shaggy/shredded) and aromatic wood.

**Table 1. Common and Scientific Names of Species and the Abbreviations used in this Study**

| Family | Common Name | Scientific Name | Abbreviations |
|---|---|---|---|
| Cupressaceae | Alaska Yellow cedar | *Callitropsis nootkatensis* | AYC |
| | Incense cedar | *Calocedrus decurrens* | IC |
| | Port-Orford cedar | *Chamaecyparis lawsoniana* | POC |
| | Western redcedar | *Thuja plicata* | WRC |
| | Western juniper | *Juniperus occidentalis* | WJ |
| Taxodiaceae | Coast redwood | *Sequoia sempervirens* | CR |

Samples of Alaska yellow cedar and Western red cedar were collected in western Washington. Samples from the other four species of tree were collected in southern Oregon. Alaska yellow cedar, incense cedar and western juniper wood samples were from relatively young trees that had not yet developed heartwood. Port-Orford cedar, coast redwood and Western red cedar wood samples were from mature trees. All wood and bark samples were frozen until cut to preserve as much as possible the original wood chemistries.

Wood and bark were obtained as stem cross-sections and cut to desired sizes. Heartwood and sapwood were cut into ≈ 2x2 cm blocks using a saw. Small pieces of bark were removed by hand and cut into approximately 1 cm squares using sturdy scissors.

All testing was done in sterile 100 mL plastic containers with screw cap lids. Acid mine drainage as seen in the Forest Products Laboratory tests typically had a low pH (below 3). A weak sulfuric acid solution was prepared (≈ pH 3) as a pre-treatment in an attempt to improve nitrate sorption ability. A sample of 0.05M sulfuric acid stock solution was diluted with distilled water to pH 3 as measured with pH test paper.

Eight samples of each tree species and tissue type (bark, sapwood, heartwood) were weighed on an electronic balance to 0.001g and the weights recorded. Samples were labeled and numbered for identification with a waterproof marker. Four samples of each tree species and tissue type were placed in separate, labeled containers. Acid solution (80 mL) was added to cover the conifer samples inside. A separate set of tissue samples was prepared and 80mL of distilled water added to each container. Containers with water served as controls. These pretreatment containers were placed in a refrigerator for 4 d at 3°C to simulate stream conditions in northwest Washington and to inhibit microbial growth which might affect results.

All containers were then removed from the refrigerator. Each tissue sample was removed from its solution and the surface dried with paper towels. Samples were then reweighed. The volume of solution absorbed by the wood sample was recorded. This was done as the maximum volume of water absorbed might be related to potential nitrate sorption. The color of each solution (water or acid) was noted to determine whether leaching of water soluble tannins might, in some way, relate to nitrate sorption. Conifer samples were then placed on a foil-lined pan in an oven at 65°C for 3 h to dry the tissues. This was done to remove water absorbed from pre-treatments without damaging tree tissues to prepare for nitrate removal tests.

Nitrate testing was done with a nitrate ion selective electrode attached to a Vernier LabQuest meter. Electrode calibration used nitrate standards of 1 and 100 mgN/L. The meter provided ≈60 readings plus mean and SD of all readings. A nitrate standard solution of 100 mgN/L was diluted with distilled water to a concentration of 25-30 mgN/L to make test solutions. This concentration is over two times the average groundwater contamination level found in eastern Washington (Nolan *et al*, 1988). The initial nitrate concentration was recorded each time new test solutions were prepared.

All tissue samples were weighed prior to testing and one sample was placed in each container. With 4 samples per tree species, tissue type (if available) and pretreatment, there was a total of 120 test containers. Bark floated in solution, so samples were weighed down with plastic-coated paper clips prior to placement in the nitrate solution. It was assumed the plastic coating of the clips would be chemically inert in the nitrate solution. Containers with bark samples had 40 mL, container with heartwood had 80 mL and those with sapwood contained 60 mL of nitrate solution. Samples were placed in a refrigerator at 3°C for 7 d. Each wood sample was removed from its container and the nitrate solution was analyzed for the final nitrate concentration.

Some bark samples removed nitrate from the prepared nitrate solution. Another test was run to determine if nitrate absorbed by these bark samples would leach out again when in contact with water. The bark samples were surface rinsed with distilled water, then dried in an oven. Plastic containers were each filled with 40mL of distilled water (pretested for nitrate concentration). The containers were again placed in a refrigerator at 3°C for seven days. The samples were then removed and nitrate levels in the distilled water re-measured. The same test was run to determine if nitrate was naturally present in bark and would be released into water using new bark samples.

