Beneficial Reuse of Dredged Materials in Upland Environments

Nicholas Wes Haus

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W. Lee Daniels (chair)
Mathew Eick
Madeline Schreiber

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ABSTRACT

Sediments excavated from dredging operations are known as dredged materials. Beneficial reuse of dredged materials in confined utilization facilities (CUFs) is a new approach that has the potential to productively utilize large quantities of dredged materials. However, several factors can inhibit the use of dredged materials in CUFs. In this study, high levels of salts and polycyclic aromatic hydrocarbons (PAHs) were investigated. In the first part of this study, 176,000 m^3 of saline dredged materials was placed into a CUF. In less than 4 years, most of the dredged materials had developed horizonation and converted to Inceptisols. The formation of pedogenic Bg horizons in these soils occurred after a polygonal prism network had developed which partially disintegrated into a blocky structured, oxidized horizon with an abundance of redoximorphic features. During the study period, the soil chemistry of the weathering dredged materials shifted from Na-dominated to a Ca and Mg-dominated system, allowing plant invasion. In the second part of the study, a bench-scale greenhouse bioremediation experiment was conducted to test the effectiveness of biosolids, compost, and straw at enhancing PAH degradation. Initial concentrations of PAHs decreased significantly after 150 days using standard methods of extraction. However, at 327 days, the concentrations of many PAHs, especially those with higher molecular weights, had rebounded close to initial levels. This indicates that PAH bioremediation studies using organic matter additions and conducted using standard methods of extraction need to be carried out for longer periods of time or that extraction methods need to be improved.

DEDICATION

To my boys, Atticus and Deacon, and to their amazing mother Allison.

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CHAPTER I

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INTRODUCTION

Sedimentation of waterways is a natural process wherein suspended particulates are deposited in environments of decreasing energies. Anthropogenic changes to natural waterways (i.e. dam creation, levees, manmade channels) change the dynamics of fluvial environments, sometimes accelerating sedimentation which can limit the depth or close navigational channels. The excavation of materials from subaqueous environments has been carried out for centuries by a process known as dredging; the excavated sediment removed by dredging operations is known as dredged materials.

The dredging process is vital to our nation's shipping, recreational boating, defense, ecosystem preservation and flood prevention, and has the following three stages: dredge planning, dredging operations, and management of the removed dredged materials. During the planning stage, the economic and technical feasibility of dredging are weighed against the environmental and societal impacts of dredging alternatives or not dredging at all. The dredging operation is the physical removal of sediments for new construction, maintenance or restoration of navigable channels. The management of dredged materials is concerned with the fate of the removed sediments and any associated contaminants and will be the primary focus of this chapter.

The responsibility for maintaining and regulating the dredging process in our nation's ~40,000 kilometers of navigation channels and 400 major and minor ports falls upon the United States Army Corps of Engineers (USACE) and Environmental Protection Agency (EPA). The dredged material resulting from maintenance dredging alone can exceed 230 million m^3 annually in the US (Brandon & Price, 2007).

Three main pathways exist for managing dredged materials: (1) open-water unconfined disposal, (2) placement into a confined disposal facility (CDF) or (3) beneficial reuse. Dredged materials in large part represent eroded and "lost" topsoil within the watershed and therefore have the potential to be a valuable natural resource. The realization of dredged material as a potential resource has added increased emphasis to beneficially reusing dredged materials for the following uses: (1) habitat restoration and development, (2) beach nourishment, (3) parks and recreation, (4) agriculture/forestry/ horticulture/aquaculture, (5) surface mine reclamation/solid waste management, (6) construction/industrial development, and (7) other multi-purpose activities (EPA & USACE, 2007). The USACE provides a detailed introduction to beneficial reuse of dredged materials at http://el.erdc.usace.army.mil/dots/budm/budm.cfm.

Due to a variety of economic, technical, and social factors, the majority of dredged material is being disposed of in the open ocean or in confined disposal facilities. Perhaps most importantly, beneficial reuse of dredged materials is commonly inhibited by: (1) high levels of soluble salts and (2) high levels of organic contamination, which will be the topics of chapters 2 and 3, respectively. Dredging operations are often conducted near coastal urban settings (see Figure 2- 1) thus many dredged materials are saline or contaminated. The research described herein seeks to aid in increasing the beneficial reuse of dredged materials with high levels of organic contamination (specifically polycyclic aromatic hydrocarbons – PAHs) and soluble salts.

Framework for Determining Dredged Material Management Alternatives

Dredging projects are regulated by the National Environmental Policy Act (NEPA), the

Clean Water Act (CWA), and the Marine Protection, Research, and Sanctuaries Act (MPRSA). The EPA and the USACE have the shared responsibility of enforcing the regulations implicit in these acts. Dredged materials disposed of in the open-ocean are regulated by the MPRSA, whereas dredged materials discharged into US waters are regulated by the CWA. The EPA authorizes the use of a particular disposal under Section 404(c) of the CWA. The CWA, and to a lesser extent the NEPA, both regulate the placement and management of dredged materials into confined disposal facilities (CDFs). Beneficial reuse of dredged materials for unconfined alternatives such as wetland restoration also falls under the CWA (all of the above mentioned alternatives will be covered in more detail in the following sections).

All three of these acts require that all reasonable alternatives be investigated. The alternative that best fits the environmental and technical feasibilities with the lowest economic cost is generally chosen as the appropriate dredged material disposal/utilization alternative (EPA & USACE, 2004). A rigorous dredged material alternative selection process is outlined in Figure 1- 1, and follows the following pathway: evaluation of the dredging project → identification of all alternatives → screening of alternatives → assess feasibility of alternatives → selection of the most appropriate alternative. The first phase of the selection process is data collection for the dredging operation including basic information such as location, extent, and volume of dredging, and characteristics of the dredged materials. The second phase is designed to identify all possible alternatives for managing the resulting dredged materials from the dredging operations. The final phases are designed to limit the number of alternatives according to their relative impacts and feasibilities until only a small selection of alternatives remain. The flow chart in Figure 1- 1 outlines the entire decision-making process. The screening, assessment, elimination and selection of alternatives is primarily based on the evaluation of the physical,

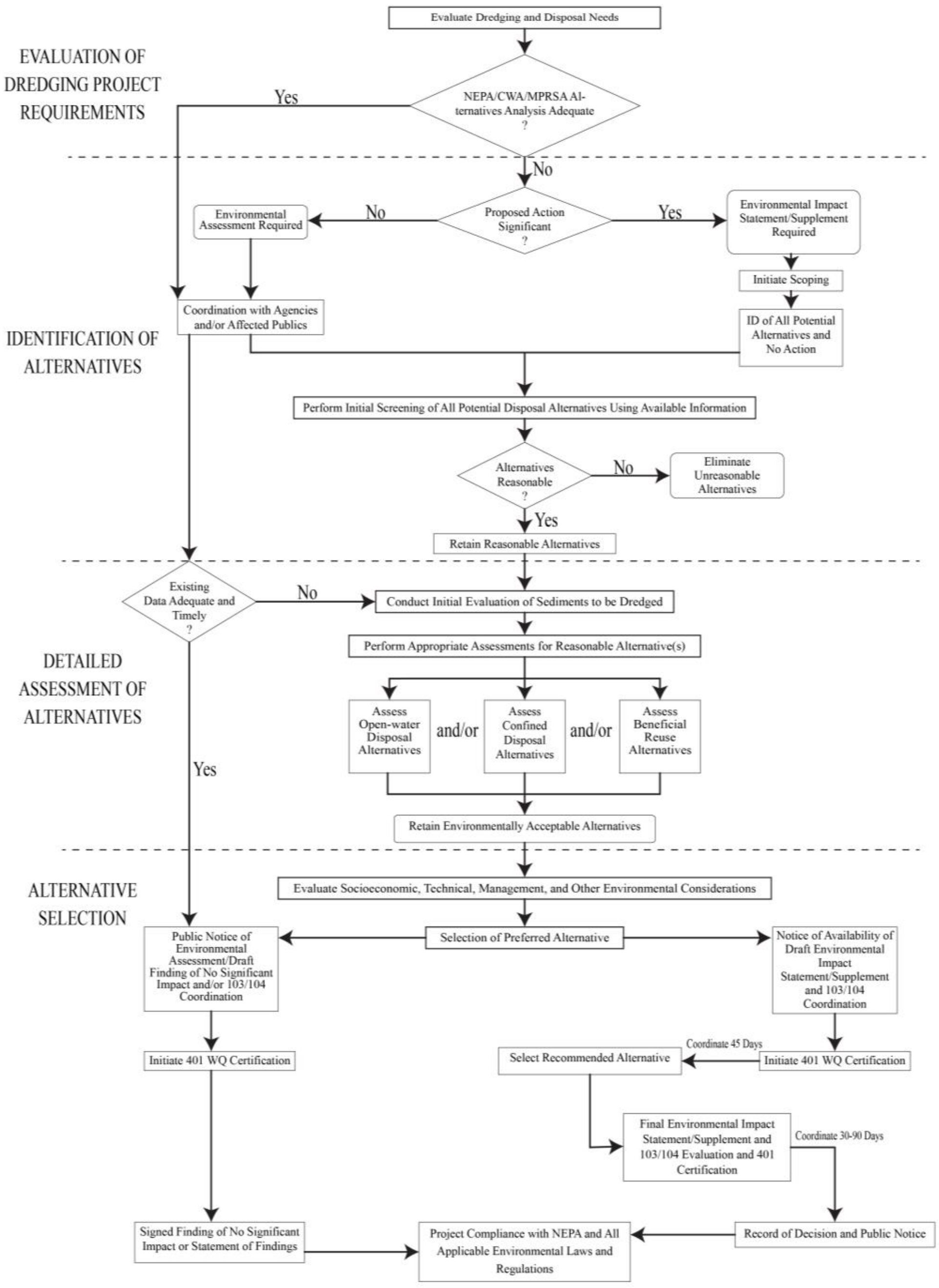

Figure 1- 1. EPA and USACE flowchart for selection of the appropriate dredged materials alternative. Modified from EPA & USACE (2004).

chemical, and contaminant properties of the dredged material; the economic, social, and environmental implications; and the technical feasibilities of the alternatives (EPA & USACE, 2004). The guidelines for testing the adverse effects of dredged materials on the environment can be found in the MPRSA Ocean Testing Manual (EPA & USACE, 1991), the CWA Inland Testing Manual (EPA & USACE, 1998) and in the Upland Testing Manual (USACE, 2003). The list of target detection limits, sampling methodologies, and sample holding times for the sediment samples is derived from QA/QC Guidance for Sampling and Analysis of Sediments, Water, and Tissues for Dredged Material Evaluations (EPA & USACE, 1995).

DREDGED MATERIAL ALTERNATIVES

As mentioned previously, dredged materials are: disposed in the open-water, confined in disposal facilities, or beneficially reused towards a productive end. Despite federal, state, and local agencies advocating for increased beneficial reuse of dredged materials, millions of cubic meters of potentially valuable dredged materials are disposed of by open-water dumping or confinement each year (Figure 1- 2). In fact, nearly 70 percent of dredged materials are currently disposed of by dumping into open-water environments or into confined disposal facilities (EPA & USACE, 2004).

A more detailed description of open-water disposal, confined disposal facilities, and beneficial reuse follows.

Open-water Disposal

Open water disposal is the placement of dredged materials onto the existing floor of inland, coastal, and oceanic water bodies. Thirty percent of all dredged materials are disposed in oceanic waters making this the most common management alternative (EPA & USACE, 2004). The primary concern with open-water disposal is adverse biological impacts (e.g. fish habitat and spawning) and impacts to other valuable economic resources (e.g. historical

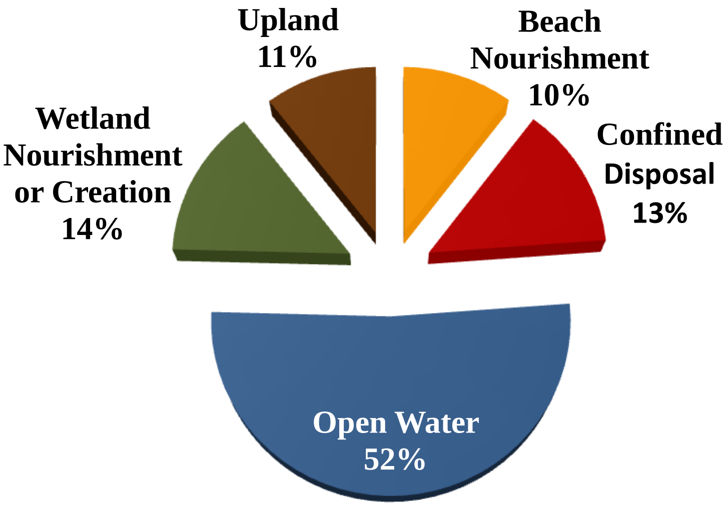

Figure 1- 2. Pie chart showing the major dredged material placement alternatives from 1997 to 2010.

artifacts, recreational activities etc.) at the disposal site. The deposition of large quantities of dredged materials into water bodies often causes irreversible damage and/or changes to many benthic communities. To ensure damage caused by open-water disposal is minimized, proper site selection is vital, including assessment of the nearby locations that could be adversely impacted by materials moving off the disposal site. In addition, the site must have the capacity to contain the specified volume of dredged material. If a site is not eliminated because of potentially adverse physical impact or inadequate site capacity, the next step is to evaluate how any contaminants present in the dredged material might impact the site and surrounding area. Sites located off the continental shelf, which have been used in the past, are generally preferred because physical impacts are reduced. Secondly, more investigations are required before dredged material can be disposed of in sites which have not been used before, particularly ones that exist closer to important estuarine environments.

Confined Disposal

Confined disposal facilities (CDFs) are diked containment facilities in upland or nearshore environments. CDFs are often filled via pipeline, and thus the initial dredged materials have very high water contents. Dewatering, consolidation and desiccation of the dredged materials allow for subsequent dredged material placement until the confined facility eventually reaches capacity. The assessment of a CDF as a dredged material management alternative is similar to, but more complex, than the assessment for open-water disposal. Because CDFs require upland or nearshore areas for permanent use and eventual abandonment, there are extra considerations (e.g. site access, real estate values, and subsurface characteristics) which need to be addressed prior to construction. The assessment of the physical impacts and site capacity of a CDF is challenging because of the potential for release of leachate, effluent and runoff from the site to the surrounding environment.

Beneficial Reuse

Beneficial reuse of dredged materials means using the dredged materials as a resource in productive ways (USACE, 2006). Most commonly, dredged materials are beneficially reused in the following ways: agriculture, habitat restoration or enhancement, beach nourishment, aquaculture, parks and recreation, forestry, horticulture, shoreline stabilization, construction fill, mined-lands reclamation, and use as an industrial product (EPA & USACE, 2007).

Another way to beneficially reuse dredged material is through confined utilization facilities (CUFs). CUFs are diked containment facilities similar to CDFs but they differ in that the goal of CUFs is the productive use of the dredged material, usually for agricultural purposes. The use of confined facilities to manage dredged materials specifically for agricultural uses is not a novel concept, although published and peer-reviewed information on the practice and management of CUFs is lacking.

When selecting the most appropriate beneficial reuse of dredged material, all potential local and productive uses are identified and considered. The selection process considers: (1) the physical and chemical suitability of the dredged material for reuse, (2) logistical factors involved in the transport and management of the dredged material, and (3) the environmental impact of the dredged material. Specific factors of concern include: grain size, mineral vs. organic matter levels, contaminant levels, salinity, transport distance, site accessibility, site capacity, and real estate considerations (EPA & USACE, 2004).

The mode of dredging can also have a dramatic effect on the beneficial reuse of dredged material. The two general means of dredging are hydraulic and mechanical. During hydraulic dredging, loose sediments are suctioned off the water body floor as sediment slurry. Mechanical dredging, on the other hand, can remove both loose and dense sediments at higher sediment-to-water contents. Post-dredging transportation and management alternatives also affect dredged material properties. Several modes of transportation exist to move dredged material to a site for disposal or for beneficial reuse, including pipeline, hopper barge, barge and truck. In many situations, especially in upland placement, a combination of these modes of transport is used. The dredging technique and post-dredging method of transportation have the greatest effect on the water content of the dredged materials.

CONFINED UTILIZATION FACILITIES

Dredged material is, by and large, eroded topsoil from agricultural settings. Unless the dredged material has obtained some negative chemical property through changes in its depositional environment (e.g. accumulation of sulfides or organic contaminants), most of dredged materials may still retain value as a natural soil resource. CUFs therefore have great potential to increase the amount of dredged material that is beneficially reused while also mitigating historic soil erosion. However, detailed information regarding the planning stages, dredged material acceptance criteria, and CUF management is lacking. The following sections introduce proposed criteria to screen dredged material before beneficial reuse, describe soil formation in CUFs, and highlight a working CUF in eastern Virginia.

Dredged Material Criteria for CUFs

Based on extensive testing of both fresh and saltwater dredged materials Daniels et al. (2009) have proposed a dredged material screening criterion to the Virginia Department of Environmental Quality. The proposal is based on EPA sediment screening levels (EPA, 2011), New Jersey dredge material management criteria (New Jersey DEP, 1997), and the authors' experience working with dredged material. A complete listing of the proposed exclusion and clean fill acceptance levels can be found in Table A- 1 in Appendix A. The user's working version of the document currently exists as an Excel spreadsheet with columns for data entry along with user instructions.

The acid forming (from sulfides) potential of the dredged material was of particular importance when developing the table and criteria. Of the 15 dredged materials evaluated by Daniels et al. (2009), over half were excluded for use in CUFs because of their excessive acid forming potential. Soil iron oxides and free sulfates undergo rapid conversion to iron sulfides in anaerobic saline environments. After excavation and exposure to an aerobic environment, the sulfides are re-oxidized, creating acid sulfate conditions if insufficient carbonates exist to neutralize the acidity generated. A useful discussion of the formation, management, and consequences of acid sulfate dredged materials can be found in Fanning et al. (2010) and Fanning & Fanning (1989).

Additional factors that should be considered in determining whether a material is suitable for reuse are the concentrations of fine grained material (silt+clay) and organic carbon. Materials with high silt+clay and/or high total organic carbon percentages are not good candidates for beneficial reuse. Silt+clay percentages exceeding values of 70% can inhibit management practices such as tillage and high total organic carbon levels can inhibit dewatering negatively affect material handling.

Soil Conversion in CUFs

Knowledge of the soil forming processes that occur in CUFs is limited. Although it is likely that many locations exist where dredged materials have been impounded in upland environments, and have since been converted to agricultural soils, few soil studies have been conducted upon these materials (Darmody & Marlin, 2002; Demas et al., 2004; Daniels et al., 2007). A freshwater CUF will be discussed at the end of this section.

The following is a brief discussion of a close analogue to soil development in CUFs which occurs in Dutch “polders”. A polder is coastal lowland at or below sea level that has been isolated from the sea by a series of dikes (Siderius & de Bakker, 2003). Polders are comprised of alluvial marine sediments that usually exhibit a classic “fining upwards” sequence commonly observed in floodplain materials. Soil formation in polders is dominated by the process known as “ripening”. Ripening is the action of dewatering and desiccation where sediments consolidate and form a very coarse prismatic structure (provided textures are finer than coarse loamy) that eventually breaks down into smaller substructural units (de Bakker, 1971). The typical Dutch polder has an ochric epipedon, with between 2-4 percent organic matter and a subsurface horizon that is gleyed with redoximorphic concentrations and depletions (de Bakker, 1971). The horizon sequence one might expect to see is: A-Bg1-Bg2-Cg. Most polder soils will be classified by Soil Taxonomy (Soil Survey Staff, 2010) as Aquic due to wet conditions within 50 cm of the surface (wet horizons are usually identified by the suffix symbol "g", which will be described in more detail in the following section). The classification of aquic soils at the order level will be largely dependent on the original parent material. Aquic soils with textures coarser than loamy very fine sand or with fine stratifications (5mm or less thick) in over 50% of the soil profile are classified as Aquents. Soils with finer than loamy very fine sands and without fine stratifications, or where ripening and/or biological activity has destroyed over 50% of fine stratifications are classified as Aquepts (de Bakker, 1971).

Soil formation in freshwater, saline, and saline-sulfidic dredged material CUFs is similar to soil formation in polders. In all reported cases, water-logged sediments ripened and underwent very similar stages of development. For example, saline-sulfidic dredge materials described by Fanning & Fanning, (1989) developed slightly differently because of the large amounts of sulfides in the dredged materials, which resulted in the creation of a sulfuric horizon, although the ripening process still occurred. A generalized sequence of soil formation in dredged materials in CUFs would be as follows: (1) dewatering starts to occur almost immediately after deposition, (2) very coarse prisms begin to form at the surface in a polygonal network and typically extend slightly below the depth of standing water, (3) oxidation starts to occur in large prism cracks, (4) prisms begin to break up into smaller structural units that slough off into the cracks, (5) fluctuations in the depth to water cause the formation of redoximorphic iron concentrations and iron depletions, (6) plants invade the new soils and accelerate the other processes by increasing transpiration, and (7) a Bg horizon forms as the prisms disintegrate.

Soil Classification

The following is a short summary of the most likely soil features that occur throughout soil formation from dredged material in CUFs.

Initially, waterlogged dredged materials have no structure and are usually greyish black to black in color and would be identified using the "^Cg" symbol. The lack of soil structure and other pedogenic features is indicated by the master horizon "C", while the dark, low chroma colors and presence of saturated conditions is indicated by the suffix symbol "g", and the caret symbol is used to indicate human transported materials. As soil development proceeds and the materials ripen to forms prisms, blocky structures and redoximorphic features, a "^Bg" horizon develops in place of the "^Cg" horizon. The "B" horizon indicates the formation of soil structure and that the horizon color is now higher in chroma, lower in value, and/or redder in hue. The "g" suffix is still used to indicate that the horizon is dominated by wet materials that have a chroma of less than 2. If the materials oxidized sufficiently to give the majority of the horizon a chroma greater than 2, and saturated conditions ceased to prevail, than a suffix "w" would replace the "g".

At some point during the ripening process, many soils would also develop a "cambic" horizon, shifting classification from Entisols to Inceptisols. Cambics with and without aquic conditions can occur during conversion of dredged materials to soils. Generally, a cambic horizon is a horizon altered (> 50% by volume) by pedogenic processes that is greater than 15 cm thick and has a texture finer than loamy very fine sand. Additionally, in aquic conditions, cambic horizons require : (1) aquic conditions exist within 50 cm of the surface, (2) fine stratifications (less than 5mm) from the dredged material deposition are obliterated in over half the horizon, (3) the horizon color no longer changes after exposure to air, and (4) the matrix horizon color either has: (a) a value ≤ 3 with a chroma of 0; or (b) a value ≥ 4 with a chroma ≤ 1; or (c) a chroma ≤ 2 with redoximorphic concentrations present (Soil Survey Staff, 2010).

A cambic horizon without aquic conditions within 50 cm of the surface, which would likely occur subsequent to one with aquic conditions, must also have lost all fine stratifications and would need to have a higher value of chroma or a redder hue than the unaltered dredged material underlying it (Soil Survey Staff, 2010).

Freshwater Dredged Material CUF

The successful conversion of impounded, freshwater dredge material into productive agricultural soil was demonstrated at Weanack Land LLP on the James River in Charles City County, Virginia (Daniels et al., 2007). Between 2000 and 2005, approximately 450,000 m^3 of silty, uncontaminated, freshwater dredge materials were removed during the construction of the Woodrow Wilson Bridge replacement span on the Potomac River near Washington DC. Over three meters of dredge materials were impounded in a 20 ha CUF with 3-6 m dikes constructed around the perimeter. One year after placement of the main body of dredged material, dewatering and ripening had produced a polygonal prism network which extended to a depth of 50 cm with saturated conditions at 25 cm. Soil pits excavated after 2 years of soil development were described as ^Ap-^AC-^Cg1-^Cg2 and the ^Ap horizons had a blocky structure. An agricultural experiment was installed on the CUF and planted with winter wheat (*Triticum aestivum* (L.)) in the fall of 2001 and corn (*Zea mays* (L.)) in the spring of 2002. After only a single year of dewatering wheat and corn yields surpassed the county average and have continued to do so almost every year.

CONCLUSION

Dredging is a vital process to our nation's transportation network and thus management of dredged materials will continue to be a major priority. The treatment of valuable dredged materials as a presumed contaminated waste stream has increasingly come under scrutiny by local, regional, and federal agencies. Beneficial reuse of materials is now encouraged as opposed to open-water disposal or disposal in confined facilities. Confined utilization facilities where dredged materials are converted into a useful soil resource have the potential to increase the amount of dredged materials that are beneficially reused.

Investigation of soil formation in CUFs reveals an analogous process to Dutch "polders". Soil development in CUFs occurs by a process known as ripening which causes rapid soil formation by dewatering and desiccation of waterlogged sediments. After only 2 years of soil conversion, freshwater dredged materials placed into a CUF in Virginia have demonstrated agricultural yields that have outperformed county averages, indicating that beneficially reusing dredged materials in CUFs could become a major management alternative in the future.

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CHAPTER II

Beneficial Reuse of Saline Dredged Materials in a Confined Utilization Facility in Eastern Virginia

ABSTRACT

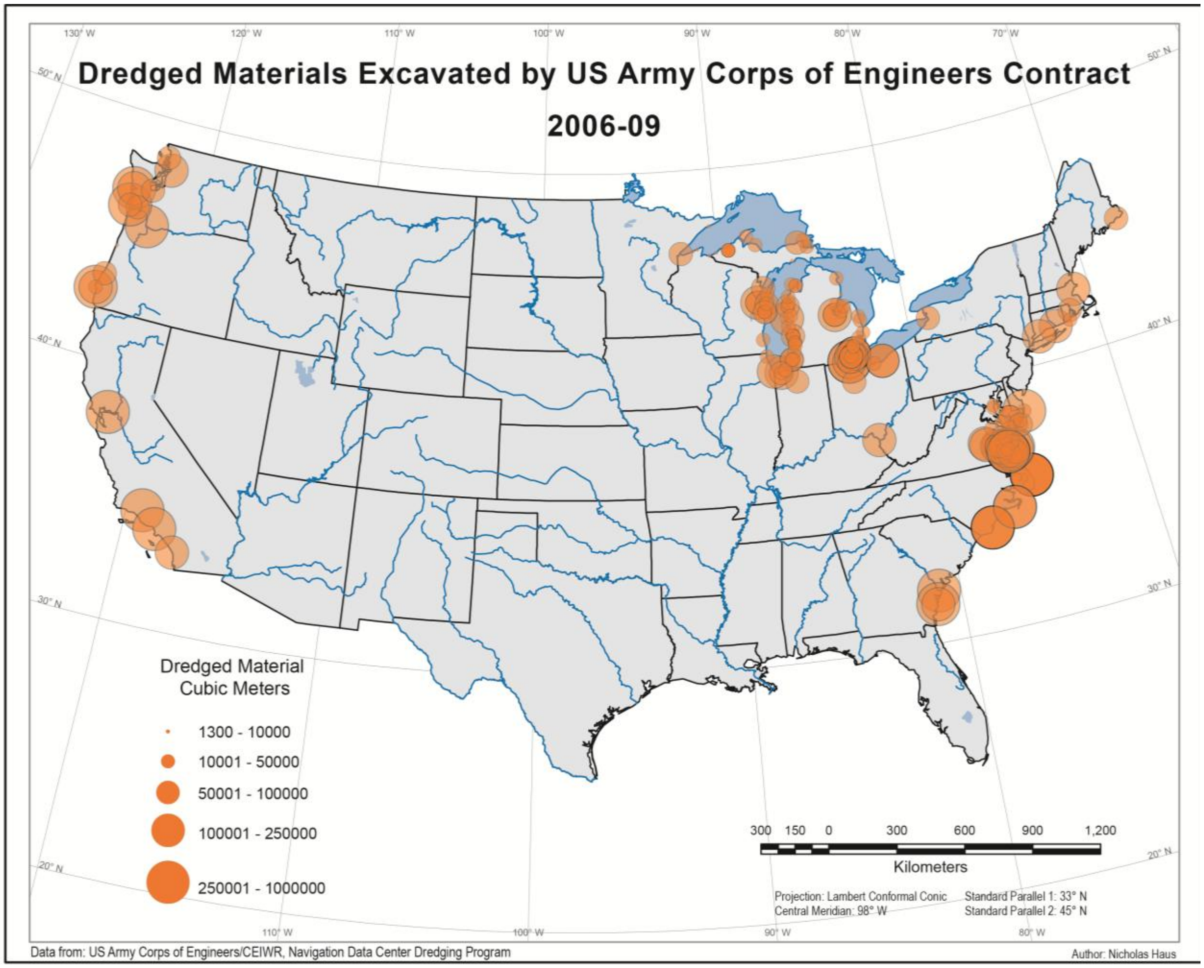
This study assessed the pedogenesis, salt redistribution and environmental impacts resulting from the placement of 176,000 m^3 of saline dredged materials into a confined utilization facility (CUF) at the Weanack Land facility in Eastern Virginia. In less than four years after placement in the CUF, the saline dredged materials had ripened sufficiently to form “wet” cambic horizons and classify as Halaquepts by Soil Taxonomy. At the subgroup level the soils were classified as Typic Halaquepts unless they contained lenses of sandy materials, in which case they were classified as Aeric Halaquepts. Large reductions in salinity (> 50% initial EC) were evident in all horizons including unaltered Cg horizons, although most of the soils would still be classified as saline-sodic for agricultural purposes. Cation redistributions on the exchange complex with depth over time suggest the soils underwent rapid pedogenesis. Large salt redistributions and reductions in the CUF soils and ponded surface waters resulted in only a minor increase of soluble chloride in one down gradient groundwater well. Preliminary findings from this study suggest that beneficially reusing saline dredged materials in CUFs could be a safe and practical method of recycling large quantities of saline sediment brought the surface annually during maintenance dredging assuming time is allowed for physicochemical ripening and that salts leaching to groundwater can be adequately contained.

INTRODUCTION

Dredging operations in the US waterways are vital to our nation's commerce, recreation and construction industries. The United States Army Corps of Engineers (USACE) is estimated to be responsible for over 40,000 kilometers of navigation channels and over 400 major and minor ports that require annual maintenance dredging exceeding 230 million m^3 of dredged material (OCRM &CPD, 2000). After excavation of a dredged material, the sediment is most often routed into one of three pathways: (1) ocean dumping, (2) confined disposal facility (CDF) or (3) beneficial reuse. Within the last few decades, regulators and private organizations have emphasized reducing the quantity of dredged material either placed in CDFs or dumped into the open ocean in favor of finding a beneficial reuse for suitable sediments. Beneficial reuse of dredged material can include any of the following: (1) habitat restoration and development, (2) beach nourishment, (3) parks and recreation, (4) agriculture/forestry/horticulture/aquaculture, (5) surface mine reclamation/solid waste management, (6) construction/industrial development or (7) other multi-purpose activities (EPA & USACE, 2007). The decision to dump, dispose or reuse is determined by both the chemical and physical properties of the dredged materials and the location, nature and cost of potential beneficial reuse projects.

At present, no national criteria exist to assess the potential of a dredged material for beneficial reuse. However, some states such as New York and New Jersey are seeking to develop legislation that would evaluate, identify and regulate potential reuses based on dredged material characteristics (Palermo & Olin-Estes, 2001). Quantitative information of specific dredged material limitations encountered in the US is not available and at present, the USACE only states that characteristics to be considered are: grain size, level of contamination, water content, organic content, acidity, nutrient levels, engineering properties and salinity.

The majority of US ports are located in marine environments which, periodically, require maintenance dredging (Figure 2- 1). Therefore, salinity will commonly pose problems to projects attempting to reuse materials from these areas. According to the USACE Beneficial Use Planning Manual (EPA & USACE, 2007), dredged materials consist of silt and soft clays which, if from a freshwater source, are routinely used for agriculture, forestry and horticulture projects. Specifically, USACE states that freshwater silts and soft clay dredged materials are often “incorporated” or “applied” to marginal soils or farmlands. Dredged materials from marine sources have traditionally been excluded from agricultural reuse because of the need for



Data from: US Army Corps of Engineers/CEIWR, Navigation Data Center Dredging Program

Author: Nicholas Haus

Figure 2- 1. Proportional symbol map showing the quantity and location of dredging projects between 2006 and 2009 in the US.

desalinization. However, the conversion of saline dredged materials to soils in Dutch polders and other worldwide locales have demonstrated that not only could saline dredged materials be beneficially reused for agricultural purposes, if properly managed, they could produce some of our most productive lands (Hassink et al., 1991; de Bakker, 1971).

The quantity of dredged materials that can be used for agricultural incorporation or application is often limited. Confined upland facilities (CUFs) are capable of accepting very large quantities of dredged materials and potentially negate the need to dispose of otherwise favorable soil materials. The creation of CUFs could bring large quantities of saline dredged materials into upland freshwater environments typical of most agriculture areas. To date, knowledge regarding the impacts of placing large quantities of saline sediments into non-saline upland environments is lacking. The aim of this study was to develop an understanding of how a marine dredged material placed into a CUF affect the surrounding freshwater environment and to document pedogenic processes as the material was converted to an agricultural soil. Specific objectives were to: (1) determine the soluble and exchangeable ion flux, specifically for the major cations Ca^{2+}, Mg^{2+}, K^+, Na^+, and the anions Cl^- and SO_4^{2-}; (2) observe and document pedogenic changes over time, especially during the critical early drying (ripening) stages of development; and (3) fully classify the resultant soils according to Soil Taxonomy (Soil Survey Staff, 2010) through detailed description and sampling of profiles from soil pits distributed across the CUF.

EXPERIMENTAL SITE

The study was located at Shirley Plantation on the James River near Charles City, Virginia, approximately 39 kilometers southeast of Richmond, Virginia. Shirley Plantation is Virginia's oldest operating plantation, dating back to 1613 and has been family managed for 11 generations. In addition to the historic house grounds, the plantation operates two CUFs, a bioremediation pilot study and a fully functioning port (Figure 2- 2). The main activities of the plantation today are tourism while other agricultural and alternative land use activities in the surrounding ~ 250 ha property are managed by Weanack Land LLP. Through 2011, beneficial reuse activities were regulated by the Virginia Department of Environmental Quality (DEQ) via a Virginia Pollution Abatement (VPA) permit which necessitates monitoring of inbound sediment quality, ground and surface water, overall post-placement soil quality and vegetation response, hydrogeology and any related beneficial reuse studies. Since 2000, the monitoring of dredge utilization and other related research work has been conducted by Virginia Tech and Old Dominion University.

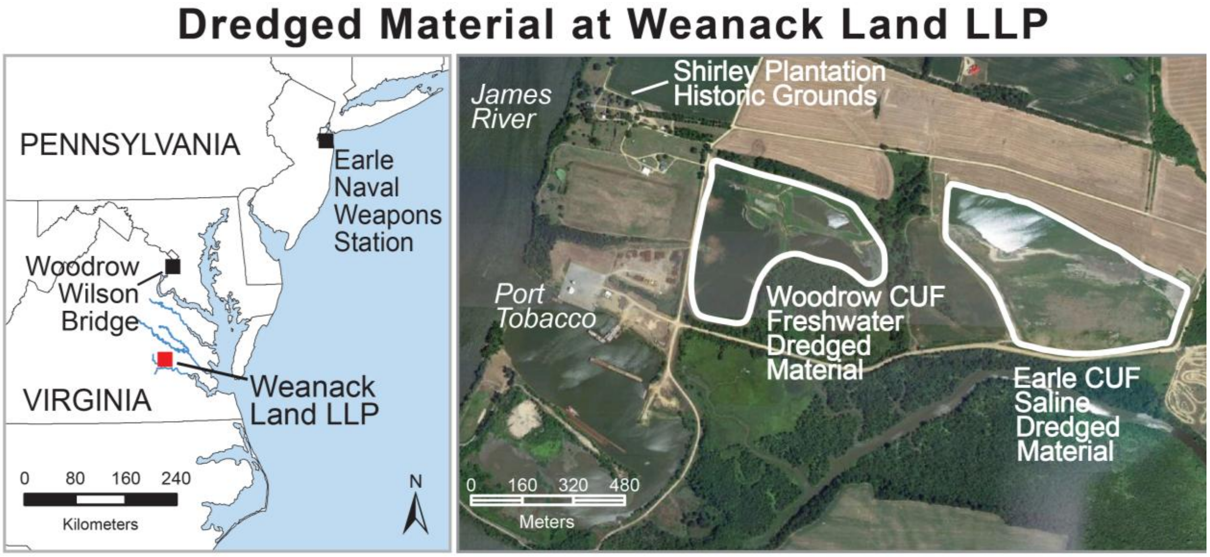


Figure 2- 2. Location of Weanack and the source of dredged material that occupies its two CUFs.

The first of two CUFs installed at Weanack were partially filled between 2000 and 2005 with approximately 450,000 m^3 of silty, uncontaminated, freshwater dredged materials from the construction of a replacement span for Woodrow Wilson Bridge on the Potomac River just south of Washington DC. The land occupied by this CUF had previously undergone approximately 50 years of sand and gravel mining, which ended in the early 1990's. After mining but prior to use as a CUF, the land was partially reclaimed for agricultural use.

In 2004, a second CUF, the focus of this study, was created in preparation for the placement of saline dredged materials from the Earle Naval Weapons Stations (ENWS) located on the New Jersey shoreline south of New York City. Thirty five deep boreholes were drilled and logged prior to the construction of the CUF (Daniels et al., 2007). The boreholes indicate that up to 5 m of fine textured (silty-clays) materials overlie beds of stratified gravels, sands, and organic-rich mud deposits which contain ancient, upright bald cypress (*Taxodium distichum* (L.)) stumps from the mid to late Pleistocene epoch (Figure 2- 3). The stratified sands and gravels act as the local aquifer, which is 2 to 10 m thick. The aquifer is very complex with several mud and ironstone deposits that serve as local aquitards. The fine textured silty-clays were the native soil materials which had suffered serious erosion and soil exhaustion from intensive agricultural use. The soils are the Yeopoim and Newflat series that classify as Hapludults and Endoaqults, respectively. The CUF was created by pushing the surface 25 to 50 cm of fine textured soil materials into approximately 2 to 5 m high berms on three sides of the CUF perimeter. The higher clay Bt and Btg horizon materials were then intentionally smeared and compacted to form a limited permeability zone under the emplaced dredged sediments. Related research work nearby indicated that the K_{sat} of these manipulated subsoils was 10^{-6} to 10^{-7} cm sec^{-1} (Tracey et al., 2008). On the northern side of the CUF, a natural escarpment from an older Coastal Plain

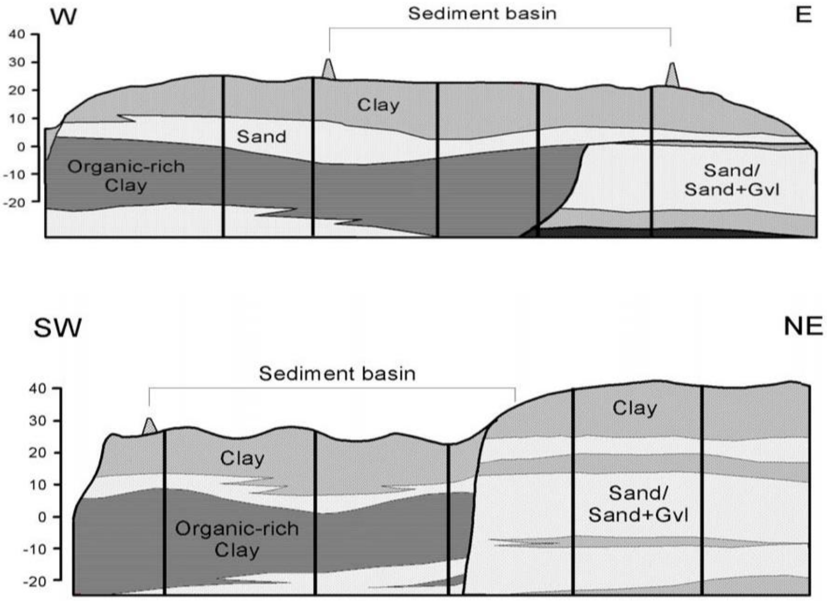


Figure 2- 3. Cross sections showing the Pleistocene formations that underlie the ENWS CUF at Weanack. Small pyramids represents manmade berms. Vertical axis is depth in meters. A natural escarpment is used as containment on the northern side of the CUF (Daniels & Whittecar, 2006).

terrace was partially utilized for containment. The majority of the CUF was contained within the concave floor of a first order drainage head that was impounded by placement of a 2 to 5 m high earthen dam across its outlet to the west. Due to lack of hydric soils and its history of agricultural use, however, this area was not a jurisdictional wetland. The CUF was designed to mimic the height of the upper stream terrace so that upon filling of the CUF, the land would appear as a natural extension of this terrace.

The first of the saline dredged materials from ENWS were hydraulically discharged into the CUF in August 2005, and placement largely continued hydraulically, and to a minor extent by local truck haul (for coarse debris), until January 2006. In total, the Earle maintenance dredging relocated almost 176,000 m^3 of saline dredged materials to Weanack. During the course of depositing the dredged material an artificial delta (Figure 2- 4) with a sandy, shell rich cap was created on the southern side of the CUF. The coarse textured cap resulted as dredging

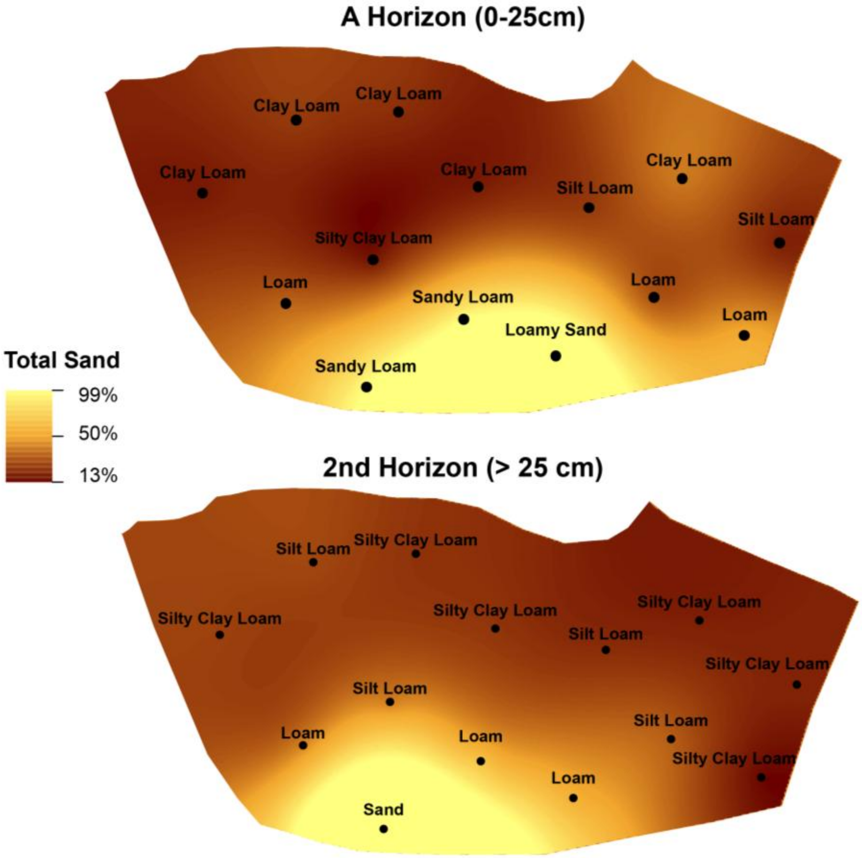


Figure 2- 4. Sand distribution in the surface and second horizon (dominantly ^Ap & ^Bg horizons, respectively) of the CUF. The hydraulic discharge of dredged materials caused coarse particles to settle proximal to the discharge points.

excavations approached the original seabed that was composed of primarily shell-rich sands with some gravel. Since these sediments were the last to be dredged, they were also the last to be deposited into the CUF. The hydraulic discharge of the sediments from south to north resulted in the deltaic shape of the sediments as the coarse textured particles preferentially settled out near the discharge pipe while the finer particles travelled to the other side of the CUF.

The toe of the artificial delta ends or thins to less than one meter along the natural escarpment to the north. Within the lower reach of the former natural drainage way, a ponded region quickly developed with waters with typical pH values around 9.0 and EC readings over 11 dS m^{-1}; values representative of the estuarine sediment environment from which the dredged material originated (Daniels and Whittecar, 2006).

METHODS AND MATERIALS

Composite sediment samples were collected from every 23,000 m^3 during dredging by the contractor at ENWS operations. Analyses were conducted by Microbac Labs® and Virginia Tech from splits of the composite samples. Analytes tested using EPA's Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (EPA, 2008) were total digestible metals (methods 6010B, 6020 and 7471A), sulfate (9038), pH (9045D), pesticides and polychlorinated biphenyls (PCBs) (8081B and 8082A) and polynuclear aromatic hydrocarbons (PAH's) (8310); those by the EPA's Clean Water Act Analytical Methods (EPA, 2010) were total Kjeldahl nitrogen (TKN) (351.3), total organic carbon (TOC) (29 3.5.2), and chlorine (325.3). The Standard Methods for the Examination of Wastewater (American Public Health Association et al, 2006) was used to analyze moisture and total solids (method 18 2540G) and ortho-phosphate (4500PE). Virginia Tech received 6 splits from every 23,000 cubic meter composite for analysis of calcium carbonate equivalence (CCE) and potential peroxide acidity (PPA). CCE was tested using a modified method of Sobek et al. (1978) and PPA by a modified method of Barnhisel & Harrison (1976).

The soils formed in the CUF dredged materials were investigated in November of 2008 and September of 2009 by a bucket auger. Soil investigations occurred at 34 regular spaced points (Figure 2- 5) on the CUF. Coordinates and elevations were recorded with a Trimble® Differential Global Positioning System (DGPS). All samples, including 3 archived composite samples, were air dried and passed through a 2-mm sieve.

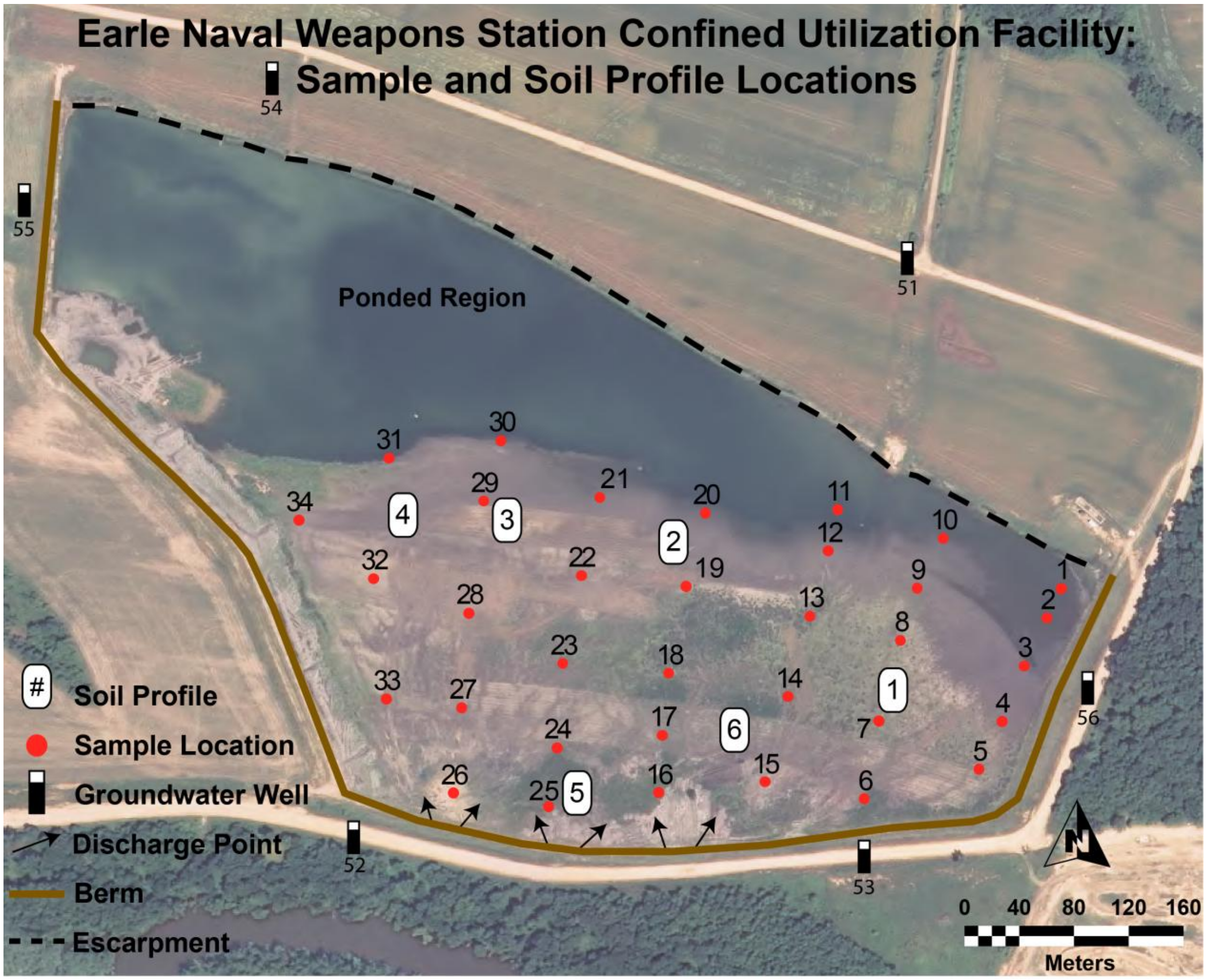


Figure 2- 5. Aerial image of the ENWS CUF showing the locations of the 34 sample points (henceforth referred to by their corresponding Arabic numeral), 6 soil pits (henceforth referred to as SP1-SP6) and 6 groundwater wells.

The following analyses were conducted on an aqueous soil extract removed from a saturated soil paste according to Soil Survey Laboratory Methods Manual (SSLMM)-4F2 (Soil Survey Staff, 1996): saturation percentage determination (SSLMM-4F2a1), electrical conductivity (EC) (SSLMM-4F2c), saturated paste pH (SSLMM-4C1a1a2), water-soluble Ca^{2+}, Mg^{2+}, K^+ & Na^+ (SSLMM-4F2c1a1-4) and water-soluble Cl^- & SO_4^{2-} (SSLMM-4F2c1b1a1-8). Determination of water-soluble Ca^{2+}, Mg^{2+}, K^+ Na^+ & SO_4^{2-} (as total S) in the aqueous soil extracts were performed on a Thermo Elemental ICAP 61E (Inductively Coupled Argon Plasma

Atomic Emission Simultaneous Spectrometer) at the Virginia Tech Soil Testing Laboratory. Chloride was determined by coulometric titration using a Labconco® Digital Chloridometer (Labconco, 2003). The sodium adsorption ratio (SAR) was also calculated based on the following relationship (SSLMM-4F3b):

$$SAR = \frac{[Na^{+}]}{\sqrt{\frac{[Ca^{2+}] + [Mg^{2+}]}{2}}}$$

where: $[Na^{+}]$, $[Ca^{2+}]$ & $[Mg^{2+}]$ = water-soluble concentrations in the saturated paste aqueous extracts ($\text{mmole}_{(\text{charge})}$ L^{-1}).

Exchangeable cations and cation exchange capacity (CEC) were approximated according to SSLMM method 4F3a2. In the presence of soluble salts, but in the absence of high amounts of carbonates or gypsum and where the electrical conductivity does not greatly exceed 20 dS m^{-1}, the exchangeable concentrations of cations may be approximated by:

Exchangeable M^{+} *= (total extractable* M^{+} *- soluble* M^{+}*)* saturation %*

where: Total extractable M^{+} (cmol kg^{-1}) = water-soluble and exchangeable cations removed by ammonium acetate extraction. Soluble M^{+} (cmol kg^{-1}) = water-soluble cations removed by saturated paste extraction. Saturation % = saturated paste weight minus oven dry weight divided by oven dry weight. CEC by method 4F3a2 is a rough approximation calculated by the summation of exchangeable calcium and magnesium minus exchangeable sodium. Method 4F3a2 is more reliable when exchangeable potassium, carbonates and gypsum concentrations are minimal.

The presence of a sulfuric horizon was tested by allowing a 1:1 water by weight sample to incubate for up to 8 weeks. Samples with a pH over 3.5 that demonstrated a drop in pH of 0.5 are considered sulfuric according to SSLMM-4C1a1a3. Organic carbon was determined using the Walkley-Black dichromate oxidation (Nelson & Sommers, 1996). Particle size distribution was determined by the pipette method (Gee & Bauder, 1986). Clay mineralogy was determined on a composite sample by x-ray diffraction (XRD) with a Scintag XDS 2000, x-ray diffractometer with Cu-Kα radiation. All necessary pretreatments were performed according to Shang & Zelazny (2008).

During July of 2009, the CUF soils had ripened sufficiently to allow for the excavation of soil pits by backhoe. Six pit locations were chosen at random within the non-ponded portion of the CUF by using the Create Random Points tool from ESRI® ArcMap™ 10.0 (Figure 2- 5). Soil pits were excavated to the depth of at least the underlying native soils (> 1.5 m). Soil profiles were described, sampled and classified according to Field Book for Describing and Sampling Soils (Soil Survey Staff, 2002) and Soil Taxonomy (Soil Survey Staff, 2010).

In accord with the Virginia's Department of Environmental Quality (DEQ) permit, groundwater quality at Weanack has been monitored since construction of the first CUF in 2000. Groundwater is monitored from 6 wells installed into the stratified sand and gravel aquifer (Figure 2- 5). Detailed analyses of groundwater chemistry and flow can be found in Daniels & Whittecar (2009).

RESULTS & DISCUSSION

After a brief discussion of the history of the CUF conditions after deposition of the dredged materials, the remainder of this section will present the following four data sets that demonstrate changes to the dredged material over the course of 4 years: (1) solution phase properties, (2) exchangeable phase properties, (3) soil morphology and classification, and (4) local groundwater properties. Table 2- 1 presents a summary of the initial inbound dredged

Table 2- 1. Chemical properties from four 23,000 cubic meter composites taken during dredging operations at the Earle Naval Weapons Station. All elemental analyses except ortho-P are totals.