To determine if a correlation existed between tree species, tissue type, and ability to remove nitrates from water, the density of each tree tissue type was determined by water displacement.

Table 2 presents the data on tannin leaching by both water and acidified water. It was interesting to **note that** neither pretreatment of Port-Orford cedar and incense cedar barks showed tannin leaching as evidenced by clear solutions. Both were also the most effective tree tissues at nitrate removal from solution.

**Table 2. Presence or Absence of Tannin Leaching by Pretreatment**

| | | Water | Acidified Water |
|---|---|---|---|
| Tannins Leached | Bark | AYC, CJ, WRC, CR | AYC, CR POC, CR |
| | Heartwood | POC, WRC, CR AYC, CJ | AYC, CJ, WRC, CR |
| | Sapwood | IC, WRC, CR | |
| Not Leached | Bark | | CJ, POC, IC, WRC |
| | Heartwood | IC, POC | WRC |
| | Sapwood | POC | IC |

Figures 1-3 present the results of absorption from water and acidified water by bark, heartwood, and sapwood samples. In most cases, the ability to absorb water versus water in an acid solution did not vary greatly.

**Figure 1.**
**Water Absorption: Bark Samples in Water and Acidified Water**
N=4 Error Bars= 1 SD

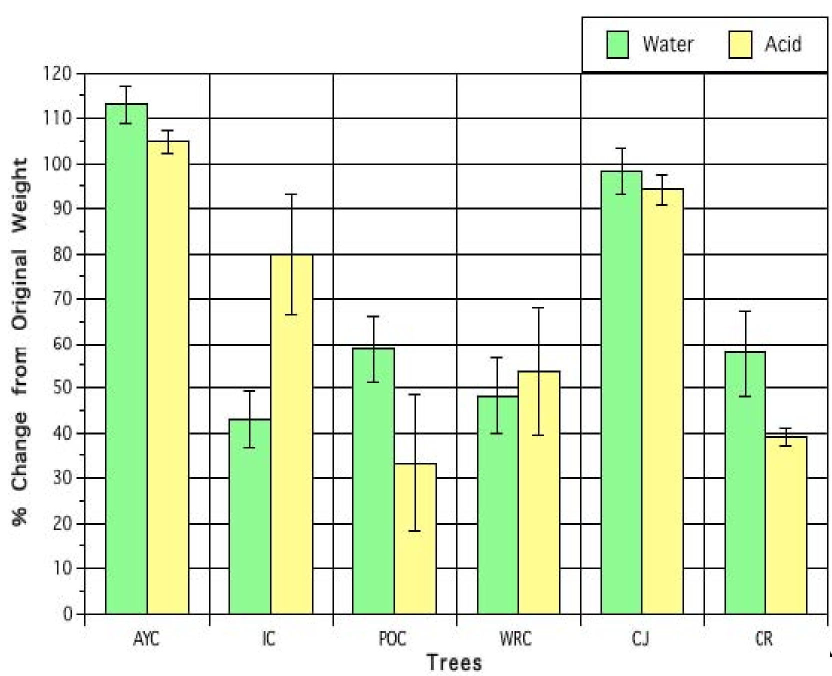


**Figure 2. Water Absorption: Sapwood Samples in Water and Acified Water**
**N=4 error bars = 1SD**

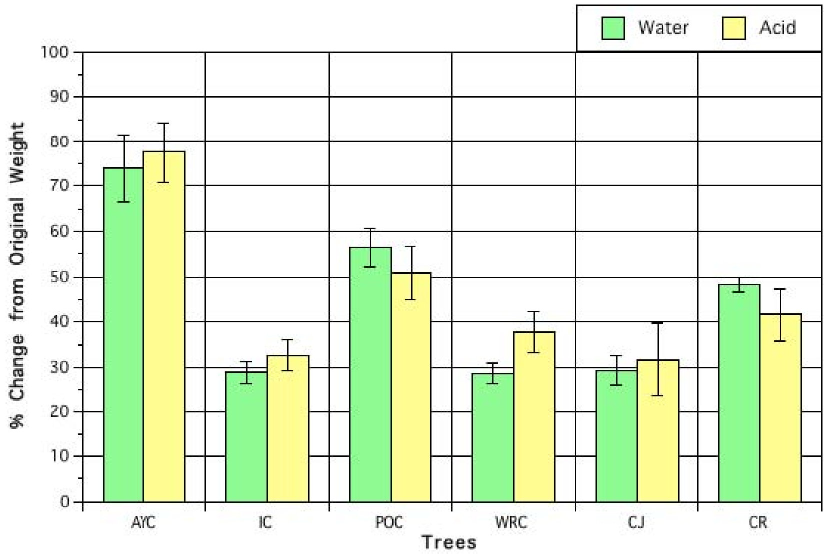
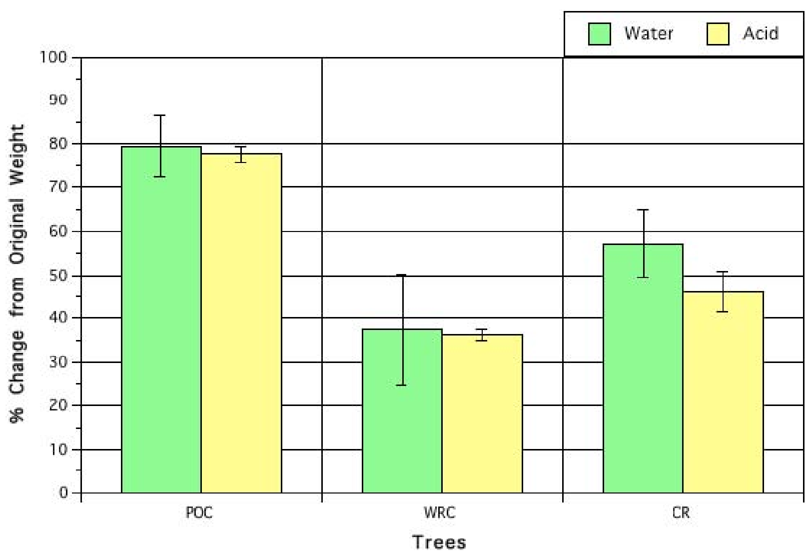



**Figure 3. Water Absorption: Heartwood Samples in Water and Acidified Water**

N=4 Error bars = 1SD



Figures 4-6 present the results of nitrate sorption by the various wood samples from both water and acidified water. Because the various bark and wood samples had different masses, nitrate removal/addition was expressed as mgN/g wood. Only IC sapwood and bark produced statistically significant ($\alpha = 0.05$, $p<0.0001$) nitrate sorption from both the water and acidified water solution. Table 2 and Figures 4-6 show that IC bark removed 50 mgN/g from water and 46 mgN/g from acidified water. PO bark removed 13 mgN/g from water and 20 mgN/g from acidified water. The WRC and POC heartwoods showed statistically significant ($\alpha = 0.05$, $p<0.0001$) nitrate sorption from the acidified water solution only. CR bark and PO heartwood samples took up little nitrate. AYC, WRC and CJ barks and all sapwoods released significant amounts of nitrates into both water and acidified water solutions.