Analysis	units	Composite Date				
		12/11/05	1/3/06	10/19/06	8/30/07	Avg.
pH		8.1	7.6	7.1	9.7	8.1
Calcium	*mg/kg*	43,000	6,500	8,400	5,200	15,775
Magnesium	*mg/kg*	5,600	4,100	6,800	1,400	4,475
Potassium	*mg/kg*	3,400	3,400	4,700	490	2,998
Sodium	*mg/kg*	10,000	6,700	NA	1,500	6,067
Chloride	*mg/kg*	9,200	8,800	12,000	150	7,538
Sulfate	*mg/kg*	2,900	1,100	2,100	350	1,613
Total Organic Carbon	*wt %*	2.8	2.8	1.7	0.1	2
Total Kjeldahl Nitrogen	*mg/kg*	11,000	3,100	3,000	35	2,045
Orthophosphate	*mg/kg*	1.3	0.7	4.9	0.2	1.8
Moisture	wt%	NA	44	60	8	37
Total Solids	wt%	46	56	40	NA	47
Calcium Carbonate Eq.	*%*	10.1	2.7	1.8	NA	4.9
Potential Peroxide Acidity	*Mg* $CaCO_3$*/Mg Material*	0.6	0.0	0.4	NA	0.3

NA, not analyzed

material properties based on composite samples taken by the dredge contractor. Additional characterization data can be found in Table B- 1, Table B- 2 and Table B- 3 of Appendix B.

CUF Conditions 2006-2009

By the spring of 2006, dewatering and desiccation of the dredged materials had created a very coarse prismatic structure in all but the submerged and coarse loamy sections of the CUF. An extensive drought in the summer of 2007 accelerated the dewatering process and caused the ponded portion of the CUF to recede into the far northwest corner. The subsequent wet spring of 2008 caused ponded conditions to return to the northwest corner of the CUF. Through the summers of 2008 and 2009, drying and/or infiltration losses to groundwater reduced the size of the ponded region to its former drought levels once again.

During the summer of 2008 common sunflower (*Helianthus annus* (L.)) and German millet (*Setaria italica* (L.)) were overseeded, but elevated levels of soluble salts in the surface soils killed or severely stunted virtually all of the plants. Prior to the spring of 2009, no vegetation took hold in the CUF with the exception of a few isolated clumps of salt-tolerant species (e.g. *Sorghum halepense* (L.) and *Echinochloa crus-galli* (L.)) and an invasion of *Phragmites australis* (Cav.) on the sandy, permeable materials on the south side of the CUF. A reduction of surface soluble salts below a critical threshold likely caused a sudden invasion of grass flora that covered > 50 % of the CUF in the spring of 2009. In September of 2009, the CUF was disked to a depth of approximately 20 cm and a crop of winter wheat (*Triticum vulgare* (L.)) was successfully established.

Solution Phase Properties

A major shift in solution chemistry of the dredged materials was observed during the study period. The ENWS dredged materials were removed from seawater, which is dominated by the ions Na^+, Mg^{2+}, Ca^{2+}, K^+, Cl^- and SO_4^{2-} at concentrations of approximately 10,760 mg L^{-1},

Table 2- 2. Solution phase properties of dredged material composites collected during dredging operations.

Analyte	unit	Composite			
		DAJ-057	DAJ-083	DAJ-050	Avg.
pH		8.4	8.4	8.3	8.3
Electrical conductivity	*dS m^{-1}*	36	40	33	36
Water soluble Ca^{2+}	*mg kg^{-1}*	161	72	249	161
Water soluble Mg^{2+}	*mg kg^{-1}*	311	451	319	361
Water soluble K^+	*mg kg^{-1}*	1,648	1,925	1,670	1,748
Water soluble Na^+	*mg kg^{-1}*	10,135	11,358	9,519	10,337
Water soluble Cl^-	*mg kg^{-1}*	17,549	19,383	16,093	17,675
Water soluble SO_4^{2-}	*mg kg^{-1}*	269	830	576	558
Sodium adsorption ratio	*ratio*	88	96	79	88
Total sand	*%*	24	66	48	46

1,290 mg L^{-1}, 411 mg L^{-1}, 399 mg L^{-1}, 19,350 mg L^{-1} and 2,710 mg L^{-1}, respectively (Drever, 1988). The composite samples removed from every 23,000 m^3 of dredged materials represent the "initial" state of the dredged materials placed into the CUF. At the initial state, the solution chemistry measured by saturated paste extract displayed a significant deviation from a purely marine chemistry (Table 2- 2). The concentration of soluble Na is only slightly less than that observed in seawater and remained the dominant cation. The concentrations of Ca, Mg, and K, however, have shifted away from a seawater composition. The preferential attraction of Ca and Mg by the soil exchange capacity is demonstrated in the decreasing concentrations of these divalent ions in solution followed by a subsequent increase of K in solution. The concentration of water-soluble sulfate in the dredged materials was lower than seawater sulfate concentrations, which is expected due to the conversion of sulfate to monosulfides, to iron disulfides, and to organic sulfides. Table 2- 2 also demonstrates that while the particle size of the dredged material may vary drastically, the salinity and pH are consistent and reflect the marine environment from which the dredged materials were removed.

In less than 3 years, the CUF dredged materials solution chemistry was more representative of an agricultural soil than of marine sediment (Table B- 4). Electrical conductivity had decreased throughout the entire CUF while increasing in the native buried cut soil horizons below. In the surface 20 cm, EC decreased from an average of 36 dS m^{-1} to under 10 dS m^{-1} over the majority of the CUF in just 3 years (Figure 2- 6).

Porewater composition likewise changed substantially. For example, Na and K decreased by about 80% and 90 % whereas Ca and Mg increased by about 65% and 25%. Large reductions in Na were expected due to the high solubility and leachability of Na. Decreases in K were not likely to be the result of leaching because corresponding large increases in K (which

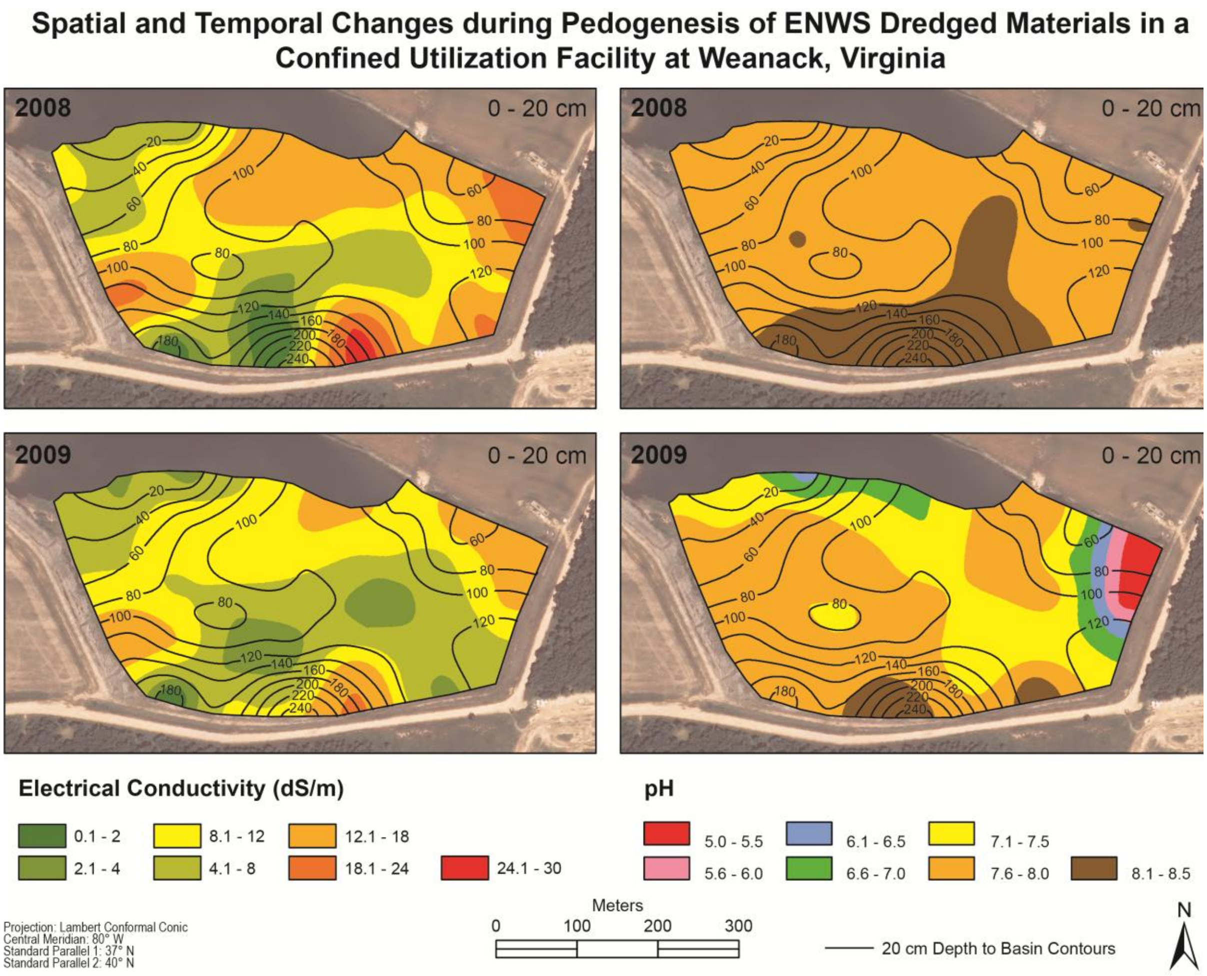


Figure 2- 6. Electrical conductivity (left column) and pH (right column) changes to the ENWS CUF during 2008 and 2009. Contour lines show depth of dredged materials.

might be expected) were not observed in the buried native soils (Table B- 4). A more plausible explanation for the almost complete reduction in soluble K is fixation by the clay fraction, which is dominated by montmorillonite, chlorite, and vermiculite (as determined for a CUF composite sample by XRD). Vermiculite, in particular, is known to "fix" K within its interlayers, thereby removing it from solution (Mcbride, 1994). Slight increases in Ca and Mg are possibly due to the dissolution of carbonates. The soils which underwent the largest deviation from the original marine-like chemistry were found at sample points 7, 13, 17, 25, and 32 in Figure 2- 5. These soils were located in one of the following three zones: (1) proximal to the discharge area in the southern part of the CUF, (2) in shallow soils on the western edge of the CUF, and (3) in a zone of silty soils with much smaller structural units in the mid-eastern part of the CUF. The flux of salts at any given location and in all horizons, including the soils underlying the CUF, steadily decreased from year to year. The lowest salt concentrations were found in the surface soils, followed by the second and third horizons in sequence (Figure 2- 7and Appendix Figure B- 1, Figure B- 2, Figure B- 3 and Figure B- 4).

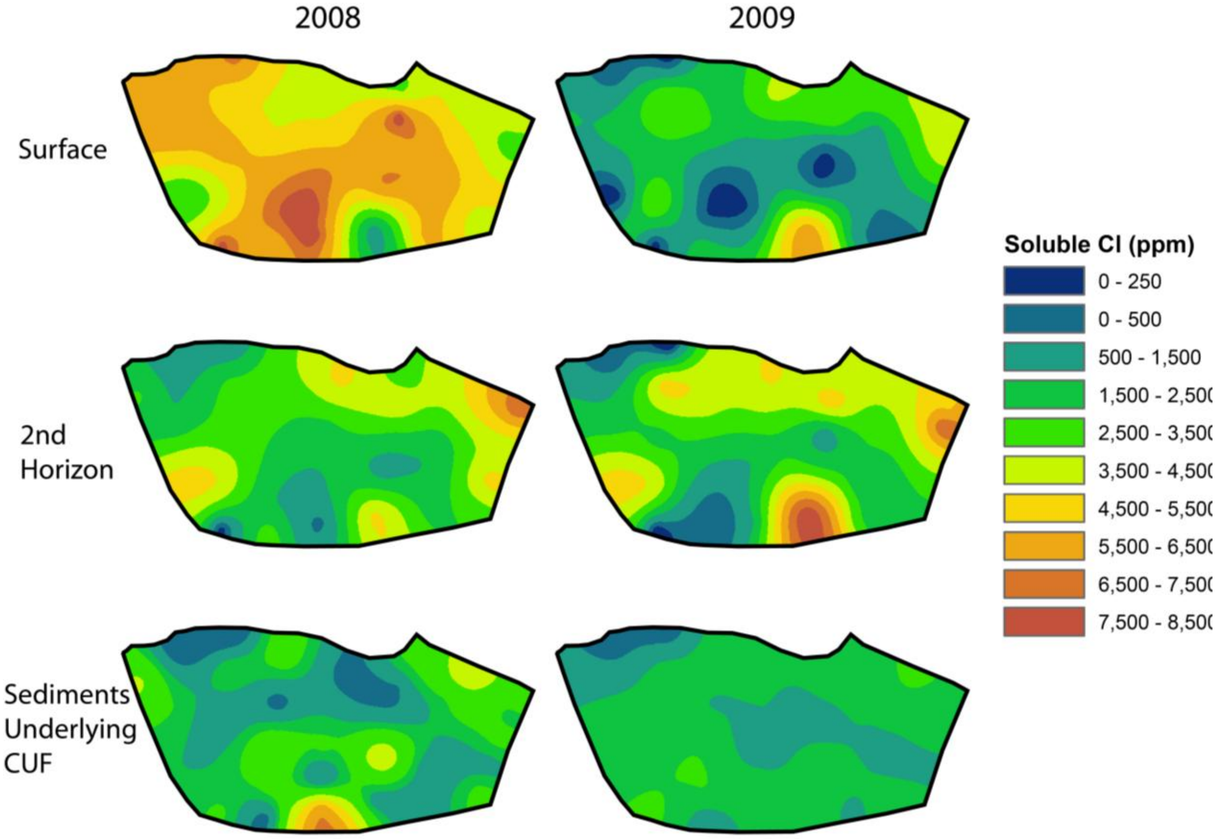


Figure 2- 7. Chloride distribution maps showing the horizontal, vertical and temporal changes to Cl between 2008 and 2009. Elevated surface Cl concentrations relative to the second horizon in 2008 was likely the result of water wicking. Overall, a downward migration of Cl into lower horizons and into the fine textured sediments under the CUF is evident.

Solid Phase Properties

The solid phase of the CUF soils exhibited properties similar to aquic soils that have large amounts of organic matter while also sharing properties common to aridic soils high in salts and carbonates. The soil textures were coarse loamy near the southern side of the CUF but mostly fine loamy silts with 2:1 layer clays and an average organic carbon content of over 4.5%. Cation exchange capacities ranged from 10 to 70 cmole kg^{-1}, with a mean CEC of ~45 cmole kg^{-1} and are completely saturated with base cations. The CEC values are 10-15 cmoles kg^{-1} higher than those reported for freshwater dredged materials removed from several locations along the Illinois River (Darmody & Marlin 2002), but the ENWS sediments contain almost twice as much organic matter. However, it should be emphasized that the CEC results of this study are only a gross approximation and that samples with very high salt contents are especially prone to overestimation of the CEC. An SAR of greater than or equal to 13 in a horizon greater than 25 cm thick within 50 cm of the soil surface is a diagnostic criterion in Soil Taxonomy. Sodium adsorption ratios remained over 13 for all but a few surface locations throughout the CUF during the course of this study (Table B- 5).

Calcium was the most abundant exchangeable cation at all locations and at all depths of the CUF. The exchangeable cation composition, as a percentage of the total for the 2008 and 2009 surface soils were: 79% Ca, 12% Mg, 3% K and 5% Na, and 82% Ca, 11% Mg, 3% K and 4% Na, respectively. Lower in the profiles, the Cg horizon exchangeable cations did not change between 2008 and 2009, and composition average was: 69% Ca, 15% Mg, 4% K and 12% Na. The exchangeable (cation) composition of the “initial” dredged materials was: 36% Ca, 44% Mg, <1% K, and 22% Na. From these data, an evolution of the CEC from “marine sediment chemistry” is evident. The most drastic and rapid change observed was the large exchange of Na

Table 2- 3. Exchangeable base cation composition of seawater sediments, ENWS sediments & freshwater dredged materials.

Soils	Exchangeable Cations (% of Total) Ca^{2+}	Mg^{2+}	K^{+}	Na^{+}	Reference
Suspended seawater clay	16	32	6	47	(Drever, 1988)
CUF initial properties	36	44	< 1	22	
CUF 2008-09 Cg horizon	69	15	4	12	
CUF 2008 surface	79	12	3	5	
CUF 2009 surface	82	11	3	4	
~25 year old freshwater DM	82	15	3	1	(Darmody & Marlin, 2002)

for Ca. Remarkably, this change was also mirrored in the Cg horizons where a lack of porosity would be thought to impede water and solute migration. Future perturbations to the CEC will likely result in a cation composition similar to that reported by Darmody & Marlin (2002) for freshwater dredged materials confined between 1981 and 1991, where Ca occupied over 80% of the CEC and Na saturated less than 1% (Table 2- 3).

Many dredged materials have the potential to form acid sulfate soils after ripening due to the presence of iron sulfides and/or organic sulfides, found in greater equivalent quantities than potentially neutralizing carbonates (Demas et al., 2004). Dredge soil pH values after oxidation did not fall below 4 and thus the formation of a sulfuric horizon is not expected. The potential acidity vs. alkalinity of the “initial” dredged materials also revealed that less than 1 ton of 100% $CaCO_3$ per ton of soil material (Table 2- 1) would theoretically be needed to neutralize any potential acidity produced from acid forming (reduced) constituents. This conclusion was verified by the observed fluctuations of sulfate released during the acid forming process that indicated that sulfide oxidation did not cause any significant lowering of the soil pH (Appendix Figure B- 5) even though substantial SO_4^{2-} was released.

Soil Development and Classification

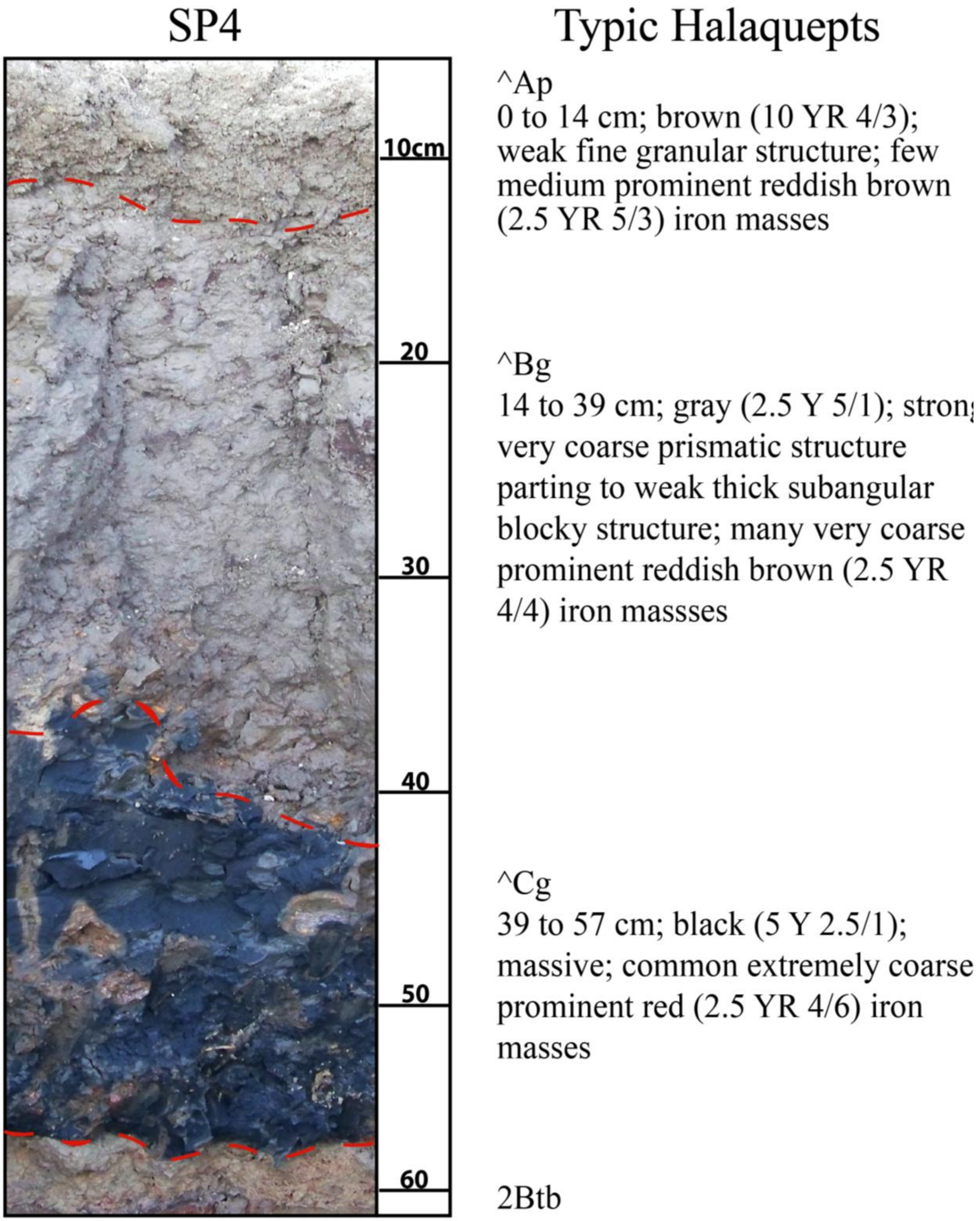
Soil development around Weanack is hastened by a mean annual rainfall of 115-140 cm, temperatures of 16-20 °C and 200-225 frost free days. However, soil formation inside the CUF was largely controlled by the restrictive nature of the CUFs internal drainage. The primary soil forming processes that occurred in the dredged materials were ripening and desalinization. Ripening is the dewatering, flocculation and desiccation (Pons & Zonneveld, 1965) of sediments which led to the consolidation of the dredged materials via irreversible flocculation and dewatering. Shrinkage of the sediments resulted in a polygonal network of coarse to very coarse prisms (25 to 50 cm diameter) that extended to a depth of approximately 50 cm (provided textures are finer than coarse loamy). Individual prisms were observed to break down to smaller sub-structural blocky units or smaller prisms near the surface of the soil.

Desalinization is the process whereby soluble salts are removed from soil (Rasulov et al., 1974). The large decrease in the soluble salts discussed previously lowered the salinity of the CUF soils below phytotoxic levels allowing for an invasion of plant growth that then accelerated the ripening process via increased transpiration. The secondary soil forming processes observed in the CUF were gleization and rubification (also referred to as ferrugination). Gleization is the reduction and mobilization of Fe under anaerobic conditions which either strips Fe from the soil resulting in a “gleyed” appearance, or reprecipitation of the Fe as brightly colored oxide masses (mottles) within a gleyed soil matrix. Rubification is the dispersion of oxidized Fe throughout a soil, imparting a higher chroma or redder hue to the soil matrix. Gleization occurred somewhat synergistically with rubification as Fe-oxides formed on the surface of prisms and blocks are sloughed off into the large vertical prism cracks. Rubification in the CUF occurred almost immediately after soil materials were exposed to oxygen as witnessed during sampling when excavated black, unoxidized sediments turn a brownish color in a matter of minutes.

Detailed morphological description of the soils surprisingly revealed that all 34 auger sample points and the six excavated soil pits were classified as Inceptisols (Soil Survey Staff, 2010) (Table 2- 4). After less than 5 years of pedogenesis, all soils shared a cambic horizon with aquic conditions within 50 cm of the soil surface (Appendix Figure B- 6, Figure B- 7, Figure B- 8, Figure B- 9 and Figure B- 9). Accelerated pedogenesis of the saline dredged materials was likely due to several factors, including: (1) fine-loamy textures (which retained high initial water contents), (2) organic carbon levels exceeding 4.5%, (3) a fluctuating water table and (4) a thermic temperature regime.

The most typical sequence of horizons encountered in the CUF was ^Ap - ^Bg - ^Cg - 2Btb. The ^Cg horizons were reduced, unstructured, nonporous sediments that had only slightly dewatered. The ^Bg horizons were well structured with many prominent iron redoximorphic features. The ^Bg horizon properties and the dynamic size of the CUF pond suggest that the moisture status is highly variable within the CUF soils.

All of the soils in the CUF were classified as Halaquepts by the summer of 2009 (Figure 2- 8). Halaquepts require the presence of a aquic cambic horizon and a SAR greater than or equal to 13 in a horizon(s) greater than or equal to 25 cm thick (Soil Survey Staff, 2010). The soils of the CUF were differentiated at the subgroup taxonomic level into either Aeric Halaquepts or Typic Halaquepts. Aeric Halaquepts are soils that have a horizon between 15 and 75 cm with a chroma greater than or equal to 3 (Appendix Figure B- 9). Aeric Halaquepts were only found on the sandy southern part of the CUF directly adjacent to the dredged materials point of discharge (Figure 2- 4). All of the remaining soils in the CUF were Typic Halaquepts (Figure 2- 8).



Typic Halaquepts

^Ap
0 to 14 cm; brown (10 YR 4/3); weak fine granular structure; few medium prominent reddish brown (2.5 YR 5/3) iron masses

^Bg
14 to 39 cm; gray (2.5 Y 5/1); stron very coarse prismatic structure parting to weak thick subangular blocky structure; many very coarse prominent reddish brown (2.5 YR 4/4) iron massses

^Cg
39 to 57 cm; black (5 Y 2.5/1); massive; common extremely coarse prominent red (2.5 YR 4/6) iron masses

2Btb

Figure 2- 8. Soil profile from the ENWS CUF at location SP4 after four years of pedogenesis.

Table 2- 4. 2009 Soil pedon descriptions and classification by Soil Taxonomy.

Horizon	Boundary		Texture	Munsell Matrix Color	Fe^{3+} Masses		Structure		Moist Constistence
	Depth (cm)	Distinctness Topography			Quantity, Contrast, Size, Color		Grade, Size	Type	
Location SP1. *fine-loamy, mixed, active, thermic Typic Halaquepts*									
^Ap	0-11	a, s	L	10 YR 4/2	f, P, 2	5 YR 5/6	2, TK	PL	fr
^Bg/Cg	11-55	c, i	SIL	2.5 Y 4/1	c, P, 4	5 YR 5/6	3, VC	PR	vfr
^Cg	55-100	a, s	SIL	5 Y 2.5/1			0	MA	lo
2Btb	100-115	-	CL	10 YR 5/3	f, P, 2	7.5 YR 5/6	2, M	SBK	fr
Location SP2. *fine-loamy, mixed, active, thermic Typic Halaquepts*									
^Ap	0-11	a, s	CL	10 YR 4/2	f, P, 3	5 YR 5/6	2, TK	PL	fr
^Bg	11-42	a, i	SICL	2.5 Y 5/1	m, P, 5	10 R 5/8	2, VC	PR	vfr
^Cg	42-119	a, c	SICL	5 Y 2.5/1			0	MA	lo
2Btgb	119-125	-	CL	2.5 Y 5/1			1, M	SBK	fr
Location SP3. *fine-loamy, mixed, active, thermic Typic Halaquepts*									
^Ap	0-9	a, s	CL	10 YR 4/2	f, P, 2	5 YR 5/6	1, F	GR	fr
^Bg	9-55	c, i	SIL	2.5 Y 5/2	m, P, 4	2.5 YR 5/8	3, VC	PR	vfr
^Cg	55-90	a, s	SICL	5 Y 2.5/1			0	MA	lo
2Btgb	-	-	CL	2.5 Y 5/1			1, M	SBK	fr
Location SP4. *fine-loamy, mixed, active, thermic Typic Halaquepts*									
^Ap	0-14	a, s	CL	10 YR 4/3	f, P, 2	2.5 Y 5/3	1, F	GR	fr
^Bg	14-39	a, i	CL	2.5 Y 5/1	m, P, 4	2.5 YR 4/4	3, VC	PR	vfr
^Cg	39-57	a, s	SICL	5 Y 2.5/1	c, P, 5	2.5 YR 4/6	0	MA	lo
2Btb	57-65	-	CL	7.5 YR 4/6	m, P, 3	10 R 5/4	2, M	SBK	fr

Table 2- 4. Continued.