**Figure 4. Changes in Dissolved Nitrate Concentration in the Presence of Bark Samples**

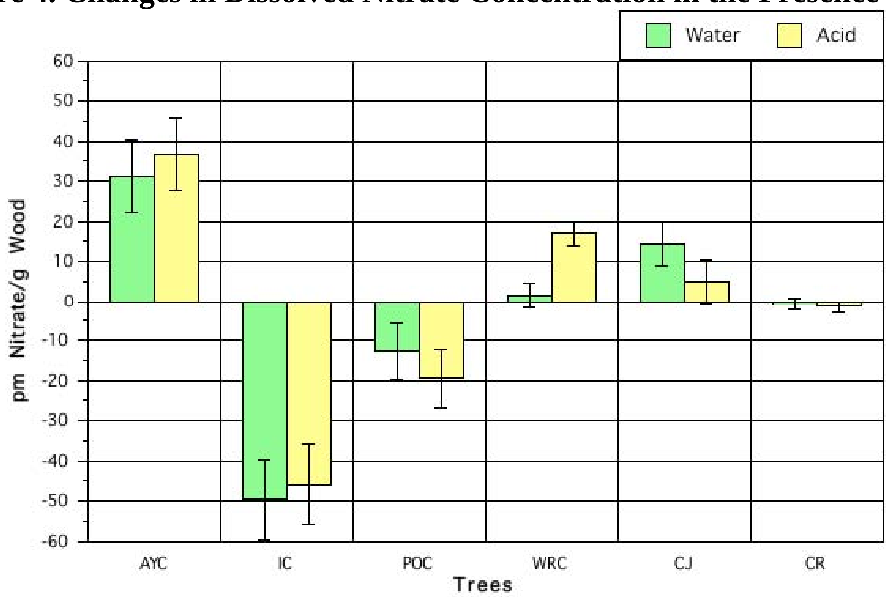



**Figure 5. Changes in Dissolved Nitrate in the Presence of Sapwood**

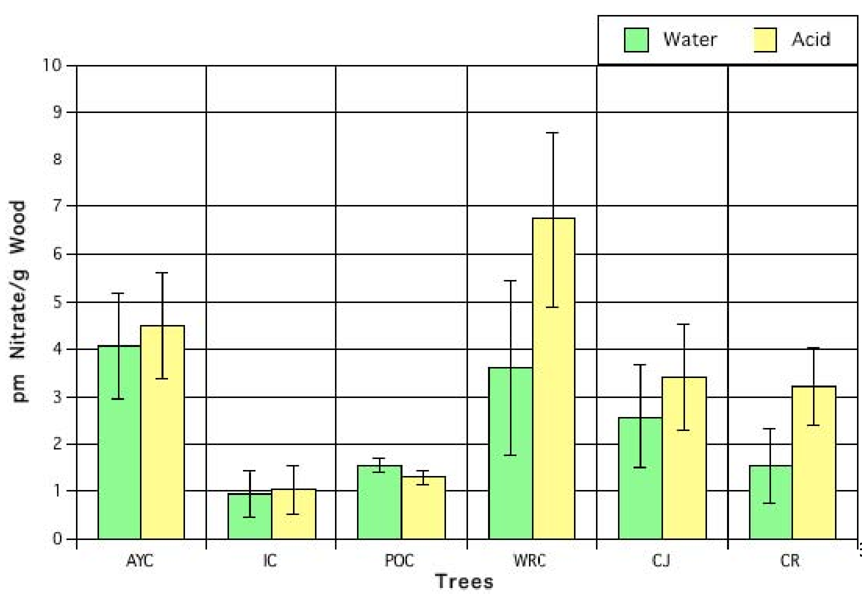


**Figure 6. Changes in Dissolved Nitrate in the Presence of Heartwood**

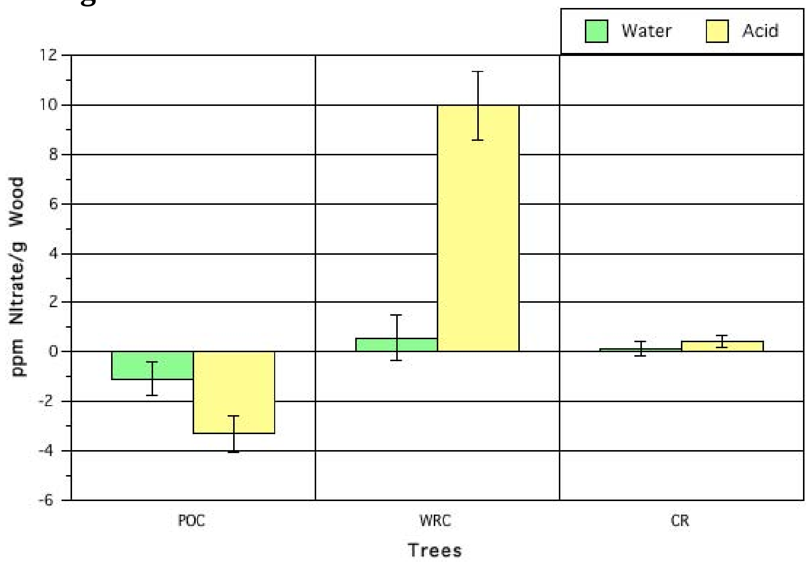



Figure 7 shows the results of tests to determine whether fresh POC and IC barks leached nitrate naturally when placed in water. Pieces of fresh bark were placed in containers of distilled water containing 2.7 mg nitrate N/L. The bark samples did not release any nitrate into the distilled water; rather they both removed significant amounts for nitrate from it (POC, 70% and IC, 80%).