Horizon	Boundary		Texture	Munsell Matrix Color	Fe^{3+} Masses		Structure		Moist Constistence
	Depth (cm)	Distinctness Topography			Quantity, Contrast, Size, Color		Grade, Size	Type	
Location SP5. *coarse-loamy, mixed, active, thermic Aeric Halaquepts*									
^Ap	0-16	a, s	SL	10 YR 4/2			1, M	GR	vfr
^Bg/BC	16-38	a, s	S	10 YR 5/2	m, P, 3	5 YR 5/6	1, TK	SBK	vfr
^BC/Bg	38-60	a, w	S	10 YR 5/4	c, D, 2	7.5 YR 5/6	0	SGR	lo
^Cg1	60-70	a, s	SL	5 Y 2.5/1	c, P, 5	10 R 5/8	0	MA	lo
^Cg2	70-87	a, w	S	2.5 Y 5/3			0	MA	lo
^Cg3	87-134	a, s	SL	5 Y 2.5/1			0	MA	lo
2Btb	134-145	-	CL	7.5 YR 5/4			2, M	SBK	fr
Location SP6. *fine-loamy, mixed, active, thermic Typic Halaquepts*									
^A	0-14	a, w	SL	10 YR 4/3			1, M	GR	vfr
^Bg	14-69	a, i	L	5 Y 4/1	m, P, 4	2.5 YR 4/6	3, VC	PR	vfr
^Cg	69-110	a, s	L	5 Y 2.5/1			0		lo
2Btgb	-	-	CL	2.5 Y 5/2			2, M	SBK	fr

Soil classification according to Soil Survey Staff (2010). Abbreviations in body of table are as follows: boundary distinctness: a=abrupt, c=clear; textural classes: CL=clay loam, L=loam, LS=loamy sand, SL=sandy loam, SIL=silt loam; Fe^{3+} Masses: f=few, c=common, m=many D=distinct, P=prominent, 1,2,3,4,5=fine, medium, coarse, very coarse, extremely coarse, respectively; structure: 0,1,2,3=structureless, weak, moderate, strong, respectively, F=fine, M=medium, TK=thick, VC=very coarse, GR=granular, MA=massive, PL=platy, PR=prismatic, SBK=subangular blocky, SGR=single grain; moist consistence: fr=friable, lo=loose, vfr=very friable.

Groundwater Flow

A review of the literature reveals that information pertaining to the impact of placing large quantities of saline dredged materials into CUFs located in freshwater environments is lacking. At other locations along the US east coast, discharges from semi-confined dredged materials have commonly been associated with acid forming conditions, metal release and fish kills (Demas et al., 2004). Monitoring of Weanack under the VPA Permit, VPA00579, includes all ground and surface waters in and around the ENWS CUF. Groundwater monitoring wells were installed prior to CUF construction and have been sampled quarterly since placement of the ENWS dredged materials in to the CUF (Figure 2- 9). Complete analysis of all monitoring

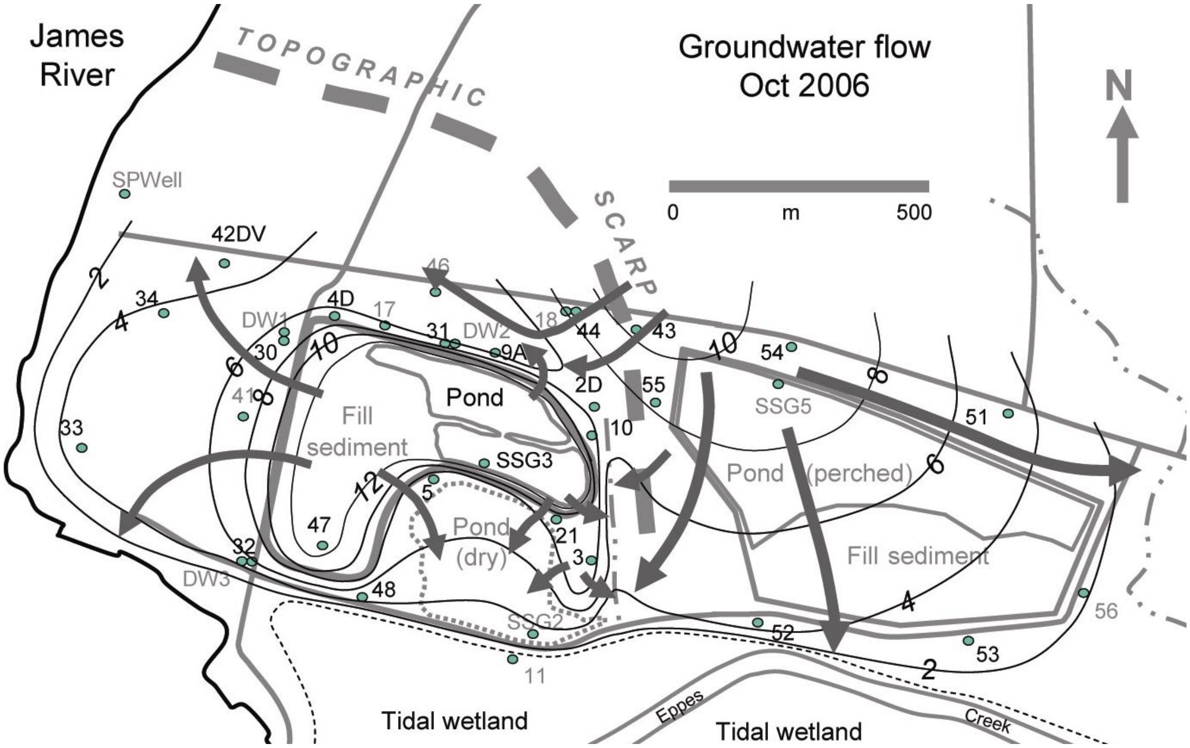


Figure 2- 9. Groundwater flow around the freshwater CUF (left) and the ENWS CUF (right). Groundwater isolines indicate feet above sea level. Groundwater direction is shown by gray arrows. Well 53 located to the southeast of the ENWS CUF is the only location thus far to indicate any saline discharge from either CUF (Daniels and Whittecar, 2009).

activities can be found in Daniels & Whittecar (2006) and Daniels & Whittecar (2009). As previously discussed, acid forming conditions do not exist in the CUF and no perturbations to the local groundwater pH are expected. The ENWS dredged materials did, however, carry a very large salt load that has been steadily declining in the CUF soils. Input of nutrients such as Ca, Mg, K, Na, NO_3 and PO_4 to groundwater and surface waters may increase the prevalence of unwanted algae blooms and undesirable organisms like *Pfisteria piscidia*. In other studies (Hesterberg et al., 2006; Vos et al., 2002; White & Broadley, 2001), Cl was used as an indicator ion for potential leaching risks (i.e. nutrients, metals and organics) due to its relative mobility and lack of attenuation by soils and sediments compared to other water soluble species. The initial mean level of water soluble Cl in the ENWS CUF was 17,675 mg kg^{-1}. Four years after placement of the dredged materials in the CUF, the water soluble Cl levels found in soils were: 1,939 mg kg^{-1} (^Ap horizon), 4,165 mg kg^{-1} (^Cg horizon) and 1,823 mg kg^{-1} (2Btb horizon).

The ponded surface waters in the CUF were also observed to decrease substantially in Cl where the initial value (17,675 mg kg^{-1}) decreased to 558 mg kg^{-1} in only 4 years. The enormous flux of Cl has at this time only resulted in a moderate but continuous increase in the Cl level of down-gradient well 53 as illustrated in Figure 2- 10. At the time of this writing an additional 53,000 m^3 of saline dredged materials was hydraulically placed on the surface of the ENWS CUF. The new influx of saline waters to the system caused Cl concentrations of the ponded region to quickly rise to 2,590 mg L^{-1}. The Cl level of well 53 has continued to steadily rise and as of October 12th of 2010 was 823 mg L^{-1} while the values of wells 51, 52 and 54 continue to remain below 25 mg L^{-1}. It is predicted that as Cl continues to migrate from the CUF that Cl levels in well 53 will continue to rise until some equilibrium is attained with the influx and outflux of Cl to the CUF.

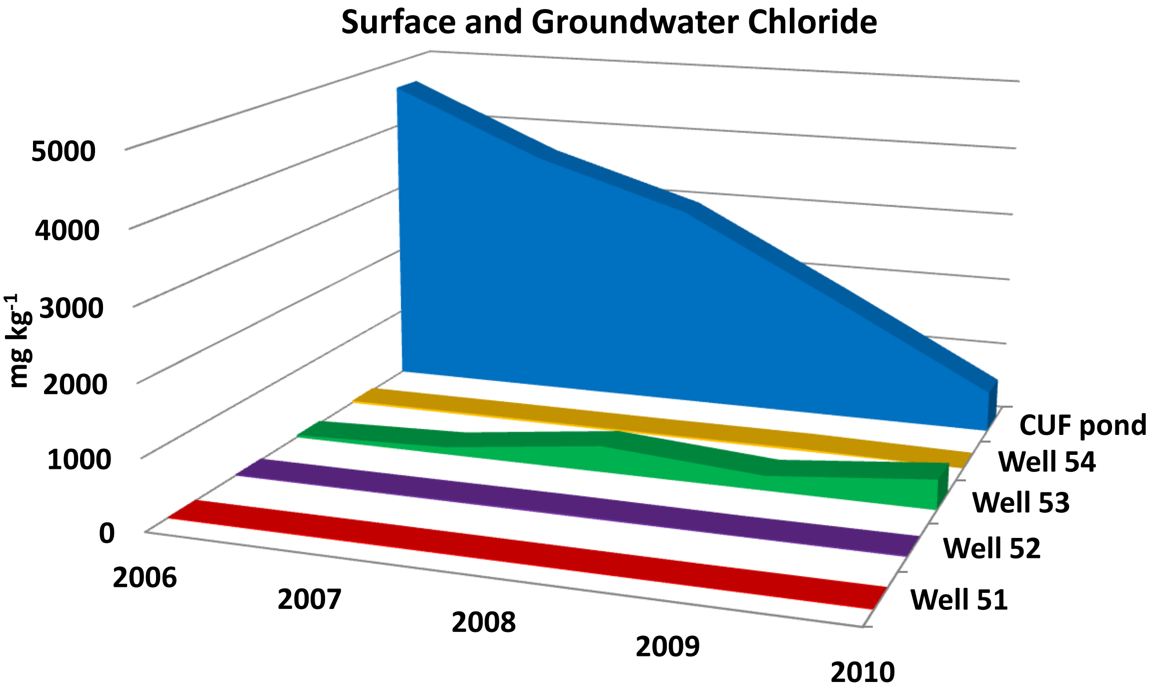


Figure 2- 10. Dissolved chloride in the down-gradient wells around the ENWS CUF and values of the surface waters ponded in the northern part of the CUF. Large reductions of chloride in the soil and surface waters have so far only resulted in a slight increase in well 53.

CONCLUSIONS

Maintenance dredging of US waterways is vital to our nation's commerce and will necessitate beneficial reuse of millions of cubic meters of saline dredged materials. The majority of these sediments are silts and clays that can be quite suitable for agricultural, horticultural, and forestry practices. Current methods of beneficial reuse such as the "incorporation" of saline dredged materials into agricultural uplands will not be sufficient to reuse millions of cubic meters of marine materials dredged annually. The use of confined utilization facilities (CUFs) has great potential for beneficial upland reuse of very large quantities of saline dredged materials. General acceptance of CUFs as a beneficial reuse will require scientific knowledge and prediction of the impacts of confining large quantities of dredged materials into foreign environments and in-depth knowledge pertaining to the genesis of the dredged materials into agricultural soils.

Pedogenesis of saline dredged materials from the ENWS was found to proceed very quickly, such that, by the fourth year after placement, all of the pedons in the CUF had evolved into Inceptisols. The formation of a cambic horizon with aquic conditions was accelerated by a fluctuating water table, a thermic temperature regime and a favorable mineralogy and texture (i.e. 2:1 layer phyllosilicates and loams). At the time of this study, nearly half of the soils were saturated with enough sodium to be classified as Halaquepts while the other more developed half was classified as Epiaquepts. Although large spatial variability existed in the CUF due to differential deposition of the dredged materials, it is likely that all soils will undergo conversion from Hydraquents to Halaquepts to Epiaquepts over time. Rapid changes to the soil pore water and solid phase chemistry suggest the pedogenic processes of ripening, desalinization, gleization, and rubification will continue towards the evolution of dynamic steady state soil that is desalinated, structured, and shares a solution and solid phase cation composition similar to reports from other freshwater confined dredged materials impounded within the last 30 years (Table 2- 3). Over more extended periods, these soils will most likely transform into Eutrudepts with great agricultural potential.

To date, no negative environmental impact has resulted from the placement of the saline dredged materials into a freshwater agricultural landscape. Large decreases of soluble salts in the soil and in ponded surface waters of the CUF have thus far only resulted in a minor increase of Cl in a down gradient well. Future monitoring of the ENWS CUF soils and groundwater will greatly benefit the understanding of the dynamics involved in using CUFs as a management alternative for saline dredged materials.

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CHAPTER III

Biodegradation of PAH-contaminated Dredged Material: Implications of Study Length on the Interpreted Effectiveness of Organic and Vegetative Treatments

ABSTRACT

In this study, a bench-scale experiment tested the effect of organic amendments and plant rooting on biodegradation of polycyclic aromatic hydrocarbon (PAH)-contaminated dredged materials from the Appomattox River Federal Navigation Channel. A completely randomized greenhouse study investigated the effects of biosolids, compost, and straw added to contaminated dredged material sediment at ratios of 24:1, 16:1, and 42:1, respectively, under unvegetated and vegetated conditions. Samples were collected at 0, 150, and 327 days, and the concentrations of 14 PAHs were analyzed by EPA SW-846 methods. The biosolids, compost, and straw treatments caused significant reductions in PAH concentrations at 150 days followed by a "rebound effect" in concentrations at 327 days. In contrast, the concentration of PAHs in the unamended control treatment either continued to decrease or remained constant. Rooted conditions resulted in significantly higher PAH concentrations, apparently due to increased desorption via rhizosphere inputs. Benzo(a)pyrene (BAP) was the only PAH found in concentrations above the EPA, Region 3, Human Health, Industrial Risk-Based Criteria during the 327 day experimental period. Concentrations of BAP did not change significantly in any of the treatments. The findings of this study suggest that future studies testing the effectiveness of organic treatments should use more extended study periods and that the relative effectiveness of the standard PAH extraction technique to adequately predict PAH bioavailability in systems such as these may be questionable.

INTRODUCTION

Dredged material

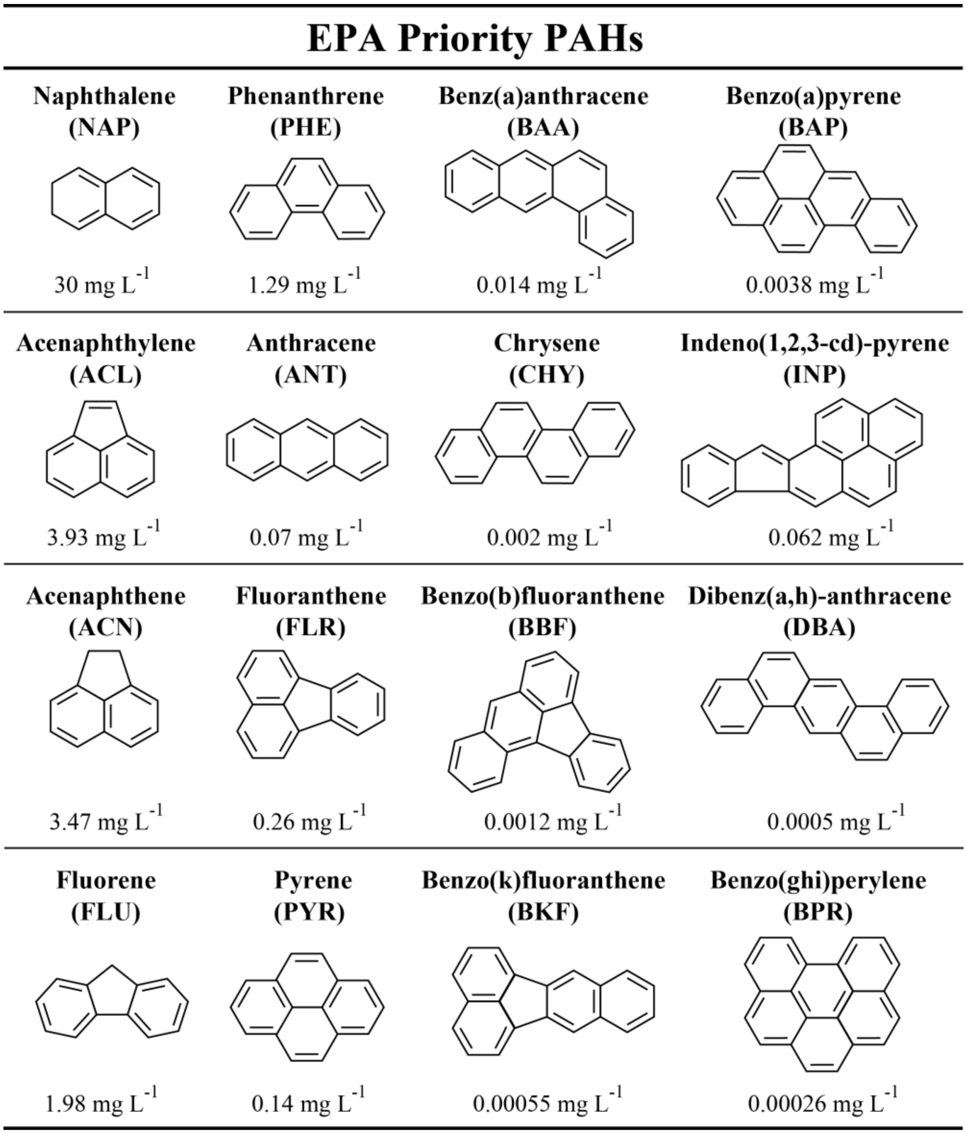
Sedimentation of waterways is a natural process wherein suspended particulates are deposited into environments of decreasing energies. Anthropogenic changes to natural waterways (i.e. dam creation, levees, manmade channels) change the dynamics of fluvial and estuarine environments, accelerating sedimentation and subsequently limiting depth of and even closing navigational channels. Maintenance and restoration of navigable channels requires sediment dredging and removal of the dredged materials; a process vital to shipping and recreational boating and to preservation of healthy ecosystems and flood prevention.

Historically, dredged materials have been pumped back into the ocean for disposal or placed into confined disposal facilities (CDFs). Within the last few decades, however, new restrictions on ocean dumping and rising prices of CDFs have encouraged local, state, and federal agencies to consider beneficial reuse of dredged materials. Dredged materials can be beneficially reused for environmental enhancement or as agriculture and engineering media (EPA & USACE, 2007). The suitability of a dredged material for beneficial reuse is primarily affected by the following characteristics: contaminants, grain size, salinity, water content, organic content, acidity, nutrient levels and engineering properties (EPA & USACE, 2007). Navigation channels in industrialized areas are particularly susceptible to contamination by heavy metals, polychlorinated biphenyls (PCB's) and polycyclic aromatic hydrocarbons (PAH's) (Ho et al., 2002). PAHs are associated with industrial and urban areas and are found increasingly in surface waters and sediments across the US (EPA, 2004). When PAH concentrations in dredged material exceed regional US Environmental Protection Agency (EPA) risk based criteria (RBC), the material is identified as contaminated hazardous waste that requires either treatment or safe disposal (EPA & USACE, 2007). Treatment options include: chemical treatment, thermal treatment, extraction/washing, immobilization, particle size separation and bioremediation (EPA, 2005). Bioremediation, specifically landfarming (discussed in more detail later), is the most economically feasible option for PAH- removal from large quantities of sediment, such as those encountered in dredging operations (Maila & Cloete, 2004).

Polycyclic Aromatic Hydrocarbons

PAHs are aromatic compounds, formed from the incomplete combustion of hydrocarbons that contain two or more fused benzene rings (Figure 3- 1). PAHs are ubiquitous in the environment due to their unusual stability, hydrophobicity and strong adsorption to soil/sediment colloids (Bamforth & Singleton, 2005; Shuttleworth & Cerniglia, 1995; Sims & Overcash, 1983; Wilson & Jones, 1993). They can form through either petrogenic or pyrogenic processes, predominantly through the former. Petrogenic PAHs form geologically, during burial of organic debris and subsequent conversion to fossil fuels such as coal and oil (Bamforth & Singleton, 2005; Sims & Overcash, 1983; Wilson & Jones, 1993). Pyrogenic PAHs form during incomplete combustion of organics in forest fires, power plants, combustion engines, and refuse incineration. Due in part to their intimate association with fine soot particles, pyrogenic PAHs can become globally distributed.

The PAHs can be categorized by type, arrangement, and number of carbon rings. Alternate PAHs contain only benzene rings (i.e. phenanthrene); non-alternates contain other types of rings (i.e. Fluorene). When rings are arranged linearly, PAHs are called acenes (i.e.



EPA Priority PAHs

Naphthalene (NAP) 30 mg L^{-1}	**Phenanthrene (PHE)** 1.29 mg L^{-1}	**Benz(a)anthracene (BAA)** 0.014 mg L^{-1}	**Benzo(a)pyrene (BAP)** 0.0038 mg L^{-1}
Acenaphthylene (ACL) 3.93 mg L^{-1}	**Anthracene (ANT)** 0.07 mg L^{-1}	**Chrysene (CHY)** 0.002 mg L^{-1}	**Indeno(1,2,3-cd)-pyrene (INP)** 0.062 mg L^{-1}
Acenaphthene (ACN) 3.47 mg L^{-1}	**Fluoranthene (FLR)** 0.26 mg L^{-1}	**Benzo(b)fluoranthene (BBF)** 0.0012 mg L^{-1}	**Dibenz(a,h)-anthracene (DBA)** 0.0005 mg L^{-1}
Fluorene (FLU) 1.98 mg L^{-1}	**Pyrene (PYR)** 0.14 mg L^{-1}	**Benzo(k)fluoranthene (BKF)** 0.00055 mg L^{-1}	**Benzo(ghi)perylene (BPR)** 0.00026 mg L^{-1}

Figure 3- 1. List of the 16 most commonly tested PAHs followed by abbreviations, structure and water solubility. Solubility data from Sims & Overcash, (1983).

anthracene); angular PAHs are called phenes (i.e. phenanthrene); peri-condensed or clustered PAHs have a ring bonded to three other rings (Harvey, 1997). The most commonly used classification of PAHs results from their number of rings or molecular weight, where PAHs containing three rings or less are called low molecular weight (LMW), while those with more than 3 rings are called high molecular weight (HMW) (Juhasz & Naidu, 2000).

Table 3- 1. Environmental Protection Agency Region 3 Human Health Risk Based Criteria (EPA, 1991, 1993 & 2011).

PAH	Industrial mg kg^{-1}	Residential mg kg^{-1}
Benzo(a)anthracene	2.1	0.15
Benzo(a)pyrene†	0.21	0.015
Benzo(b)fluoranthene	2.1	0.15
Chrysene	210	15.0
Dibenz(a,h)anthracene†	0.21	0.015
Indeno(1,2,3-cd)pyrene	2.1	0.15

† analytes with the lowest RBC's are usually the target analytes during many remediation projects

In 1984, the U.S. Environmental Protection Agency (EPA) ranked PAHs according to their toxicity, using benzo(a)pyrene (BAP) as a reference point. The ranking classified PAHs as either carcinogenic or noncarcinogenic. A subsequent study found benzo(a)pyrene, chrysene (CHY), benzo(b)fluoranthene (BBF), benzo(k)fluoranthene (BKF), indeno(1,2,3-cd)pyrene (INP), and dibenzo(a,h)anthracene (DBA) (all HMW PAHs) to be the most toxic PAHs commonly assessed by risk based criteria (RBC) (EPA, 1984). BAP and DBA have the most stringent RBCs and therefore usually represent the target analytes during bioremediation (Table 3- 1) of PAH contaminated sediments.

Biodegradation

The widespread distribution and persistence of PAHs in the environment has resulted in several organisms, including humans, developing the ability to metabolize PAHs to various oxidized products via enzymatic pathways. Since the mid-20th century, several bacterial and fungal species that can degrade PAHs have been identified. There are two general pathways of microbial biodegradation. The first, accomplished via intracellular oxygenase enzymes (enzymes that add oxygen), is used by bacteria and by non-lignolytic fungi, and will be discussed in greater detail below. The second occurs via extracellular peroxidase enzymes (enzymes that increase oxidation state) in lignolytic fungi (Bamforth & Singleton, 2005). While both enzymatic pathways catalyze the initial oxidation of one of the PAH rings, intracellular enzymes are proteins associated within microbial cells whereas extracellular enzymes or soil enzymes are proteins that are secreted into the environment. The exact mechanism of the peroxidase pathway is still unclear, but it is likely that the addition of oxygen to a ring occurs by a free radical intermediate produced when peroxidase reacts with lignolytic materials. The oxidized metabolites of both classes of enzymes undergo ring fission and subsequent oxidation steps by other enzymatic pathways (Bamforth & Singleton, 2005).

Ten of the most common bacteria genera possessing the ability to degrade PAHs are: *Agrobacterium, Bacillus, Burkholderia, Comamonas, Gordona, Mycobacterium, Pseudomonas, Rhadococcus, Sphingomonas, Stenotrophomonas* (Cerniglia & Sutherland, 2006; Juhasz & Naidu, 2000). Bacterial degradation of PAHs is commonly an aerobic process using two general intracellular enzymatic pathways. The first utilizes cytochrome P450 monoxygenase enzymes which creates trans-dihydrodiols. This pathway is very similar to the way in which the human liver metabolizes PAHs to epoxides. The second pathway utilizes dioxygenase enzymes which create cis-dihydrodiols that are subsequently oxidized to phenols by dehydrogenases and ultimately undergo ring cleavage by other enzymes (Bamforth & Singleton, 2005; Cerniglia & Sutherland, 2006; Johnsen et al., 2005).

Most fungal species that possess the ability to degrade PAHs are white rot, lignolytic fungi of the Basidiomycetes phylum. Ten commonly cited genera are: *Aspergillus, Bjerkandera, Candida, Coriolopsis, Cunninghamella, Fusarium, Irpex, Pleurotus Phanerochaete, Pleurotus, Syncephalastrum, Trametes* (Cerniglia & Sutherland, 2006; Juhasz & Naidu, 2000). Microbial degradation of both lignin and PAHs is thought to occur by similar processes because lignin is structurally similar to PAHs, composed of a random structure of linked aromatics. Lignolytic fungi metabolize PAHs using three different extracellular “soil enzymes” (Johnsen et al., 2005): lignin peroxidases (LiP), manganese peroxidases (MnP), and laccases. The degradation pathway proceeds via oxidation of PAHs to quinones which subsequently undergo ring fission and further oxidation by other enzymes and microbes (Bamforth & Singleton, 2005; Cerniglia & Sutherland, 2006; Johnsen et al., 2005). Extracellular enzymes have the capability of entering much smaller soil/sediment pore spaces than intracellular enzymes carried on cellular bodies. Extracellular enzymes are secreted into the environment at concentrations independent of the carbon source and thus do not pose threshold limits (the minimum concentration of a contaminant and degrading organism, below which no degrading enzymes are produced) (Cerniglia & Sutherland 2006; Johnsen et al., 2005).

The susceptibility to degradation of PAHs decreases as the number of fused rings increases. To date, very few studies report microorganisms capable of utilizing PAHs with more than four rings as their sole carbon source (Juhasz & Naidu, 2000; Kanaly & Harayama, 2000). PAHs with greater than four rings do undergo environmental degradation, suggesting co-metabolic and cooperative processes work together to degrade HMW PAHs (Johnsen et al., 2005). During co-metabolism, the resulting intermediate metabolite is utilized cooperatively by other fungi or bacteria.

Bioremediation

Bioremediation is the process of reducing contaminant toxicity in the environment by degradation, adsorption, and volatilization due to natural biological processes. PAH contaminated materials in the field are bioremediated by bioaugmentation and/or biostimulation strategies which are dependent on PAH bioavailability, concepts which are discussed in further detail below. Briefly, bioaugmentation introduces PAH-degrading organisms; biostimulation increases the population of these organisms; and bioavailability is the availability of a given PAH to these organisms. In the practice of landfarming, the PAH-degrading microflora that is found in or introduced into contaminated sediment is treated as the “crop”, and similar to conventional farming, the goal of landfarming is to increase the yield of only the desired microfloral crop. Typically, microflora populations increase with available oxygen and nutrients, thus the soil is mechanically tilled and fertilized (often heavily) on a regular basis (Harmsen et al., 2007; Saison et al., 2004; Straube et al., 2003).

Bioavailability of PAHs, roughly defined as the accessibility of a contaminant to a particular organism (Alexander, 2000), decreases with: increasing contaminant-sediment interactions, increasing organic matter, and decreasing particle size (Alexander, 2000; Bogan & Sullivan, 2003; Chiou et al., 1998). Because PAHs are extremely hydrophobic, they slowly diffuse from the hydrophilic environment surrounding soil inorganic particles towards the more lipid-like environments that occur near organic matter. Intimate interactions between PAHs and organic matter result in sorption by chemical processes (e.g. van der Waals and covalent bonding). This process of diffusion followed by sorption is defined as sequestration (Alexander, 2000). Bioavailability and sequestration of PAHs are inversely related, which contributes to the recalcitrance of PAHs in the environment as well as to a reduced biotoxicity of sequestered compounds. In bioremediation, bioavailability is often enhanced by tillage and inputs of biosurfactants. Tillage mechanically mixes contaminated soil and thus enhances bioavailability by redistributing contaminants, nutrients, microbes and soil pores (Harmsen et al., 2007; Saison et al., 2004; Straube et al., 2003). Biosurfactants are amphiphilic compounds produced by microbes which form micelles that surround PAHs and increase their solubility (Mulligan, 2005). Biosurfactants may be artificially produced ex-situ and introduced into a contaminated site or alternatively, microbes that can produce biosurfactants may be added or stimulated in-situ.

Bioaugmentation aims to increase the genetic diversity of the contaminant-degrading microbial community by increasing the number of species and/or increasing the spatial distribution of individual species (Dejonghe et al., 2001; Hamdi et al., 2007). A vast amount of research has been conducted to identify and to isolate PAH-degrading organisms from contaminated soils, to inoculate these populations in laboratory, and to later introduce these microbes to PAH contamination contaminated sites (Cerniglia & Sutherland, 2006; Herwijnen et al., 2006; Johnsen et al., 2005). The results of this large research and demonstration effort have been mixed, and some studies show that allochthonous strains have difficulty competing with indigenous microbial populations (Chavez-Gomez et al., 2003; Straube et al., 1999). In fact, diverse dredged materials have previously been shown to possess an indigenous microbial population capable of degrading PAHs (Ferdinandy-van Vlerken, 1998; Harmsen et al., 2007). Some studies have indicated that successful bioaugmentation may also be achieved through the addition of an alternative natural carbon such as biosolids (or sewage sludge), wheat straw, rice hulls, compost, poultry litter, corn cobs, mushroom spawn, etc. (Bamforth & Singleton, 2005; Hamdi et al., 2006; Herwijnen et al., 2006), a process which is much simpler than microbial extraction, replication, and reintroduction.

Biostimulation is the action of manipulating soil conditions to stimulate an increase in the PAH degrading population (Liebeg & Cutright, 1999). This is usually accomplished by optimizing the following soil properties: temperature, acidity, salinity, moisture, oxygen, nutrients and the rhizosphere (Bamforth & Singleton, 2005). Of these, oxygen, nutrients, and the rhizosphere are the most manipulated variables in biostimulation. Biodegradation has been found to occur from the equator to the poles, although rates vary with temperature (Coulon et al., 2005). Acidity can also affect the rate of biodegradation and PAH-degrading organisms favor circum-neutral pH environments (Bamforth & Singleton, 2005). Salinity as measured by electrical conductivity (EC) is usually kept below 2 dS m^{-1} in bioremediation experiments. The optimal range of moisture for bioremediation is between 30-90% field capacity (FC) (Bamforth & Singleton, 2005; Hansen et al., 2004).

Oxygen in soils acts as the terminal electron acceptor for aerobic degrading organisms and recurring tillage events maintain the oxic conditions necessary for optimal bioremediation. Studies have shown, however, that routinely tilling a soil to add oxygen is not necessary because the initial placement of material, at the initiation of a field or lab study, provides adequate oxygen for PAH degradation and ultimately, tillage may decrease biostimulation by disturbing bacterial and fungal substructures (e.g. biofilms and mycelium) (Grant et al., 2007; Hansen et al., 2004).

The most significant limitation to bioremediation is nutrients. High C:N ratios associated with large quantities of carbon-rich contamination restrict biodegradation to the rate of nitrogen mineralization in the system. Laboratory and field trials have demonstrated that additions of both macro- and micronutrients can stimulate microbial activity and enhance degradation (Chaineau et al., 2005; Liebeg & Cutright, 1999). Much of the literature suggests that optimal biodegradation of PAHs occurs at bulk soil/sediment C:N ratios of 10:1, approaching that found in microbial biomass. However, net biodegradation has been found to occur with C:N ratios two to three times that value (Bamforth & Singleton, 2005; Chaineau et al., 2005; Liebeg & Cutright, 1999).

Finally, the rhizosphere activity (via root exudates, redox and microbial effects) is cited to have conflicting effects, and researchers have reported both increased and decreased PAH degradation due to plant rooting and associated rhizosphere activity. The rhizosphere is thought to enhance PAH degradation through destabilization of soil organic matter by root exploration and exudates, through increased distribution of PAH-degrading rhizobacteria in the soil, and through inputs of rhizosphere enzymes that can co-metabolize PAHs (Joner et al., 2002; Parrish et al., 2005). Grasses from the monocotyledon family, *Pocaceae*, have been reported to be the most significant enhancer of PAH degradation, likely because of very extensive root distributions (Chen et al., 2003; Olson et al., 2007). On the other hand, commonly cited causes of decreased PAH degradation include: the presence of a more easily degraded organic carbon; nutrient immobilization by plants; and increased PAH extractability due to biosurfactants which could inhibit degradation in the short term (Corgie et al., 2003; Saison et al., 2004).

EXPERIMENTAL SITE

Project History

The Appomattox River Federal Navigation Channel is being restored through the joint efforts of the city of Petersburg, VA, and the U.S. Army Corps of Engineers-Norfolk District (USACE-NAO). The Channel is in the vicinity of the Interstate 95 Richmond-Petersburg Turnpike Bridge (37°14’8.21”N 77°23’43.99”W) in downtown Petersburg. A century-long history of intervention and non-maintenance has led to the restoration project. In an effort to control siltation problems, the Appomattox River was first diverted into a manmade channel north of the original navigation channel in the 1920s. The navigation channel was open and accessible to watercraft until 1949, when maintenance dredging halted. Post-dredging construction and flooding events led to the silting-in and complete closure of the navigation channel by the late 1980s (Figure 3- 2). In 1991, the USACE-NAO began a dredging project to restore the navigation channel. However, high levels of total petroleum hydrocarbons (TPH) associated with creosote in the channel sediment were discovered as the project began, and because the level of contamination is sufficient to warrant sediment treatment or disposal, dredging operations were immediately suspended (Tracey et al., 2008).

Creosote is approximately 85-90% PAHs (Mueller et al., 1991), and in the channel, it is non-uniformly distributed throughout layers of gravel, sands and loamy sands. In 1994, additional USACE sampling revealed gravelly layers high in total PAH (greater than 1,000 mg kg^{-1}) occurring at depths greater than 7 meters from the sediment surface. Above the contaminated gravels lie predominantly sandy textured sediments, with a lens at between 4.9-6.7

Figure 3- 2. Aerial photographs taken in 1961 (left) and 2010 (right) showing the extent of siltation in the Appomattox Federal Navigation Channel (lower channel) (historic photo on left from http://www.petersburg-va.org/dredging/index.asp).

meters below surface containing total PAHs of approximately 100-500 mg kg^{-1}. Additional testing did not reveal any further contamination, beside the PAHs, nor any negative handling properties that might affect post-dredging uses (e.g. high organic matter or sulfides), making the channel sediments ideal for biodegradation and beneficial reuse.

The tentative dredge plan is to excavate the sandy materials above the deeper highly contaminated gravels. The total dredged material to be excavated will exceed 268,000 m^3, of which some 46,000 m^3 would require treatment. Bioremediation and subsequent agricultural beneficial reuse are options currently being explored by USACE-NAO and Weanack Land LLP, located in Charles City County, VA, 10 km by river from the James and Appomattox River confluence. Bench-scale studies were initiated in 2007 by USACE-NAO in partnership with Science Applications International Corporation (SAIC) to investigate the feasibility of bioremediation. Collaborative bench-top and field-scale pilot studies ensued, using proprietary nutrient blends, microbial consortia from Russian oilfields, and enzyme accelerator treatments. In both the bench-top and the field pilot study, large decreases in total PAHs were observed but several HMW PAHs remained above the EPA, Region 3, Human Health RBC. Complete information of the dredging plan, bench-top study and landfarm pilot study can be found in (Tracey et al., 2008).

METHODS AND MATERIALS

Sediment Collection

Channel sediments were collected using a 15 cm hollow stem auger, 125 meters west of Interstate 95 Richmond-Petersburg Turnpike Bridge (37°14’5.26”N 77°23’50.19”W). The sample location correlated with the zone of highest contamination as identified by USACE borings in 1994. Samples were collected between 4.9 to 6.7 meters below the sediment surface from auger blades, transferred to 15 liter plastic containers, and immediately placed on ice until storage in a 4° C cooler at Virginia Tech Soils Laboratory. Table 3- 2 lists the properties of unamended sediment/soil after mixing. Preliminary testing of the samples revealed total petroleum hydrocarbons-diesel range organics (TPH-DRO) contamination ranging from 21 to 2620 mg kg^{-1}. To replicate the action of dredging and deposition within a confined facility, the homogenized sediment was neither air-dried nor screened prior to homogenization. The sediment moisture content remained near 100% of saturation before the experiment began. The

Table 3- 2. Properties of Appomattox Channel sediments (unlimed & unammended).

Physical-chemical Properties†		*Exchange Capacity*†	
Texture (USDA class)	sand	CEC ($cmol_c$ kg^{-1})	5.4
Organic Matter (%)	0.8	Base Cations (%)	85
pH	6.0		
Available Macronutrients† *(mg kg^{-1})*		*Available Micronutrients* † *(mg kg^{-1})*	
Total Kjeldahl Nitrogen	320	B	0.3
Available P	65	Cu	2.7
K	26	Fe	568
Ca	767	Mn	32
Mg	67	Mo	< 5
S	120	Zn	15.8

† *Analysis by Virginia Tech Soil Testing Laboratory*
(Maguire & Heckendorn, 2011)

pH of the homogenized soil was adjusted to 7.5 with the addition of lime in the form of calcium hydroxide according to the Mehlich Single Buffer Method outlined in Sims (1996).

Organic Treatments

Biosolids, compost, and straw were chosen as experimental organic treatments because of their availability and frequent use in the literature as well as in the Petersburg, VA area. Table 3-3 lists their nutrient properties. The amendments were obtained from the following sources: (1) biosolids from the Alexandria Sanitation Authority, Alexandria, VA; (2) compost from Yard Works LLC/Grind-All LLC, Richmond, VA; (3) and wheat straw was obtained from a local farm cooperative in Christiansburg VA. The biosolids were anaerobically digested and dewatered and had been used by our research group with positive results in a wide range of mined land

Table 3- 3. Amendment properties analyzed from frozen subsamples prior to mixing with sediment.

	Biosolids	Compost	Straw
Total Macronutrients (mg kg^{-1})			
TKN	54,900	8,400	20,200
Total P	33,500	900	800
K	1,300	2,600	6,000
Ca	21,900	16,300	3,800
Mg	3,900	2,800	1,200
S	8,700	1,400	600
Total Micronutrients (mg kg^{-1})			
B	NA	NA	5
Ni	17	72	1
Cu	314	32	3
Fe	54,000	10,510	145
Mn	560	433	55
Mo	8	BLD	0.1
Zn	732	112	11

BLD, below detection limits; NA, not analyzed remediation studies. The compost was produced from chipped/shredded wood and twig+leaf debris. The wheat straw was chopped to < 3 cm size fractions to mimic the effects of a mulch blower or combine.

Amendments were added on a dry weight basis to achieve soil to amendment ratios of 15:1, 25:1, and 40:1 or rates of approximately 90, 55 and 150 Mg ha^{-1} for biosolids, compost, and straw, respectively (Table 3- 4). Ratios were chosen based on typical quantities used for soil restoration (Cogger, 2005).

Greenhouse Experimental Design

Four treatments, including an unamended control, were tested in conditions both unvegetated and vegetated with tall fescue (*Schedonorus phoenix* (Scop.) Holub) and each treatment combination was replicated four times. The seven-liter pots (Figure 3- 3) were mixed at day 0 and again at day 150, when they were also re-sampled. The bottom of each pot was lined with 1.25 kg of clean, coarse sand and covered with plastic mesh fabric to ensure a

Table 3- 4. Amendment ratios, nutrient at day 0 and status of pots at 150 days. Nutrients are those available to plants analyzed by a 1:5 soil to Mehlich 1 solution.

	Control	Biosolids	Compost	Straw
% Amendment	0	4.1	6.1	2.4
Soil:Amendment (dry wt.)	-	24:1	16:1	42:1
Nutrients: day 0 (before fertilization)				
C:N	27	11	29	81
C:N:P	225:8:1	64:6:1	519:20:1	542:9:1
Pot Status: day150				
P (kg ha^{-1})	60	405	85	63
K (kg ha^{-1})	31	27	78	68
Ca (kg ha^{-1})	1,707	2,302	2,422	1,397
Mg (kg ha^{-1})	141	279	196	140
SS (mg kg^{-1})	589	1,472	1,578	877
pH	5.7	4.9	5.2	5.3
Base Saturation (%)	96	79	87	87
Avg. Monthly Veg. (dry g)	5.5	7.0	4.6	4.6

saturated zone did not exist in the contaminated sediments. Soil moisture was maintained at 80% field capacity daily by placing the pots on a balance and adding water until they reached their predetermined 80% FC mass. The 100% FC point was determined by thoroughly saturating each pot and weighing the pots after all "free water" had ceased to drain. Temperatures were maintained between 23 and 27° C during the study.

Nutrients varied by treatment due to large differences inherent to each amendment. The optimal nutrient ratio reported in literature is approximately C:N:P 100:10:1 (as totals of the elements per dry weight of material), but adding amendments to the pots at this ratio would translate to fertilizer rates exceeding agronomic rates by at least 10 times. This study used nutrient recommendations for tall fescue determined by routine soil testing (Maguire & Heckendorn, 2011). Fertilizer was applied to all pots after germination and establishment of tall fescue via a solution of KNO_3, NH_4NO_3 and Triple superphosphate (TPS), to avoid excess salt build-up on the sediment surface. The seeding rate was 50 kg ha^{-1}, and grass was clipped to 10 cm to maximize growth and encourage a uniform mat of culms across the pot surfaces. The

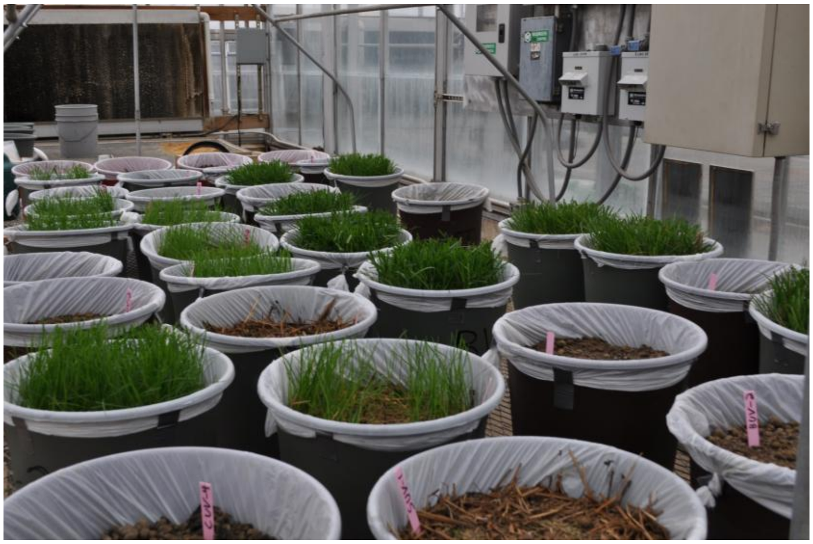


Figure 3- 3. Experimental pots shortly after establishment of vegetation.

clipped biomass was dried at 60°C and the dry mass recorded in Table 3- 3.

Sampling and PAH Analysis

At 0, 150 and 327 days, 100 grams of soil was collected and stored in a 4°C cooler until analysis. Day 0 samples were collected in replicate from the bulk treatments prior to placement of the treatments into the pots (e.g. biosolids were mixed with the sediment, the bulk material from this *treatment* was sampled, then the biosolids treatment was placed into individual pots). Samples collected at 150 and 327 days were collected from all pots for analysis. Individual pots were sampled by homogenizing 3 vertical transects (surface to bottom) of the pot sediment.

PAH extraction and analysis was performed by a certified EPA Contract Laboratory Program (CLP) (Air, Water and Soil Laboratories, Inc. in Richmond, VA) that uses analytical methods in compliance with EPA Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846) to extract, detect and quantify target analytes (EPA, 2007). PAHs were prepared by method 3550C, Ultrasonic Extraction; the samples were mixed with anhydrous sodium sulfate, forming a free flowing powder, followed by extraction with 100% methylene chloride and separation by gravity filtration through a bed of anhydrous sodium sulfate. Detection was performed by method 8270D, Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS) in a methylene chloride solution by elution through a fused-silica capillary column. In short, this procedure does not necessarily quantify the total PAH content of a given substrate but analyzes the mix of PAH’s that are available to the extractant (methylene chloride) at that time.

Statistics

This study was analyzed by analysis of variance using Proc Mixed in SAS (Proc Mixed, SAS Institute, 2004). Repeated measures analysis was used to test the main effects for sampling event (0, 150, and 327 days), treatment (control, biosolids, compost, and straw), and vegetation (vegetated and unvegetated), as well as all two-way interaction, and the three way interaction. A compound symmetry (CS) covariance structure was added to account for the variance due to repeated measurements taken on the same pot. The final statistical model included all three main effects, all two-way interactions, the three-way interaction, a covariance structure, and the experimental error (Littell et al., 1998).

RESULTS & DISCUSSION

Statistical analyses indicated that PAHs containing the same number of benzene rings behaved similarly (Table 3- 5). Three- and four-ring PAHs were significant at the two-way treatment by event interaction; five-ring PAHs were significant at the two-way vegetation by event interaction; and six-ring PAHs were significant at the three-way treatment by vegetation by event interaction. In addition, the main effect of vegetation was also significant for all 3- and 4-ring PAHs, except for PYR. Over the 327-day study period, decreases in concentration were highest for PAHs that contained the least number of benzene rings. In this study, large decreases in the concentration of 3- and 4-ring PAHs were observed at the 150 day sampling event for all three organic treatments, both vegetated and unvegetated, and the control treatment, as shown in Table 3- 6 and Table 3- 7 (raw data can be found in Appendix Table C- 1). Surprisingly, at the subsequent sampling event at 327 days, the concentrations of the PAHs increased, or “rebounded,” relative to the 150 day concentrations, and nearly all returned to their initial values with the exception of the control treatments. The apparent dip and rebound in PAH-contaminant concentration is interpreted to be a relic of the extraction procedure as discussed in detail later.

Table 3- 5. Summary of statistical analysis.

Source	ACN	ACL	ANT	BAA	BAP	BBF	BPR	CHR	FLR	FLU	INP	NAP	PHE	PYR
Trt	**	NS	*	**	**	**	**	**	**	**	**	**	**	NS
Veg	**	*	*	*	**	**	**	*	*	*	**	**	**	NS
TRT*VEG	NS	NS	NS	NS	NS	NS	**	NS	NS	NS	**	NS	NS	NS
Event	**	**	**	**	**	**	**	**	**	**	**	**	**	**
TRT*event	**	**	*	**	**	**	**	**	*	*	**	**	*	**
veg*event	NS	NS	NS	NS	**	**	**	NS	NS	NS	**	*	NS	NS
trt*veg*event	NS	NS	NS	NS	NS	NS	**	NS	NS	NS	**	NS	NS	NS

TRT, Treatment; VEG, Vegetation; NS, Not significant; * significant at $P < 0.05$, ** significant at $P < 0.01$.

Table 3- 6. Initial, midpoint and final concentrations (μg kg^{-1}) in pots for 3 and 4 ring PAHs.

	Control			**Biosolids**			**Compost**			**Straw**		
Days	0	150	327	0	150	327	0	150	327	0	150	327
3 Ring PAHs												
Acenaphthene	335 a	125 b	140 b	397 a	127 c	175 b	262 a	99 b	132 b	363 a	90 c	168 b
Acenaphthylene	139 a	91 b	77 b	118 a	56 b	124 a	95 a	53 b	121 a	126 a	55 c	95 b
Anthracene	976 a	259 b	270 b	813 a	294 c	449 b	773 a	200 b	249 b	890 a	155 c	417 b
Fluorene	198 a	73 b	87 b	165 a	68 c	97 b	151 a	52 b	76 b	191 a	50 c	114 b
Phenanthrene	1,117 a	455 b	438 b	911 a	356 c	590 b	802 a	284 b	401 b	1,105 a	340 c	612 b
4 Ring PAHs												
Benz(a)anthracene	883 a	715 b	590 b	798 b	422 c	1,051 a	620 a	362 b	557 a	1,053 a	438 c	728 b
Chrysene	726 a	609 ab	514 b	670 b	371 c	918 a	518 a	314 b	494 a	911 a	376 c	625 b
Fluoranthene	1,215 a	766 b	727 b	991 a	511 b	966 a	776 a	436 b	624 a	1,190 a	575 b	983 a
Pyrene	2,345 a	2,253 a	1,326 b	2,060 a	1,054 b	2,183 a	1,830 a	974 b	1,709 a	2,690 a	1,478 b	1,680 b

Means for each PAH x amendment combination followed by the same letters are not significantly different at $P < 0.05$.

Table 3- 7. Percent reduction of PAHs at 150 and 327 days.

	Control		**Biosolids**		**Compost**		**Straw**	
Days	150	327	150	327	150	327	150	327
3 Ring PAHs								
Acenaphthene	63	58	68	56*	62	50	75	54*
Acenaphthylene	35	45	53	0*	44	0*	56	25*
Anthracene	73	72	64	45*	74	68	83	53*
Fluorene	63	56	59	41*	66	50	74	40*
Phenanthrene	59	61	61	35*	65	50	69	45*
4 Ring PAHs								
Benz(a)anthracene	19	33	47	-32*	42	0*	58	31*
Chrysene	16	29	45	-37*	39	0*	59	31*
Fluoranthene	37	40	48	0*	44	0*	52	0*
Pyrene	0	43	49	0*	47	0*	45	38

* PAH concentrations significantly rebounded from samples analyzed at 150 days

As previously mentioned, PAH analysis during this study was conducted by a certified EPA contract laboratory by EPA SW-846 methods. The SW-846 methods have been utilized since 1980 for complying with Resource Conservation and Recovery Act (RCRA) regulations and as such the SW-846 methods are the most common method for analysis of dredged materials outside of research laboratories (EPA, 2007). Ultrasonic extraction of PAHs according to SW-846 method 3550C, utilizes organic solvents such as 1:1 acetone/hexane, 1:1 acetone/methylene chloride or 100% methylene chloride. The concentration of PAHs extracted by method 3550C is validated by analysis of laboratory analyzed samples that are spiked with known concentration of PAHs. Spiked samples have very limited sediment-contaminant interaction times and thus, the actual total concentration of PAHs in "aged" samples (field samples with much longer contaminant-particle interaction times) may be underestimated. Furthermore, previous studies have shown that PAHs can strongly adsorb to the organic fraction of sediments within a matter of hours (Pignatello & Xing, 1996). It is suspected that the rebound in PAH concentrations observed during this study from 150 to 327 days was caused by the fast uptake of PAHs by the organic treatments (biosolids, compost and straw) followed by the subsequent release of the PAHs as extractability increased. The lack of a "rebound effect" in the PAH concentrations of the control treatment samples supports this conclusion.

Our results indicate that unvegetated treatments had significantly lower PAH concentrations than vegetated treatments (Table 3- 8). Higher PAH concentrations of the vegetated treatments in the study were most likely not associated with lower degradation rates in these treatments but instead with increased desorption from bound phases due to rhizosphere effects and the subsequently higher levels of extractability or "rebound". Thus, PAH desorption was likely increased due to biosurfactants produced in rhizosphere. For INP and BPR (6 ring HMW PAHs) in unvegetated organic treatments, PAH concentrations decreased significantly from day 0 to day 150 (Table 3- 9). However, at day 327, there was a rebound back to initial values in the unvegetated biosolids and compost treatments. The vegetated biosolids and compost treatments, on the other hand, showed a larger rebound in INP and BPR concentrations such that levels at 327 days actually exceeded the initial concentrations. These results suggest that day 0 concentrations for INP and BPR in the biosolids and compost treatments may have underestimated actual concentrations due to extremely rapid adsorption to the organic

Table 3- 8. Statistical means for the main effect of vegetation for PAHs which were significantly different at $P < 0.05$.

	Unvegetated.	**Vegetated**
PAH	*($\mu g\ kg^{-1}$)*	
FLU	103 b	117 a
FLR	763 b	864 a
CHR	549 b	625 a
BAA	639 b	730 a
ANT	442 b	516 a

Means for each PAH followed by the same letters are not significantly different at $P < 0.05$.

Table 3- 9. Statistical means found during treatment * vegetation * time interactions of the 6 ring PAHs.