**Figure 7. Nitrates Leached from Untreated Fresh Bark Samples into a Solution Containing an Initial Nitrate Level of 2.7 mgN/L.**

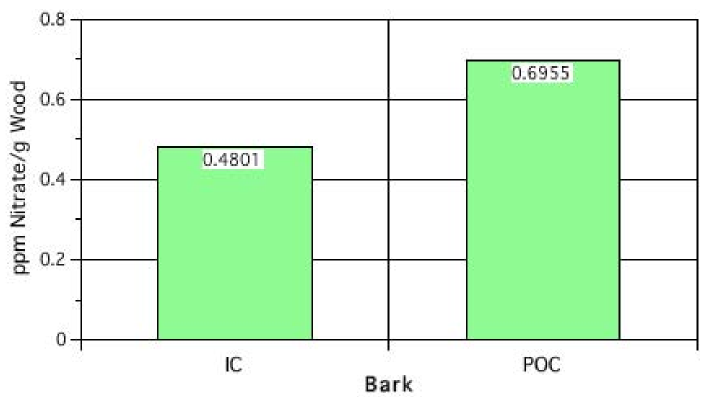
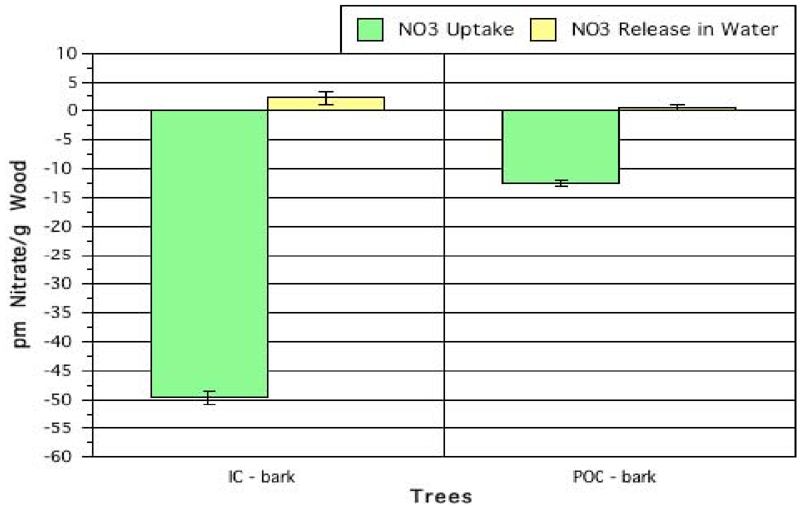


**Figure 8. Nitrates Leached from Bark Samples in Nitrate Removal/Addition Experiment**




The POC and IC barks from the nitrate absorption experiment shown in Figure 7 were placed in distilled water and the amount of nitrate leached back into solution was determined. Figure 8 shows that <5% of the absorbed nitrate was returned to solution and it is possible that this small amount may have been due to inadequate rinsing of the bark surface rather than from leaching from the bark itself.

**Table 3. Statistics for Nitrate Removal/Addition versus Density**

**Bark samples** (Alpha 0.05)

- water pretreatment p-value 0.8037
- acid pretreatment p-value 0.8940

**Sapwood samples** (Alpha 0.05)

- water pretreatment p-value 0.0149
- acid pretreatment p-value 0.0212

**Heartwood samples** (Alpha 0.05)

- water pretreatment p-value 0.3176
- acid pretreatment p-value 0.6805

## 4. DISCUSSION

The physical structure of some barks may play a role in nitrate absorption, but the main factor is believed to be bark chemistry. The chemical components of bark include lignin and polyphenols, polysaccharides, hydroxyl acid complexes and extractives (such as tannins). Bark is also high in inorganic ions (Na, K, Ca, Mg, Mn, P, and Zn) (Rowell, 2005). The specific chemical reactions which occur to remove nitrate from solution are not known, but cations and compounds are both available to which nitrate ions might chemically bond. POC and IC barks are effective at nitrate removal from aqueous solutions. This ability is enhanced through acidification of the bark for IC but not for POC bark. Both the POC and IC sequester the removed nitrate rather than releasing it back into the aqueous solution. The bark from these two tree species is not of commercial value. A system of bark filter units might be effective as a temporary solution to nitrate pollution from point sources, such as failing septic systems near the Hood Canal. They could also be placed periodically in ditches to lower nitrate levels in irrigation water caused by fertilizer run-off.