Vegetation	Days	Control	Biosolids	Compost	Straw
Indeno(1,2,3-cd)-pyrene (µg kg^{-1})					
N	0	379 a	240 a	210 ab	396 a
N	150	306 a	116 b	148 b	184 b
N	327	328 a	222 a	269 a	185 b
Y	0	379 a	240 b	210 b	396 a
Y	150	376 a	225 b	208 b	199 b
Y	327	237 b	654 a	366 a	262 b
Benzo(ghi)perlyene (µg kg^{-1})					
N	0	436 a	291 a	254 ab	442 a
N	150	356 a	140 b	163 b	222 b
N	327	422 a	265 a	327 a	268 b
Y	0	436 a	291 b	254 b	442 a
Y	150	522 a	298 b	241 b	243 b
Y	327	308 b	848 a	420 a	293 b

Means for each PAH x amendment x vegetative status combination followed by the same letters are not significantly different at $P < 0.05$.

amendments. This conclusion is again supported by a lack of rebound from 150 to 327 days in INP and BPR concentrations for the control treatments. In fact, the vegetated control treatment concentrations for INP and BPR were observed to decrease slightly from day 0 to day 327. These results suggest that vegetation is not only increasing the availability of PAHs to extraction but that the presence of vegetation also increases the bioavailability of PAHs to biodegradation.

At the onset of the study, only the concentration of BAP exceeded the industrial RBC of 210 µg kg^{-1} (Table 3- 1), and BAP did not decrease below the RBC for any treatment at any time during the study (see Table C- 1 for BAP concentrations). The mean BAP concentrations were 967 and 724 µg kg^{-1} for the vegetated biosolids and compost treatments respectively, whereas the nonvegetated biosolids (670 µg kg^{-1}) and compost (552 µg kg^{-1}) treatments had concentrations that were significantly lower at $P < 0.05$. Vegetated and unvegetated control and straw treatments did not differ significantly. Vegetation by event interactions for BAP concentrations resulted in decreases at 150 days followed by a relative increase at 327 days for both the vegetated and unvegetated treatments (Figure 3- 4). In all vegetated pots, the BAP concentrations rebounded back to initial concentrations at 327 days, whereas they rebounded slightly less in the unvegetated pots.

The mean minimum BAP concentration attained at 150 days was 487 µg kg^{-1} for the unvegetated treatments. Although this value still exceeds the industrial RBC (210 µg kg^{-1}), such a large apparent reduction in 150 days could lead to the erroneous conclusion that the treatments were successfully achieving degradation at an acceptable rate if the study was halted before a

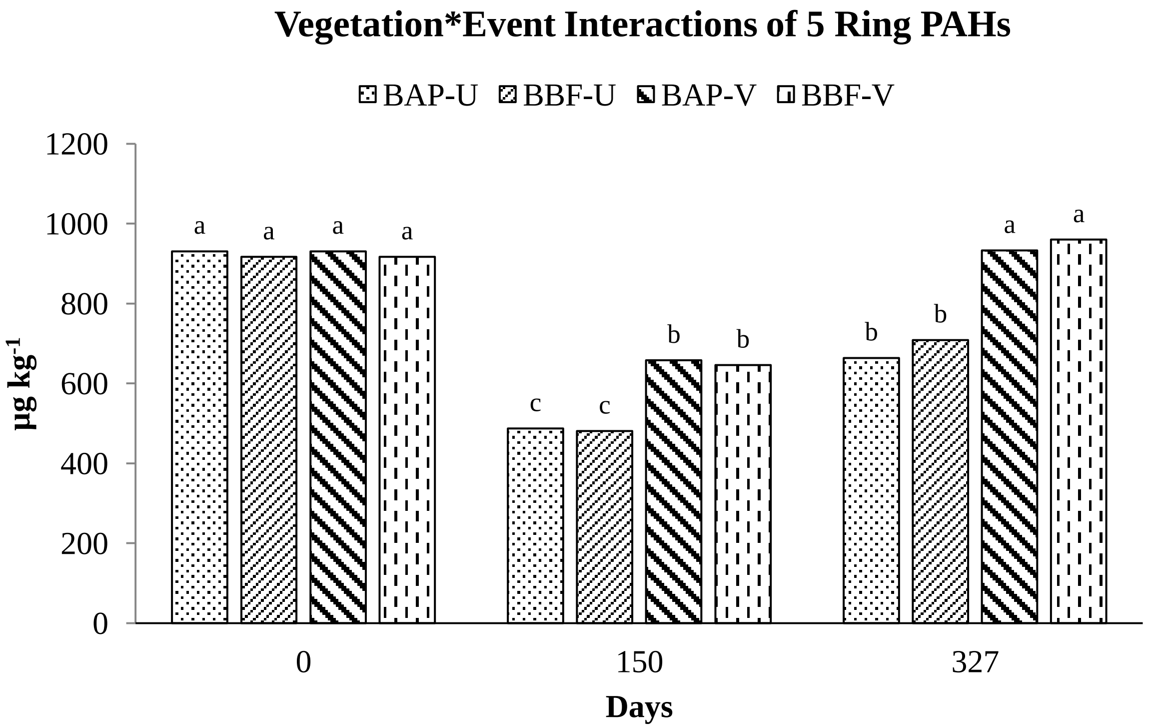


Figure 3- 4. The vegetation*event interactions of 5 ring PAHs. BAP, benzo(a)pyrene; BBF, benzo(b)fluoranthene; U, unvegetated; V, vegetated. Bars represent means of PAHs. Means for each PAH x vegetative status combination followed by the same letter are not statistically different at $P < 0.05$.

rebound of PAH concentrations had occurred. Alternatively, if the study were carried out for 327 days, the observation that BAP concentrations had decreased at 150 days and subsequently rebounded back to the initial concentration may provide the impetus to carry out the study for a longer period to determine if the increased availability of BAP under vegetated conditions would result in biodegradation.

CONCLUSION

Biodegradation can effectively lower PAH concentrations in contaminated, naturally-aged dredged materials. Organic treatments, including straw, biosolids, and compost amendments, caused a decrease in PAH concentrations during the first 150 days of the study, but by 327 days, PAH concentrations had rebounded relative to 150 day concentrations and approached original levels for recalcitrant PAHs like BAP. Ultrasonic extraction using organic solvents is the most commonly used extraction method and is preferred by the EPA. Our findings show, however, that this method potentially underestimates PAH concentrations in aged sediments possessing complex organic fractions or at a minimum, may not accurately reflect the levels of PAHs in materials such as these vs. their true bioavailability to degrading organisms and enzyme systems over time.

The presence of vegetation in this study resulted in PAH concentrations rebounding significantly higher than when vegetation was lacking. Additionally, the presence of vegetation caused increased bioavailability and biodegradation of INP and BPR, both HMW PAHs with 6 rings.

Benzo(a)pyrene was the only PAH found to have concentrations exceeding the EPA Regions III industrial RBC and no treatment significantly changed the concentration of BAP over the full course the study. Our findings suggest that when organic treatments are used for bioremediation of PAH contaminated sediments and analysis proceeds by standard EPA extraction methods, the study period must be longer than examined here. Pilot studies conducted outdoors with variable moisture and temperature conditions would likely require even longer times to account for PAH rebound effects and to accurately assay true biodegradation rates.

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CHAPTER IV

Summary and Overall Conclusions

Beneficial reuse of dredged materials offers an alternative to the disposal of a valuable natural resource. Unfortunately, millions of cubic meters of potentially suitable dredged materials that could be utilized as a productive resource are disposed of every year by open-water dumping or confinement in a disposal facility. The use of confined upland facilities (CUFs) with conversion to agricultural or similar uses is a new approach that has the potential to mitigate this problem.

Two factors were investigated during these thesis projects that inhibit the beneficial reuse potential of dredged materials in CUFs: (1) high levels of salinity, and (2) polycyclic aromatic hydrocarbon (PAH) contamination.

In the first study, 176,000 m^3 of saline dredged materials were placed into a CUF. In less than 4 years, rapid soil formation driven by ripening and desalinization of the dredged materials occurred. A polygonal prism network formed, exposing increasing amounts of unoxidized dredged materials with depth to oxidizing conditions, resulting in a better soil structure through disintegration of the larger prisms. As ripening continued, gleization, rubification, and pedoturbation (mainly by surface materials sloughing into the prismatic cracks) resulted in a Bg horizon with blocky structure, redoximorphic features and a redder hue than the underlying unripened dredged materials. Another notable observation was the dramatic shift in sediment chemistry that moved the saline sodium-dominated solution and solid phase chemistry to a desalinated chemistry dominated by calcium, magnesium, and potassium. The soils that resulted from these processes were classified as Inceptisols by Soil Taxonomy and in general, were well structured and very high in organic matter and exchangeable bases. It is expected that continued ripening of the saline dredged materials within the CUF will result in highly productive agricultural soils.

In the second study, bioremediation of PAH contaminated dredged materials was investigated through the additions of organic treatments (biosolids, compost and straw) which we presumed would enhance PAH degradation. The results indicated a dramatic decrease in PAHs during the first 150 days using standard methods of extraction and analysis. However, after an additional 150 day, many of the high molecular weight PAHs were observed to rebound back towards their initial concentrations. We believe that this may have been due to initial sorption/sequestration of the PAH's by the added organic substrates followed by increased extractability over a longer period of time. This important finding suggests that any future investigations that test the effectiveness of organic substrates to aid in bioremediation of PAHs must be carried out for periods longer than studied here if the current standard methods for extraction and analysis are used. Investigations conducted for shorter time periods could result in the erroneous conclusion that a treatment successfully reduced PAH concentrations when in fact, they had simply suppressed their "extractability" for some period of time. If a full scale remediation project was carried under this premise, project planners could be left with extremely large management and/or cleanup costs.

In conclusion, the beneficial reuse of dredged materials will become increasingly important as society becomes more aware of the potential that dredged materials have to be productive resources. As such, it is vital to continue to research different methodologies that allow for the beneficial reuse of a variety of different dredged materials.

APPENDICES

APPENDIX A

Table A- 1. Proposed sediment screening criteria for Virginia dredged material (Daniels et al., 2009).

PARAMETER	NJDEP (1997) Residential Soil Cleanup Criteria[3]	EPA Region 3 Screening Levels (EPA, 2008)[1]		Proposed VA Exclusion Criteria[2, 5]	Proposed VA Clean Upland Fill Criteria[2, 6]
		Industrial Soil	Residential Soil		
Metals (mg kg^{-1})					
Aluminum	NA	990,000	77,000	NA	NA
Antimony	14	410	31	410	14
Arsenic	20	1.6	0.39	41	20
Barium	700	19,000	15,000	19,000	700
Beryllium	1	2,000	160	2,000	160
Cadmium	39	810	70	810	39
Calcium	NA	NA	NA	NA	NA
Chromium	NA	200	39	1,200	200
Cobalt	NA	300	23	300	NA
Copper	600	41,000	3,100	4,300	1,500
Iron	NA	720,000	55,000	150,000	150000
Lead	400	800	400	800	300
Magnesium	NA	NA	NA	NA	NA
Manganese	NA	NA	NA	NA	NA
Mercury	14	100	7.8	100	14
Nickel	250	69,000	14,000	1,000	250
Potassium	NA	NA	NA	NA	NA
Selenium	63	5,100	390	5,100	63
Silver	110	5,100	390	5,100	110
Sodium	NA	NA	NA	NA	NA
Thallium	2	NA	NA	2	2
Vanadium	370	5,200	390	5,200	370
Zinc	1,500	310,000	23,000	7,500	1,500
Cyanide, Total	1,100	20,000	1,600	20,000	1,100
PCBS (mg kg^{-1})					
Aroclor 1016	NA	21	3.9	21	NA
Aroclor 1221	NA	0.62	0.17	0.62	NA
Aroclor 1232	NA	0.62	0.17	0.62	NA
Aroclor 1242	NA	0.74	0.22	0.74	NA
Aroclor 1248	NA	0.74	0.22	0.74	NA
Aroclor 1254	NA	0.74	0.22	0.74	NA

Table A- 1. Continued.

PARAMETER	NJDEP (1997) Residential Soil Cleanup Criteria[3]	EPA Region 3 Screening Levels (EPA, 2008)[1]		Proposed VA Exclusion Criteria[2, 5]	Proposed VA Clean Upland Fill Criteria[2, 6]
		Industrial Soil	Residential Soil		
Aroclor 1260	NA	0.74	0.22	0.74	NA
Total Aroclor[4]	0.49	25.2	5.1	25.2	0.49
Pesticides (mg kg^{-1})					
Dieldrin	0.042	0.11	0.03	0.11	0.042
Endosulfan	NA	3,700	370	3,700	NA
Endrin	17	180	18	180	17
Endrin aldehyde	NA	NA	NA	NA	NA
Endrin ketone	NA	NA	NA	NA	NA
Heptachlor	0.15	0.38	0.11	0.38	0.15
Heptachlor epoxide	NA	0.19	0.053	0.19	NA
Methoxychlor	280	3,100	310	3,100	280
alpha-BHC	NA	NA	NA	NA	NA
beta-BHC	NA	NA	NA	NA	NA
delta-BHC	NA	NA	NA	NA	NA
gamma-BHC (Lindane)	0.52	NA	NA	0.52	0.52
Toxaphene	0.1	1.6	0.44	1.6	0.1
alpha-Chlordane	NA	NA	NA	NA	NA
gamma-Chlordane	NA	NA	NA	NA	NA
Aldrin	0.04	0.11	0.029	0.11	0.04
4,4'-DDD	3	7.2	2	7.2	3
4,4'-DDE	2	5.1	1.4	5.1	2
4,4'-DDT	2	7	1.7	7	2
Semivolatiles (mg kg^{-1})					
Acenaphthene	3,400	33,000	3,400	33,000	3,400
Diethyl phthalate	10,000	490,000	49,000	490,000	10,000
2,4-Dimethylphenol	1,100	12,000	1,200	12,000	1,100
Dimethyl phthalate	10,000	NA	NA	10,000	10,000
Di-n-octyl phthalate	1,100	NA	NA	1,100	1,100
4,6-Dinitro-2-methylphenol	NA	NA	NA	NA	NA
2,4-Dinitrophenol	110	1,200	120	1,200	110
2,4-Dinitrotoluene	NA	1,200	120	1,200	NA
2,6-Dinitrotoluene	1	620	61	620	61
Anthracene	10,000	170,000	17,000	170,000	10,000
Fluoranthene	2,300	22,000	2,300	22,000	2,300
Fluorene	2,300	22,000	2,300	22,000	2,300
Hexachlorobenzene	0.66	1.1	0.3	1.1	0.66
Hexachlorobutadiene	1	22	6.2	22	1
Hexachlorocyclopentadiene	400	3,700	370	3,700	400

Table A- 1. Continued.

PARAMETER	NJDEP (1997) Residential Soil Cleanup Criteria[3]	EPA Region 3 Screening Levels (EPA, 2008)[1]		Proposed VA Exclusion Criteria[2, 5]	Proposed VA Clean Upland Fill Criteria[2, 6]
		Industrial Soil	Residential Soil		
Hexachloroethane	6	120	35	120	6
Indeno(1,2,3-cd)pyrene	0.9	2.1	0.15	2.1	0.9
Isophorone	1,100	1,800	510	1,800	1,100
2-Methylnaphthalene	NA	4,100	310	4,100	NA
2-Methylphenol	2,800	NA	NA	2,800	2,800
4-Methylphenol	2,800	NA	NA	2,800	2,800
Naphthalene	230	20	3.9	230	20
2-Nitroaniline	NA	NA	NA	NA	NA
3-Nitroaniline	NA	82	18	82	NA
4-Nitroaniline	NA	82	23	82	NA
Nitrobenzene	28	280	31	280	28
2-Nitrophenol	NA	NA	NA	NA	NA
4-Nitrophenol	NA	NA	NA	NA	NA
Benzo(a)anthracene	0.9	2.1	0.15	2.1	0.9
N-Nitroso-di-N-propylamine	0.66	0.25	0.069	0.66	0.25
N-Nitrosodiphenylamine	140	350	99	350	140
Benzo(b)fluoranthene	0.9	2.1	0.15	2.1	0.9
Benzo(k)fluoranthene	0.9	21	1.5	21	0.9
Benzo(ghi)perylene	NA	NA	NA	NA	NA
Benzo(a)pyrene	0.66	0.21	0.015	0.66	0.21
Pentachlorophenol	6	9	3	9	6
Phenanthrene	NA	NA	NA	NA	NA
Phenol	10,000	180,000	18,000	180,000	10,000
Pyrene	1,700	17,000	1,700	17,000	1,700
1,2,4-Trichlorobenzene	68	400	87	400	68
2,4,5-Trichlorophenol	5,600	62,000	6,100	62,000	5,600
2,4,6-Trichlorophenol	62	160	44	160	62
Carbazole	NA	NA	NA	NA	NA
bis(2-Chloroethoxy)methane	NA	1800	180	1,800	NA
bis(2-Chloroethyl) ether	0.66	0.9	0.19	0.9	0.66
bis(2-Ethylhexyl) phthalate	49	120	35	120	49
4-Bromophenyl phenyl ether	NA	NA	NA	NA	NA
2,2'-oxybis(1-Chloropropane)	2,300	NA	NA	2,300	2,300
Butyl benzyl phthalate	1,100	910	260	1,100	910
Acenaphthylene	NA	NA	NA	NA	NA
4-Chloroaniline	230	NA	NA	230	230
4-Chloro-3-methylphenol	10,000	NA	NA	10,000	10,000

Table A- 1. Continued.

PARAMETER	NJDEP (1997) Residential Soil Cleanup Criteria[3]	EPA Region 3 Screening Levels (EPA, 2008)[1]		Proposed VA Exclusion Criteria[2, 5]	Proposed VA Clean Upland Fill Criteria[2, 6]
		Industrial Soil	Residential Soil		
2-Chloronaphthalene	NA	NA	NA	NA	NA
2-Chlorophenol	280	5,100	390	5,100	280
4-Chlorophenyl phenyl ether	NA	NA	NA	NA	NA
Chrysene	9	210	15	210	9
Dibenz(a,h)anthracene	0.66	0.21	0.015	0.66	0.21
Dibenzofuran	NA	NA	NA	NA	NA
Di-n-butyl phthalate	5,700	NA	NA	5,700	5,700
1,2-Dichlorobenzene	5,100	10,000	2,000	10,000	5,100
1,3-Dichlorobenzene	5,100	NA	NA	5,100	5,100
1,4-Dichlorobenzene	570	13	2.6	570	13
3,3'-Dichlorobenzidine	2	3.8	1.1	3.8	2
2,4-Dichlorophenol	170	1,800	180	1,800	170
Dioxin and Furans (ng kg^{-1})					
2,3,7,8-TCDD	NA	18	4.3	18	4.3

Table A- 1. Continued.

Additional Analyses	Units/Reporting convention	Method	Proposed VA Exclusion Criteria[5]	Proposed VA Clean Fill Criteria[6]
Acid-base accounting (all samples > 0.25% total S)	Tons CCE acid demand per 1000 Tons Material	EPA 600-2-78-054	15 T/1000 T	5 T/1000 T
Soluble Salts	mmhos cm^{-1} or dS m^{-1}	Saturated paste extract	NA	4

1. EPA Region 3 SSLs have been merged into a regional document developed with input from Regions III, VI, and IX. Values from September 12, 2008 version. Values listed for: antimony (metallic), arsenic (inorganic), chromium VI (particulates), lead and compounds, manganese and cadmium values are for diet, methyl mercury, nickel refinery dust, vanadium and compounds. (EPA, 2011)
2. One-half the reporting limit (RL) assumed for chemicals reported as non-detect or < RL, however, these values will not be used for exclusionary purposed unless other evidence indicates such.
3. (New Jersey DEP, 1997).
4. Total Aroclor concentrations reported as sum of seven individual aroclors.
5. The proposed Virginia exclusion standards generally represent the higher of EPA RBC Industrial, NJDEP or EPA 503 EQ levels for a given parameter.
6. Proposed VA clean fill criteria are based primarily on NJDEP residential cleanup criteria and manually adjusted for known issues with agricultural production/bioavailability.

APPENDIX B

Table B- 1. Total metal analysis of four 23,000 cubic meter composites taken during dredging operations at the Earle Naval Weapons Station.

Analyte	Units	Composite Date			
		12/11/05	1/3/06	10/19/06	8/30/07
Aluminum	mg/kg	NA	57,700	49,282	NA
Antimony	mg/kg	2	2	< 0.5	< 2
Arsenic	mg/kg	5	9	7	4
Beryllium	mg/kg	< 0.5	< 2	0	< 0.5
Cadmium	mg/kg	1	1	0	< 0.5
Chromium	mg/kg	61	48	85	6
Copper	mg/kg	17	44	74	4
Lead	mg/kg	14	44	30	17
Iron	mg/kg	34,000	23,000	38,000	4200
Manganese	mg/kg	430	180	390	56
Mercury	mg/kg	2	1	1	< 0.5
Nickel	mg/kg	97	14	28	3
Selenium	mg/kg	< 0.5	< 5	< 0.5	< 0.5
Silver	mg/kg	< 0.5	1	1	< 0.5
Thallium	mg/kg	< 0.5	0	< 0.5	< 0.5
Zinc	mg/kg	35	100	72	51

Table B- 2. Polycyclic aromatic hydrocarbon concentrations in four 23,000 cubic meter composites taken during dredging operations at the Earle Naval Weapons Station.

Analyte	Units	Composite Date			
		12/11/05	1/3/06	10/19/06	8/30/07
Acenaphthene	µg/kg	500	NA	100*	NA
Acenaphthylene	µg/kg	13*	NA	100*	NA
Anthracene	µg/kg	80	NA	100*	1
Benzo(b)fluoranthene	µg/kg	300	NA	110*	0
Benzo(a)anthracene	µg/kg	350	NA	200	0
Benzo(a)pyrene	µg/kg	100	NA	150	0
Benzo(ghi)perylene	µg/kg	200	NA	100*	0*
Benzo(k)fluoranthene	µg/kg	100	NA	120	0
Chrysene	µg/kg	500	NA	230	0
Dibenzo(a,h)anthracene	µg/kg	400	NA	100*	0*

* analytes concentration reported at 50% of reporting limit at the time of analysis.

Table B- 2. Continued.

Analyte	Units	Composite Date			
		12/11/05	1/3/06	10/19/06	8/30/07
Fluoranthene	µg/kg	850	NA	450	1
Fluorene	µg/kg	13*	NA	100*	1
Indeno(1,2,3-cd)pyrene	µg/kg	100	NA	100*	0*
Naphthalene	µg/kg	1800	NA	100*	0
Phenanthrene	µg/kg	400	NA	130	2
Pyrene	µg/kg	500	NA	400	NA

* analytes concentration reported at 50% of reporting limit at the time of analysis.

Table B- 3. Pesticide and polychlorinated biphenyls concentrations in four 23,000 cubic meter composites taken during dredging operations at the Earle Naval Weapons Station.

Analyte	Units	Composite Date			
		12/11/05	1/3/06	10/19/06	8/30/07
alpha-BHC	µg/kg	55*	45*	60*	27*
beta-BHC	µg/kg	55*	45*	60*	27*
gamma-BHC	µg/kg	55*	45*	60*	27*
delta-BHC	µg/kg	55*	45*	60*	27*
Heptachlor	µg/kg	55*	45*	60*	27*
Aldrin	µg/kg	55*	45*	60*	27*
Heptachlor epoxide	µg/kg	55*	45*	60*	27*
gamma-Chlordane	µg/kg	110*	90*	125*	55*
Endosulfan I	µg/kg	110*	90*	125*	55*
alpha-Chlordane	µg/kg	110*	90*	125*	55*
Dieldrin	µg/kg	110*	90*	125*	55*
4,4'-DDE	µg/kg	110*	90*	125*	55*
Endrin	µg/kg	110*	90*	125*	55*
Endosulfan II	µg/kg	325*	270*	375*	160*
4,4'-DDD	µg/kg	325*	270*	375*	160*
Endrin aldehyde	µg/kg	325*	270*	375*	160*
Endosulfan sulfate	µg/kg	325*	270*	375*	160*
4,4'-DDT	µg/kg	325*	270*	375*	160*
Endrin Ketone	µg/kg	325*	270*	375*	160*
Methoxychlor	µg/kg	550*	445*	600*	270*

* analytes concentration reported at 50% of detection limit at the time of analysis.

Table B- 3. Continued.

Analyte	Units	Composite Date			
		12/11/05	1/3/06	10/19/06	8/30/07
Toxaphene	µg/kg	3250*	2700*	3750*	550*
Technical Chlordane	µg/kg	1100*	900*	1250*	1600*
Aroclor 1016	µg/kg	1100*	900*	1250*	550*
Aroclor 1221	µg/kg	1100*	900*	1250*	550*
Aroclor 1232	µg/kg	1100*	900*	1250*	550*
Aroclor 1242	µg/kg	1100*	900*	1250*	550*
Aroclor 1248	µg/kg	1100*	900*	1250*	550*
Aroclor 1254	µg/kg	1100*	900*	1250*	550*
Aroclor 1260	µg/kg	1100*	900*	1250*	550*
Total PCBs	µg/kg	1100*	900*	1250*	550*

* analytes concentration reported at 50% of reporting limit at the time of analysis.

Table B- 4. Solution phase properties of the ENWS CUF 3 (2008) and 4 (2009) years after placement.

2008									2009								
Horizon	Depth	EC	Ca^{2+}	Mg^{2+}	K^{+}	Na^{+}	Cl^{-}	SO_4^{2-}	Horizon	Depth	EC	Ca^{2+}	Mg^{2+}	K^{+}	Na^{+}	Cl^{-}	SO_4^{2-}
	cm	*dS m^{-1}*	*mg L^{-1}*							*cm*	*dS m^{-1}*	*mg L^{-1}*					
Sample Point 3									*Sample Point 3*								
^AC	0-25	17	582	482	145	2233	3041	1315	^Ap	0-20	12	514	1126	169	2621	3278	2373
^Cg1	25-45	18	587	560	161	2715	3893	1424	^Bg	15-60	15	598	798	178	3582	4674	1880
^Cg2	45-110	24	662	708	212	3780	5384	1706	^Cg	60-102	19	606	868	205	4410	6757	1886
2Btb	110-115	9.5	318	180	70	1595	2710	438	2Btb	102-107	7.2	158	135	50	1345	2308	195
Sample Point 5									*Sample Point 5*								
^Ap	0-25	18	559	701	135	2449	3006	1657	^Ap	0-20	5.8	561	376	98	761	701	1151
^Bg	25-65	18	563	704	160	2507	3349	1725	^Bg	15-82	10	549	623	134	2156	2201	1821
^Cg	65-127	23	575	591	181	2968	3716	1611	^Cg	82-109	16	616	863	191	3857	4733	2367
2Btb	127-132	7.3	57	105	33	1636	2603	162	2Btb	109-114	7.7	153	183	38	1620	2024	577
Sample Point 7									*Sample Point 7*								
^Ap	0-25	7.1	579	252	63	647	828	852	^Ap	0-20	4.7	587	223	130	438	728	712
^Bg	25-57	10	588	563	152	2347	1787	1647	^Bg	20-75	9.8	513	815	150	1776	1704	2155
^Cg	57-115	24	584	608	168	2714	3254	1747	^Cg	75-100	11	584	685	140	2446	2580	1985
2Btb	115-120	10	181	182	64	1453	1716	649	2Btb	100-105	6.1	126	135	32	1271	1538	538
Sample Point 9									*Sample Point 9*								
^AC	0-30	8.6	594	306	96	1312	1669	1054	^Ap	0-20	7.0	614	343	111	1114	1296	1119
^Cg1	30-59	18	632	520	159	2515	3231	1439	^Bg	20-30	11	587	569	131	2269	2994	1482
^Cg2	59-69	22	627	582	160	2855	3964	1523	^Cg	30-66	12	654	620	146	2650	3455	1679
2Btgb	69-74	11	273	236	82	1747	2450	640	2Btb	66-71	7.9	578	281	73	1534	2237	864
Sample Point 13									*Sample Point 13*								
^Ap	0-30	7.9	531	343	106	983	1112	1028	^Ap	0-20	3.9	540	241	46	360	328	827
^Bg	30-73	17	532	500	131	2136	2592	1389	^Bg	20-50	7.3	504	456	92	1235	1254	1372
^Cg	73-108	18	565	648	164	2603	3325	1650	^Cg	50-92	9.5	577	581	134	1893	1858	1743
2Btb	108-113	11	270	285	91	1507	1763	882	2Btb	92-97	5.9	360	255	78	1084	1030	959

Table B- 4. Continued.

2008									2009								
Horizon	Depth	EC	Ca^{2+}	Mg^{2+}	K^{+}	Na^{+}	Cl^{-}	SO_4^{2-}	Horizon	Depth	EC	Ca^{2+}	Mg^{2+}	K^{+}	Na^{+}	Cl^{-}	SO_4^{2-}
	cm	*dS m^{-1}*	*mg L^{-1}*							cm	*dS m^{-1}*	*mg L^{-1}*					
Sample Point 15									*Sample Point 15*								
^A	0-30	24	636	600	246	3920	5775	1463	^Ap	0-20	16.7	799	578	350	3695	5976	1315
^Cg	30-150	31	308	572	223	4036	6437	957	^Bg	20-137	21.0	819	919	281	5272	8153	2082
2Btgb	150-155	6.6	133	92	45	1057	1941	128	2Btb	137-142	5.2	156	78	28	863	1799	89
Sample Point 17									*Sample Point 17*								
^Ap	0-25	3.7	530	117	39	239	118	644	^Ap	0-20	3.2	537	96	109	116	336	471
^Cg1	25-48	14	602	676	161	2841	3704	0	^Bg	20-49	7.0	528	317	56	1088	1207	1058
^Cg2	48-115	20	605	613	171	2946	3739	1744	^Cg	49-101	12.6	619	699	152	2955	3325	2099
2Btb	115-120	8.2	34	42	13	955	1633	40	2Btb	101-106	6.2	82	72	16	1273	1882	281
Sample Point 19									*Sample Point 19*								
^Ap	0-20	14	530	472	118	1676	2047	1282	^Ap	0-20	9.0	561	380	90	1162	1692	1049
^Bg	20-67	19	486	708	148	2086	2544	1762	^Bg	20-61	14.6	579	754	123	2508	3183	1879
^Cg	67-101	22	651	399	140	2056	2521	1375	^Cg	61-89	15.0	674	655	115	2726	3290	1976
2Btb	101-106	6.6	45	61	39	1175	1870	112	2Btb	89-94	6.8	96	113	39	1102	1503	367
Sample Point 21									*Sample Point 21*								
^EC	0-30	14	593	401	128	1963	2627	1238	^Ap	0-20	9.2	654	470	167	1434	1988	1238
^Cg1	30-60	20	620	449	146	2332	3219	1266	^Bg	20-50	14.4	678	765	144	2797	4059	1617
^Cg2	60-97	28	555	577	166	2741	3728	1575	^Cg	50-86	16.9	786	832	155	3777	4970	2225
2Btb	97-102	7.8	152	121	37	1673	2680	221	2Btb	86-91	8.3	434	336	62	1460	1858	1114
Sample Point 23									*Sample Point 23*								
^Ap	0-20	6.9	540	265	84	843	994	954	^Ap	0-20	4.5	618	197	72	370	490	746
^Cg	20-73	14	563	425	128	1791	2130	1233	^Bg	20-67	12.8	606	679	109	2500	1680	1607
2Btb	73-78	12	419	347	94	2121	3065	883	2Btb	67-72	8.4	383	211	39	1378	2319	533

Table B- 4. Continued.

2008									2009								
Horizon	Depth	EC	Ca^{2+}	Mg^{2+}	K^{+}	Na^{+}	Cl^{-}	SO$_4^{2-}$	Horizon	Depth	EC	Ca^{2+}	Mg^{2+}	K^{+}	Na^{+}	Cl^{-}	SO$_4^{2-}$
	cm	*dS m^{-1}*				*mg L^{-1}*				*cm*	*dS m^{-1}*				*mg L^{-1}*		
Sample Point 25									*Sample Point 25*								
^A	0-25	4.2	410	139	57	941	1385	518	^Ap	0-20	7.7	640	232	68	1067	1882	772
^Cg1	25-55	11.9	719	313	121	2024	2816	1089	^Bg	20-56	3.5	506	97	35	317	291	623
^Cg2	55-158	12.4	717	571	211	2548	4094	1368	^Cg	56-160	8.3	599	367	119	1635	2035	1242
2Btb	158-163	4.8	45	39	9	889	1456	71	2Btb	160-165	5.0	82	70	14	933	1160	318
Sample Point 27									*Sample Point 27*								
^AC	0-20	16.3	555	423	136	2311	2958	1331	^Ap	0-20	12.2	844	547	130	2400	3432	1369
^Cg1	20-50	24.2	633	635	189	3227	4296	1605	^Bg	20-48	13.7	736	620	149	2982	4154	1574
^Cg2	50-104	23.8	675	683	203	3548	5349	1596	^Cg	48-109	21.0	754	871	228	4844	7065	1926
2Btgb	104-109	7.6	116	88	51	1204	2213	99	2Btb	109-114	7.5	262	149	49	1296	2355	318
Sample Point 29									*Sample Point 29*								
^AC	0-20	11.3	575	426	124	1846	2106	1361	^Ap	0-20	11.7	654	642	187	2330	3384	1470
^Cg1	20-36	14.1	578	456	132	2128	2674	1328	^Bg	20-53	15.7	665	1050	186	3380	4710	2166
^Cg2	36-70	25.1	688	632	158	2807	3657	1834	^Cg	53-72	20.4	768	973	181	4350	6414	2147
2Btgb	70-75	10.0	125	118	38	1544	2461	164	2Btb	72-77	7.4	322	205	22	1240	1811	562
Sample Point 32									*Sample Point 32*								
^AC	0-20	6.6	505	249	77	756	769	945	^Ap	0-20	8.0	732	380	125	1185	1633	1144
^Cg	20-60	18.2	557	515	131	2300	3160	1398	^Bg	20-63	9.3	567	451	91	1651	2000	1289
2Btb	60-65	11.5	485	310	59	1678	2450	999	2Btb	63-68	6.5	265	166	14	1154	1704	532

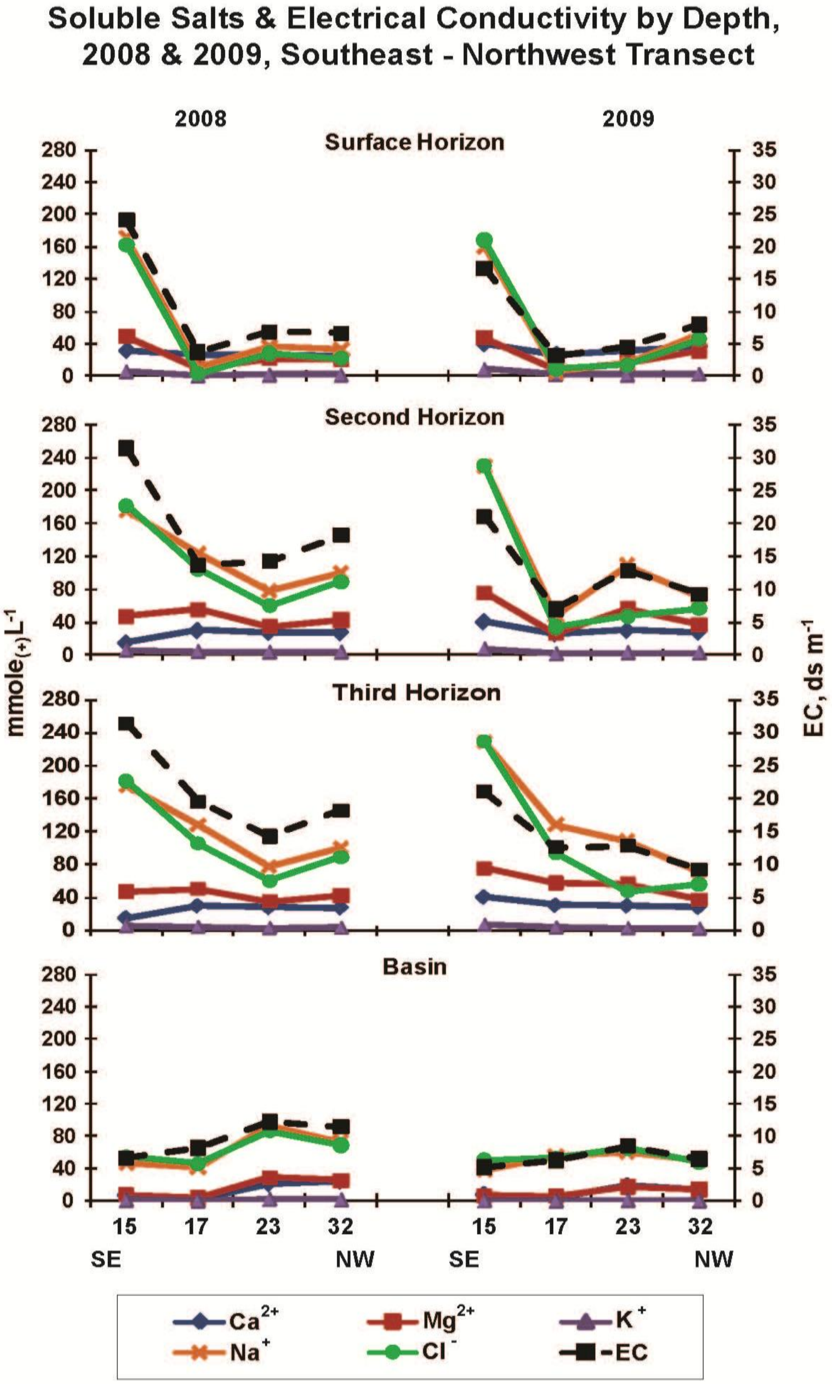


Figure B- 1. Water soluble salt compositions along cross section of the CUF. Concentrations in the order of highest to lowest are: sodium, magnesium, calcium and potassium. The composition is similar to the cation composition found in seawater. The dominant soluble cation, sodium, is paired with chloride as observed by their similar concentrations in solution. The sodium chloride ion pair is also observed to have the greatest influence on the EC .

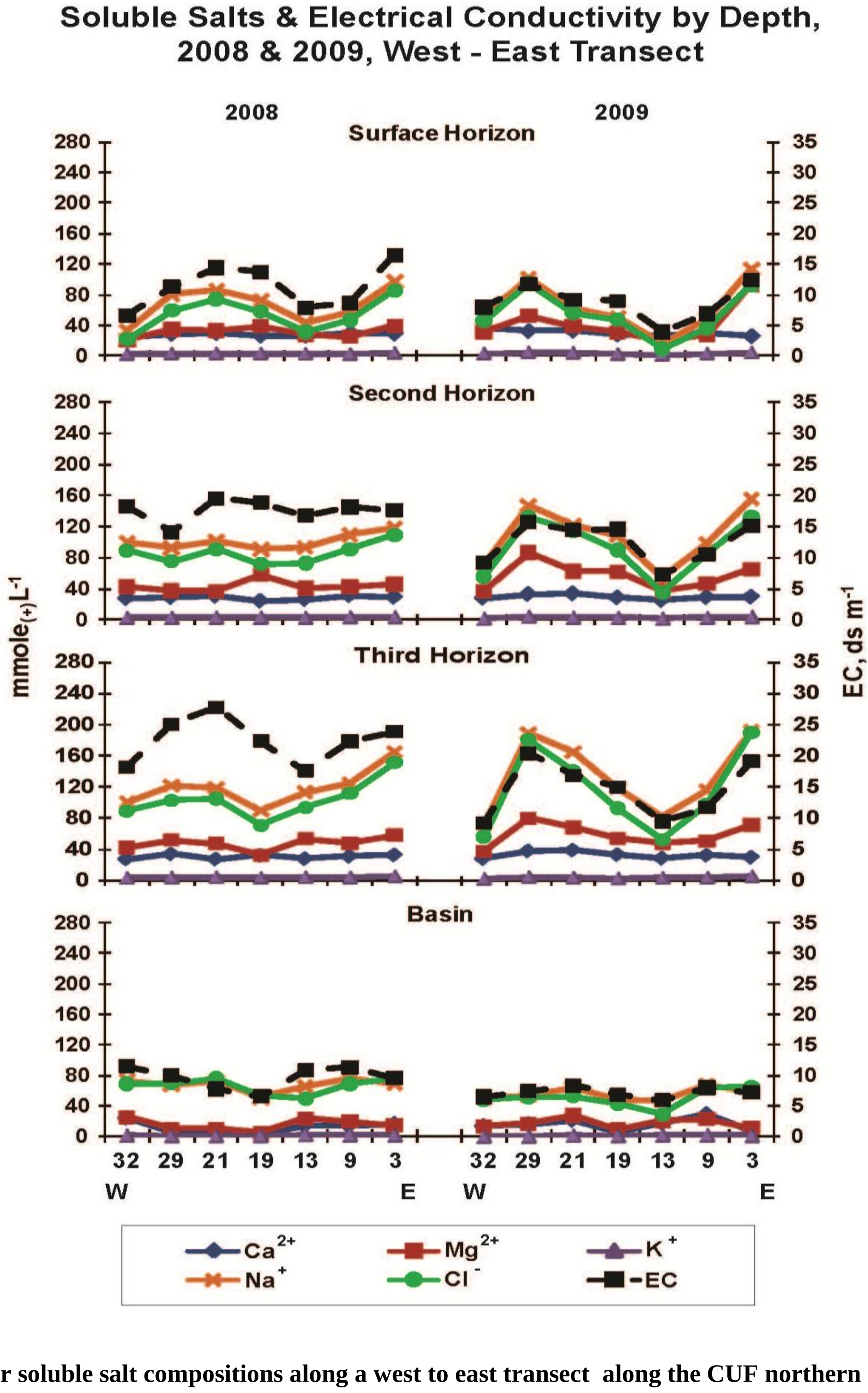


Figure B- 2. Water soluble salt compositions along a west to east transect along the CUF northern edge, immediately adjacent to the fluctuating saline pond. Local increases in the sodium chloride and other cations from 2008 to 2009 are the result of fluctuating saline conditions in the adjacent ponded region of the CUF. Although slight increases of specific cations are observed total salinity as measured by EC still decreases.

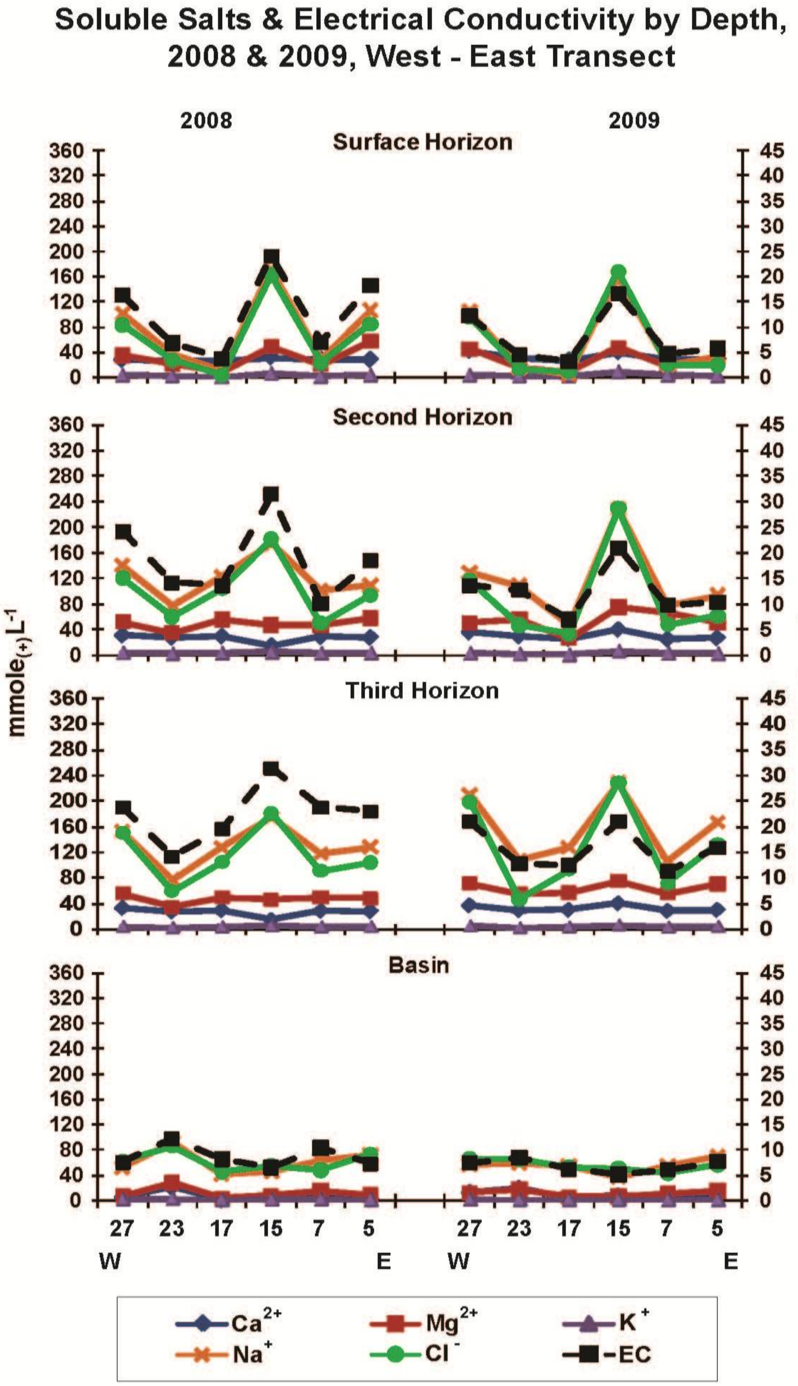


Figure B- 3. Water soluble salt compositions for a west to east transect along the CUFs southern edge, immediately adjacent to the discharge area. Large spatial variability is the result of a complex relationship between soil depth, texture and the internal CUF water table fluctuations.

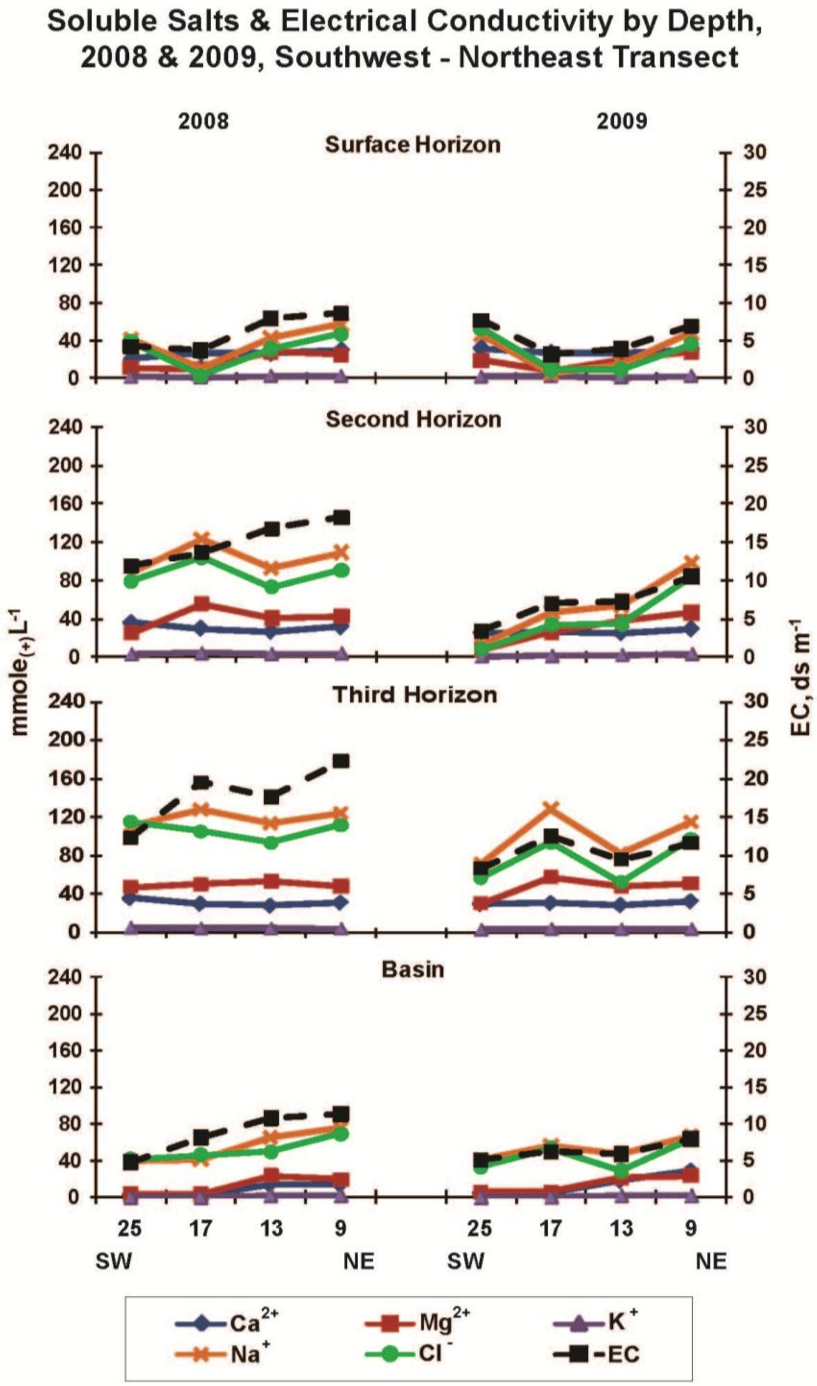


Figure B- 4. Water soluble salt concentrations in ENWS CUF along a cross section radiating from the discharge point. Sodium and chloride values mirror one another and buffer the EC of the pore waters. The high leaching potential of sodium and chloride is evident by large surface reductions and subsequent increases in the underlying native soil. Increasing salt concentrations from the southwest to the northeast result from ponded saline waters that fluctuate in the northeastern side of the CUF.

Table B- 5. Solid phase properties of the ENWS CUF 3 (2008) and 4 (2009) years after placement.

2008									2009								
Horizon	Depth	pH	Ca^{2+}	Mg^{2+}	K^{+}	Na^{+}	CEC*	SAR	Horizon	Depth	pH	Ca^{2+}	Mg^{2+}	K^{+}	Na^{+}	CEC*	SAR
	cm		$cmol_c\ kg^{-1}$							*cm*		$cmol_c\ kg^{-1}$					
Location EAC 3									*Location EAC 3*								
^AC	0-25	7.8	42.3	9.9	2.6	5.7	47	23	^Ap	0-20	5.5	49.8	8.3	2.3	5.0	53	21
^Cg1	25-45	7.9	38.3	8.7	2.3	5.3	42	27	^Bg	15-60	7.6	45.9	11.3	2.6	8.4	49	32
^Cg2	45-110	7.7	31.1	8.4	2.2	8.5	31	34	^Cg	60-102	7.8	26.0	10.1	2.5	10.8	25	38
2Btb	110-115	7.5	4.1	1.4	0.4	0.9	4.6	25	2Btb	102-107	8.0	2.6	1.8	0.5	1.8	2.6	27
Location EAC 5									*Location EAC 5*								
^Ap	0-25	7.7	63.2	9.2	1.8	5.1	67	23	^Ap	0-20	7.2	66.4	8.0	2.0	3.1	71	8.6
^Bg	25-65	7.8	51.4	8.9	1.9	5.5	55	24	^Bg	15-82	7.5	48.3	9.1	2.3	5.0	52	21
^Cg	65-127	7.7	36.3	8.8	2.1	8.9	36	30	^Cg	82-109	7.9	35.1	9.9	2.4	6.9	38	33
2Btb	127-132	7.2	1.8	2.9	0.4	3.3	1.5	42	2Btb	109-114	6.7	2.1	3.0	0.6	2.4	2.7	30
Location EAC 7									*Location EAC 7*								
^Ap	0-25	7.9	58.4	6.0	1.4	1.9	62	8	^Ap	0-20	7.1	62.9	5.4	2.7	1.5	67	5.5
^Bg	25-57	7.8	52.6	6.7	1.2	0.0	59	24	^Bg	20-75	4.8	55.8	5.3	1.7	2.8	58	16
^Cg	57-115	7.8	41.1	9.5	2.2	8.3	42	25	^Cg	75-100	8.4	43.7	11.6	2.4	10.5	45	23
2Btb	115-120	7.6	4.4	3.2	0.4	2.3	5.4	26	2Btb	100-105	6.4	2.6	3.4	0.5	2.5	3.6	27
Location EAC 9									*Location EAC 9*								
^AC	0-30	7.9	45.9	6.4	2.1	2.6	50	12	^Ap	0-20	7.2	61.2	8.0	2.7	3.5	66	13
^Cg1	30-59	8.0	32.7	7.5	2.1	3.2	37	23	^Bg	20-30	7.7	50.0	9.4	2.3	6.0	53	23
^Cg2	59-69	7.8	40.3	6.9	2.2	3.3	44	25	^Cg	30-66	7.0	49.1	9.1	2.4	6.8	51	25
2Btgb	69-74	7.7	5.4	2.3	0.4	1.4	6.3	22	2Btb	66-71	7.5	5.2	1.9	0.6	0.7	6.4	19

* CEC values are only rough approximations calculated by the summation of exchangeable calcium and magnesium minus exchangeable sodium.

Table B- 5. Continued.