## 5. CONCLUSIONS

It appears that both Port-Orford and incense cedar barks are effective at nitrate removal from water solution. This ability is enhanced by acid pre-treatment for incense cedar bark and is not affected (or decreases slightly) for Port-Orford cedar bark. These two types of bark were collected within 3-4 months of use, while other bark samples were older. The bark chemistry could change as the cut wood ages and starts decomposition, possibly making nitrate removal less effective. But the common juniper bark was also freshly collected and proved ineffective at nitrate removal

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### Author

I have lived in Sequim, WA my entire life and have always had a fascination with natural systems, their ecology and chemistry. In my four years of high school I ran on the cross country and track teams, participated in community service projects with the International Order of the Rainbow for Girls, and was an active member of my school district's science club, serving as president for two years. In science club I learned to conduct independent research and compete successfully at the state, regional, national, and international levels with my research. This year I will be beginning my college career at The Evergreen State College in Olympia, WA, majoring in ecology and creative writing. I hope to give back to the science community by volunteering as a science mentor and science fair judge in my future years.

## 8. REFERENCES

'A Cheaper Way to Clean Water' Forest Products Laboratory *Newsline* Vol. 1 Issue 2 Spring 2002

Barett, J.M., Abramoff, P., Kumaran A.K. and Millington W.F. 'Biology' Prentice-Hall Pg 944-945 1986

Chasan D.J. 'Hood Canal: It's not always greener over the septic tank' Crosscut: News of the Great Nearby 09-23-2008

Nitrate/Nitrite Toxicity CDC: Agency for Toxic Substances and Disease Registry 1995 atsdr.cdc.gov/csem/nitrate

Nitrate Contamination in the Mid-Columbia Basin Ecology Publications Office July 2002 ecy.wa.gov/programs/wq/grndwtr

Rowell, R.M. Handbook of Wood Chemistry and Wood Composites CRC Press 2005 pg 35-73, 99-119, 303-347, 381-419

## 9. BIBLIOGRAPHY

Acid Mine Drainage Fact Sheet

Acid Mine Drainage www.fs.fed.us

Acid Mine Drainage-AMD www.scrip.pa-conservation

Environmental Impacts of Hardrock Mining in Eastern Washington University of Washington College of Forest Resources

Hood Canal www.en.wikipedia.org

Tannins www.ansci.cornell.edu

The Science of Acid Mine Drainage and Passive Treatment www.dep.state.pa.us

Upper Hood Canal Restoration Project Kitsap County Health District

Han, S., hur, N., Choi, B. and Min, S.H. 'Removal of Phosphorus using Chemically Modified Lignocellulosic materials' Land and Water Use Planning and Management Conference Spain 2003

Han, J.S., Min, S.H. and Kim, Y.K. 'Removal of Phosphorus using AMD-treated Lignocellulosic Material' Journal of Forest Products Vol 55 Issue 11 pg 48-53 2005

Henderson, R.W., Andrews, D.S., Lightsey, G.R. and Poonawala, N.A. 'Reduction of Mercury, Copper, Nickel, Cadmium and Zinc Levels in Solution by Competitive Adsorption onto peanut Hulls and Raw and Aged Bark' Bulletin of Environmental Contamination and Toxicology Vol. 17 No 3 pg355-359 1977

Shin, E.J., Lauve, A. Carey, M. Bukovsky, E., Ranville, J.F. Evans, R.J. and Herring, A.M. 'The development of bio-carbon adsorbents from Lodgepole Pine to remediate acid mine drainage in the Rocky Mountains' Biomass and Bioenergy Vol. 32 pg 267-276 2008

Takano, T., Maurakami, T., Kamitakahara, H. And Makatsubo, f. 'Formaldehyde adsorption by karmatsu (*Larix leptolepis*)bark' Journal of Wood Science Vol 54 pg 332-336 2008]

Vazquez, G., Gonzalez-Alvarez, J., Freire, M.S., Lopez-Lorenzo, M. and Antorrena, G. 'Removal of cadmium and mercury ions from aqueous solution by sorption on treated *Pinus pinaster* bark: kinetics and isotherms' Bioresource Technology Vol 82 pg 247-251 2002

Wan Ngah, W.S. and Hanafiah, M.A.K.M. 'Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: A review' Bioresource Technology Vol 99 pg 3935-3948 2008