2008									2009								
Horizon	Depth	pH	Ca^{2+}	Mg^{2+}	K^{+}	Na^{+}	CEC^{*}	SAR	Horizon	Depth	pH	Ca^{2+}	Mg^{2+}	K^{+}	Na^{+}	CEC^{*}	SAR
	cm		*$cmol_c$ kg^{-1}*							*cm*		*$cmol_c$ kg^{-1}*					
Location EAC 13									*Location EAC 13*								
^Ap	0-30	8.1	42.8	7.8	2.2	2.3	48	12	^Ap	0-20	7.7	57.9	6.6	1.7	1.5	63	4.6
^Bg	30-73	7.9	41.2	9.8	2.1	6.1	45	23	^Bg	20-50	7.7	60.5	9.1	2.2	4.5	65	14
^Cg	73-108	7.8	37.9	7.5	1.7	4.5	41	25	^Cg	50-92	8.4	45.2	9.6	2.5	5.3	50	19
2Btb	108-113	7.7	4.7	2.9	0.7	1.6	6.0	22	2Btb	92-97	7.3	7.0	3.4	0.8	1.2	9.2	15
Location EAC 15									*Location EAC 15*								
^A	0-30	8.1	19.6	2.8	0.6	2.7	20	38	^Ap	0-20	7.3	16.9	2.4	0.7	0.7	19	34
^Cg	30-150	7.9	23.9	6.4	1.5	5.0	25	47	^Bg	20-137	8.6	18.8	5.0	1.4	2.6	21	43
2Btgb	150-155	7.0	4.7	2.1	0.4	2.0	4.8	24	2Btb	137-142	7.1	6.0	2.1	0.3	1.5	6.6	20
Location EAC 17									*Location EAC 17*								
^Ap	0-25	8.0	34.4	3.2	0.9	1.0	37	3	^Ap	0-20	7.8	19.1	2.2	1.3	0.4	21	1.7
^Cg1	25-48	8.0	54.3	10.1	1.9	12.0	53	27	^Bg	20-49	7.6	54.9	6.8	1.4	3.7	58	13
^Cg2	48-115	7.6	35.5	7.5	1.6	5.0	38	29	^Cg	49-101	7.9	40.8	8.7	1.8	6.2	43	27
2Btb	115-120	7.3	2.5	2.2	0.2	2.5	2.1	37	2Btb	101-106	7.4	2.5	2.8	0.4	2.9	2.4	35
Location EAC 19									*Location EAC 19*								
^Ap	0-20	7.8	49.9	8.7	2.0	3.7	55	18	^Ap	0-20	7.3	62.6	7.7	2.1	3.7	67	13
^Bg	20-67	4.5	51.0	6.9	1.8	5.6	52	20	^Bg	20-61	7.2	57.3	6.4	1.6	2.8	61	23
^Cg	67-101	7.7	29.6	10.7	1.9	9.9	31	23	^Cg	61-89	6.8	42.9	9.8	2.0	7.1	46	25
2Btb	101-106	7.6	2.9	1.9	0.4	1.9	2.9	38	2Btb	89-94	7.8	2.3	2.1	0.4	1.6	2.9	26

* CEC values are only rough approximations calculated by the summation of exchangeable calcium and magnesium minus exchangeable sodium.

Table B- 5. Continued.

2008									2009							
Horizon	Depth	pH	Ca^{2+}	Mg^{2+}	K^{+}	Na^{+}	CEC*	SAR	Horizon	Depth	pH	Ca^{2+}	Mg^{2+}	K^{+}	Na^{+}	CEC*	SAR
	cm		$cmol_c\ kg^{-1}$							*cm*		$cmol_c\ kg^{-1}$					
Location EAC 21									*Location EAC 21*								
^AC	0-30	7.9	42.1	7.4	2.0	3.3	46	22	^Ap	0-20	7.2	53.5	8.6	2.8	3.7	58	15
^Cg1	30-60	7.9	35.1	7.4	1.9	6.2	36	25	^Bg	20-50	8.1	51.4	9.0	2.0	5.2	55	25
^Cg2	60-97	7.9	40.1	9.6	2.0	8.9	41	28	^Cg	50-86	7.9	29.2	9.7	2.0	8.8	30	32
2Btb	97-102	7.9	3.6	1.8	0.3	0.9	4.4	35	2Btb	86-91	6.7	3.6	2.3	0.5	1.5	4.3	18
Location EAC 23									*Location EAC 23*								
^Ap	0-20	7.9	34.9	7.1	1.9	2.4	40	11	^Ap	0-20	7.4	41.2	5.2	2.0	1.2	45	4.7
^Cg	20-73	7.9	35.5	7.7	1.7	4.2	39	22	^Bg	20-67	7.8	52.1	7.3	1.5	3.1	56	23
2Btb	73-78	7.7	4.8	2.0	0.4	1.4	5.4	26	2Btb	67-72	7.1	3.7	1.6	0.4	1.3	4.1	20
Location EAC 25									*Location EAC 25*								
^A	0-25	8.1	13.7	1.3	0.4	0.3	15	15	^Ap	0-20	8.0	29.7	2.8	0.8	1.5	31	13
^Cg1	25-55	8.1	20.3	2.0	0.5	1.9	20	22	^Bg	20-56	7.7	9.9	0.7	0.2	0.2	10	4.8
^Cg2	55-158	7.9	9.7	1.2	0.2	0.9	10	24	^Cg	56-160	7.9	9.9	1.1	0.3	0.8	10	18
2Btb	158-163	7.4	2.9	2.3	0.3	2.5	2.7	33	2Btb	160-165	6.8	3.1	3.2	0.4	1.9	4.4	26
Location EAC 27									*Location EAC 27*								
^AC	0-20	7.9	37.3	5.6	1.4	3.1	40	25	^Ap	0-20	7.8	46.5	5.9	1.5	3.8	49	22
^Cg1	20-50	7.3	48.1	7.2	1.7	4.7	51	31	^Bg	20-48	7.0	47.1	7.4	1.7	5.5	49	28
^Cg2	50-104	7.7	23.9	5.2	1.4	3.7	26	33	^Cg	48-109	8.2	23.9	7.3	1.9	5.4	26	40
2Btgb	104-109	8.0	5.2	2.2	0.4	2.2	5.2	29	2Btb	109-114	8.2	4.1	1.9	0.5	1.7	4.4	22

* CEC values are only rough approximations calculated by the summation of exchangeable calcium and magnesium minus exchangeable sodium.

Table B- 5. Continued.

2008									2009								
Horizon	Depth	pH	Ca^{2+}	Mg^{2+}	K^{+}	Na^{+}	CEC*	SAR	Horizon	Depth	pH	Ca^{2+}	Mg^{2+}	K^{+}	Na^{+}	CEC*	SAR
	cm		*$cmol_c$ kg^{-1}*							*cm*		*$cmol_c$ kg^{-1}*					
Location EAC 29									*Location EAC 29*								
^AC	0-20	7.7	42.9	7.3	2.0	1.7	49	20	^Ap	0-20	7.8	59.4	9.2	2.6	4.0	65	22
^Cg1	20-36	7.8	31.4	7.9	2.0	3.4	36	23	^Bg	20-53	7.9	55.9	11.7	2.2	10.8	57	27
^Cg2	36-70	7.9	39.0	7.8	1.9	4.3	43	26	^Cg	53-72	7.6	42.6	11.2	2.1	10.6	43	35
2Btgb	70-75	7.9	3.1	1.6	0.2	1.3	3.5	34	2Btb	72-77	7.4	2.9	1.4	0.2	0.2	4.2	19
Location EAC 32									*Location EAC 32*								
^AC	0-20	7.7	44.4	7.1	1.7	2.6	49	10	^Ap	0-20	7.6	42.5	7.0	2.3	2.5	47	13
^Cg	20-60	7.6	49.2	8.3	1.9	5.4	52	20	^Bg	20-63	7.8	48.5	8.1	1.9	4.1	52	18
2Btb	60-65	6.9	7.5	3.3	0.4	3.0	7.8	20	2Btb	63-68	6.6	3.9	2.9	0.3	2.6	4.3	19

* CEC values are only rough approximations calculated by the summation of exchangeable calcium and magnesium minus exchangeable sodium.

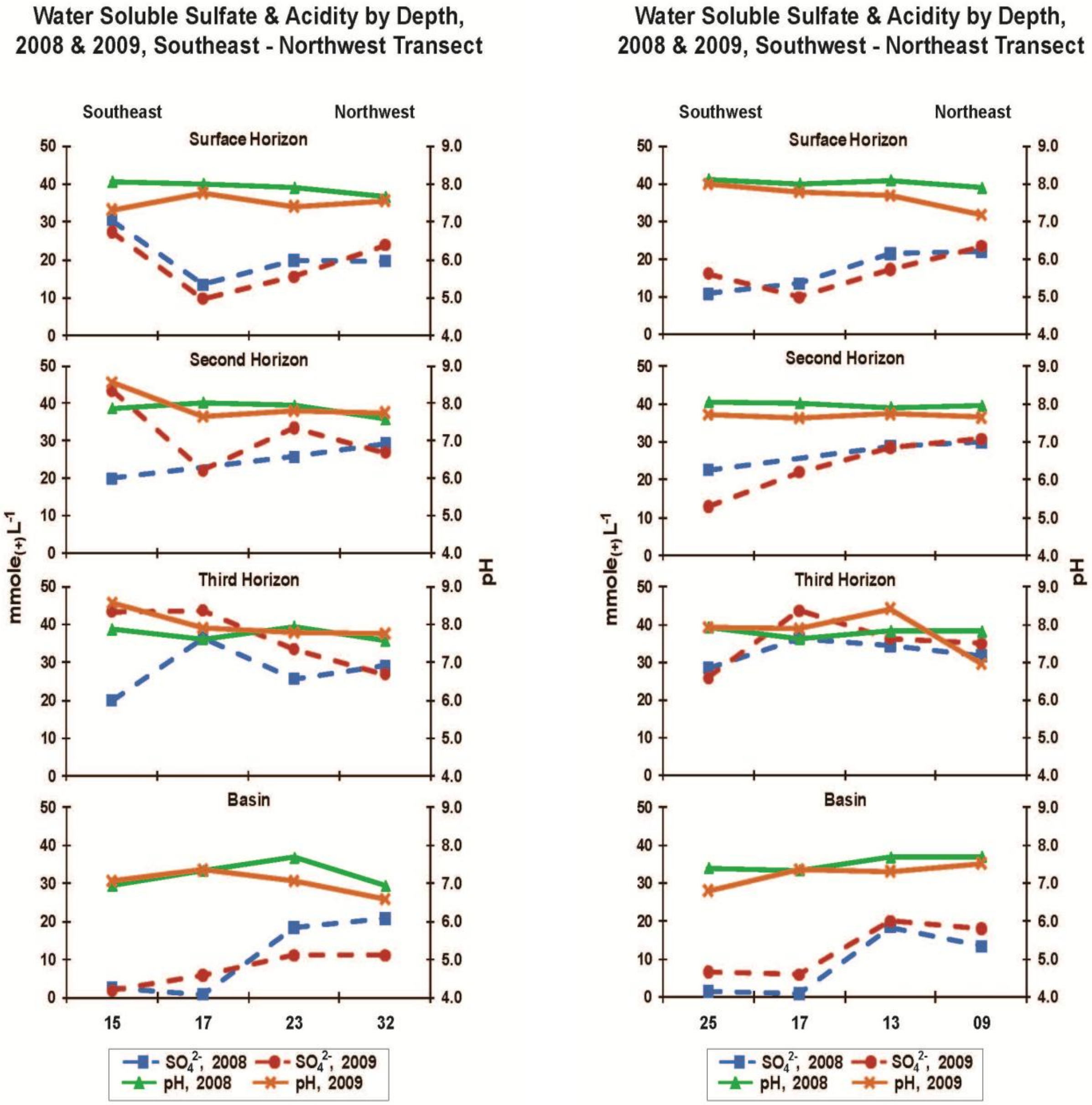
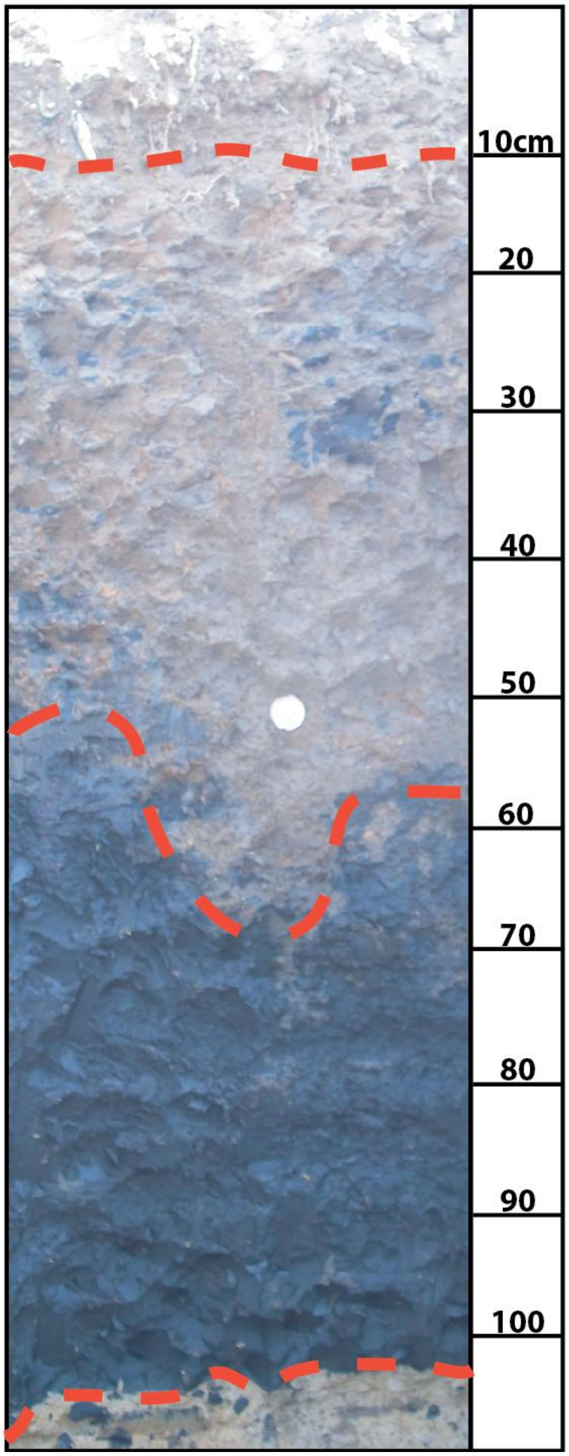


Figure B- 5. Spatial and temporal data for water soluble sulfate and acidity measured from saturation extracts. The transects represent cross sections radiating from the point of discharge on the southern side of the CUF. Neither transect displays an inverse relationship between sulfate and pH, demonstrating that the CUF has adequate buffering capacity to prevent acid sulfate soil formation. A lag in sulfate generation below the surface horizon can also be observed as increased concentrations in 2009 compared with 2008. Subsurface sulfate concentrations will likely be similar to the surface values if vertical oxidation continues.

SP1

Typic Halaquepts



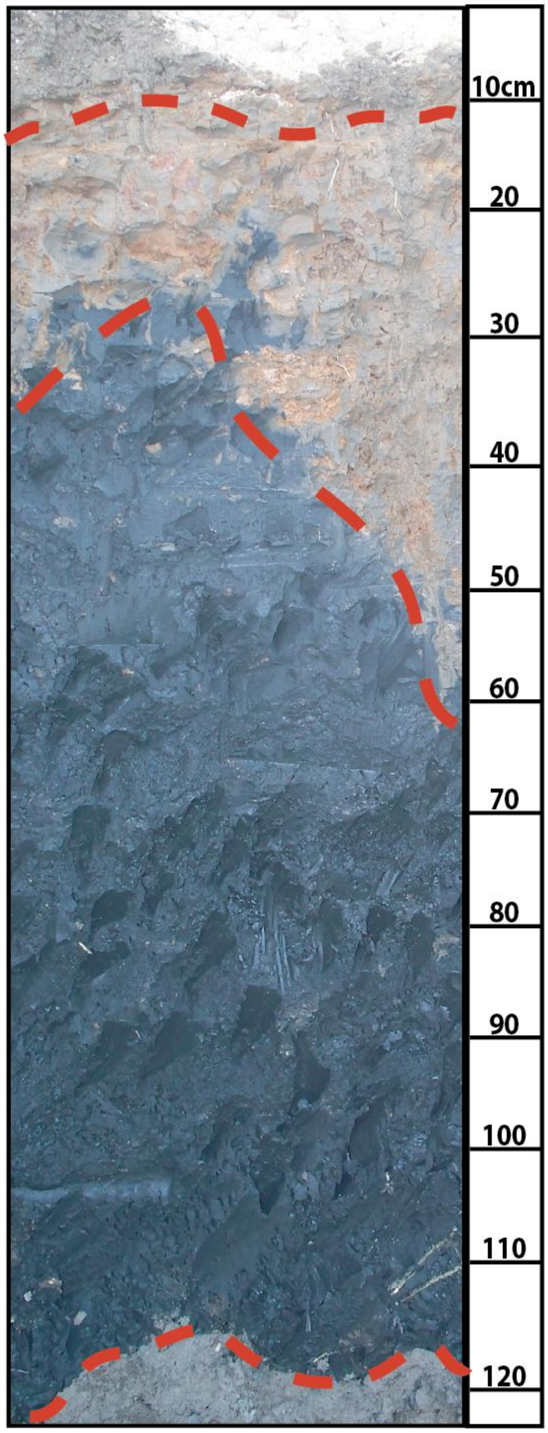
^Ap
0 to 11 cm; dark grayish brown (10 YR 4/2); moderate thick; few medium prominent yellowish red (5 YR 5/6) iron masses

^Bg/Cg
11 to 55 cm; dark gray (2.5 Y 4/1); strong very coarse prismatic structure parting to weak thick subangular blocky structure; common very coarse prominent yellowish red (5 YR 5/6) iron masses

^Cg
55 to 100 cm; black (5 Y 2.5/1); massive

2Btb

Figure B- 6. Soil profile from the ENWS CUF at location SP1 after four years of pedogenesis.



SP2

Typic Halaquepts

^Ap
0 to 11 cm; dark grayish brown (10 YR 4/2); moderate thick platy structure; few very coarse prominent yellowish red (5 YR 5/6) iron masses

^Bg
11 to 42 cm; black (2.5 Y 5/1); medium very coarse prismatic structure parting to weak thick subangular blocky structure; many extremely coarse prominent red (10 R 5/8) iron masses

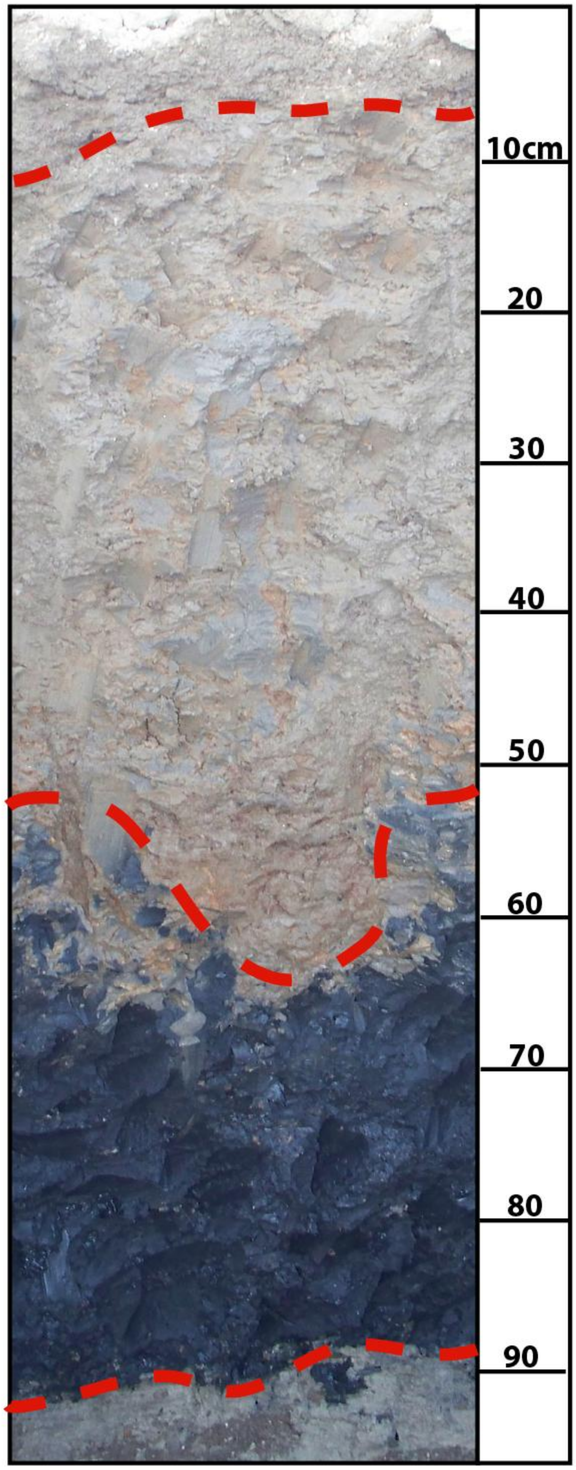
^Cg
42 to 119 cm; black (5Y 2.5/1); massive

2Btgb

Figure B- 7. Soil profile from the ENWS CUF at location SP2 after four years of pedogenesis.

SP3

Typic Halaquepts



^Ap
0 to 9 cm; dark grayish brown (10 YR 4/2); weak fine granular structure; few medium prominent yellowish red (5 YR 5/6) iron masses

^Bg
9 to 55 cm; grayish brown (2.5 Y 5/2); strong very coarse prismatic structure parting to weak thick subangular blocky structure; many very coarse prominent red (2.5 YR 5/8) iron masses

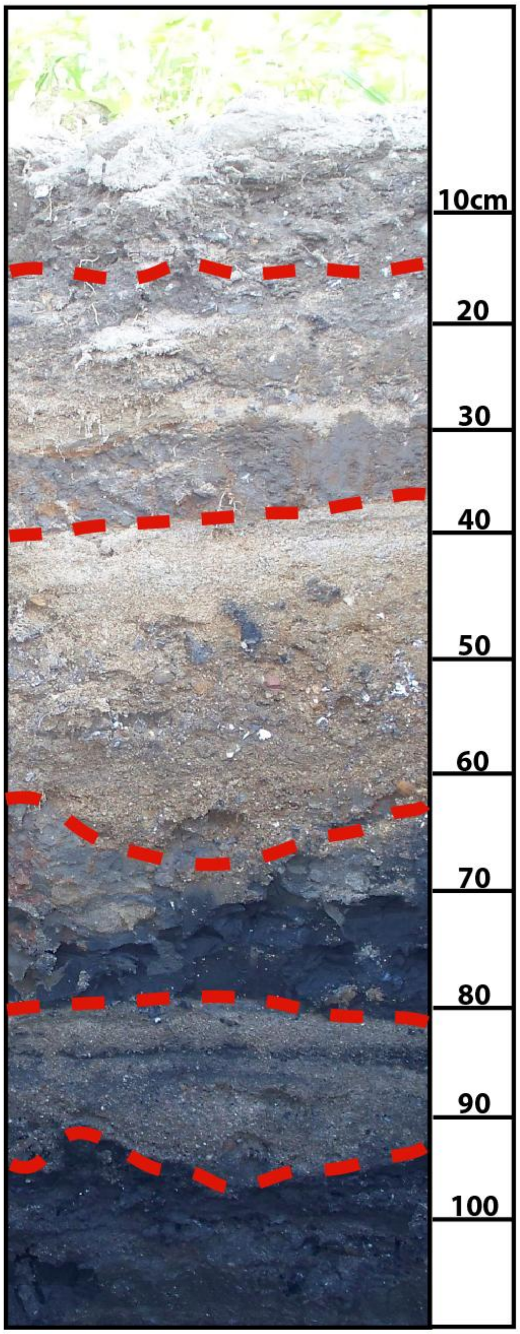
^Cg
55 to 90 cm; black (5 Y 2.5/1); massive

2Btgb

Figure B- 8. Soil profile from the ENWS CUF at location SP3 after four years of pedogenesis.

SP5

Aeric Halaquepts



^Ap
0 to 16 cm; dark grayish brown (10 YR 4/2); weak medium granular structure; few shell fragments

^Bg/BC
16 to 38 cm; grayish brown (10 YR 5/2); weak thick subangular blocky structure

^BC/Bg
38 to 60 cm; grayish brown (10 YR 5/4); single grain; common medium distinct strong brown (7.5 YR 5/6) iron masses

^Cg1
60 to 80 cm; black (5 Y 2.5/1); massive; common extremely coarse prominent red (10 R 5/8) iron masses

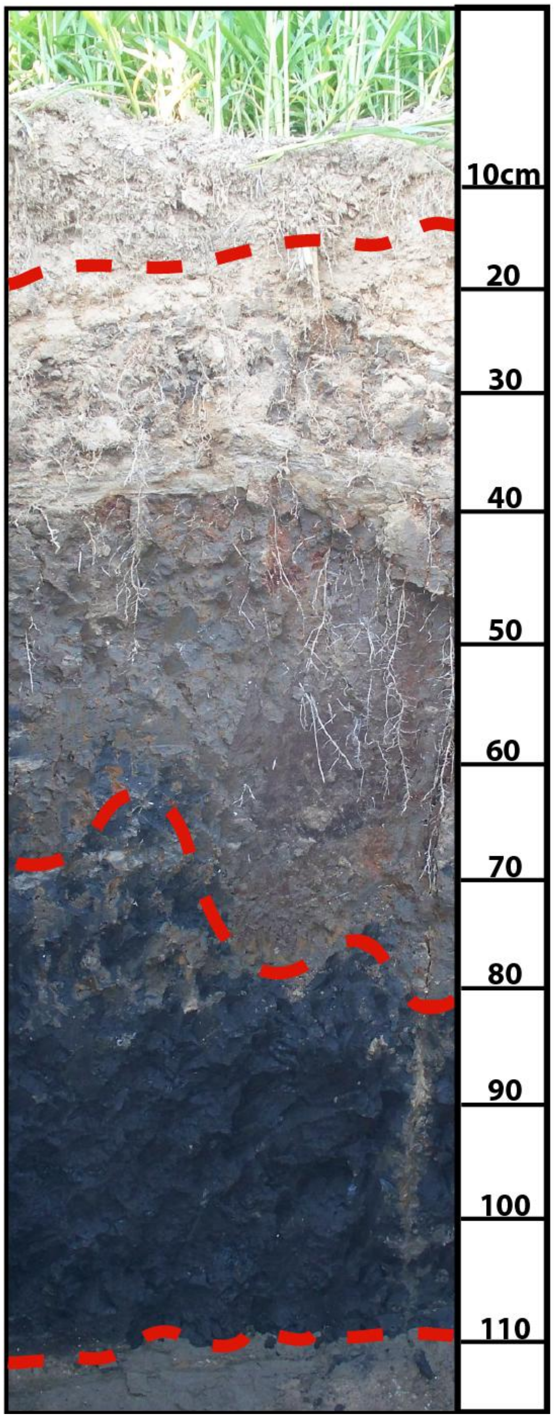
^Cg2
80 to 93 cm; light olive brown (2.5 Y 5/3); massive

^Cg3
93 to 130 cm; black (5 Y 2.5/1); massive

Figure B- 9. Soil profile from the ENWS CUF at location SP5 after four years of pedogenesis.

SP6

Typic Halaquepts



^A
0 to 14 cm; brown (10YR 4/3);weak medium granular structure

^Bg
14 to 69 cm; dark gray (5 Y 4/1); strong very coarse prismatic structure parting to weak thick subangular blocky structure; many very coarse prominent red (2.5YR 4/6) iron masses; upper half of horizon has common very coarse sandy inclusions

^Cg
69 to 110 cm; black (5Y 2.5/1); massive

2Btb

Figure B- 10. Soil profile from the ENWS CUF at location SP6 after four years of pedogenesis.

APPENDIX C

Table C- 1. PAH concentration data for all replicates, treatments and sampling events.

	ACN	ACL	ANT	BAA	BBF	BKF	BPR	BAP	CHR	FLR	FLU	INP	NAP	PHE	PYR
Sample*								*($\mu g\ kg^{-1}$)*							
1-CONTROL; UV; 0	378	139	1060	918	1010	324	488	1030	741	1310	222	432	260	1260	2390
2-CONTROL; UV; 0	292	139	892	847	952	371	383	983	711	1120	174	325	199	974	2300
1-CONTROL; V; 0	378	139	1060	918	1010	324	488	1030	741	1310	222	432	260	1260	2390
2-CONTROL; V; 0	292	139	892	847	952	371	383	983	711	1120	174	325	199	974	2300
1-CONTROL; UV; 150	102	73.7	147	472	513	154	279	583	325	481	55.4	245	87.9	294	1060
2-CONTROL; UV; 150	221	339	20100	3070	2420	618	1200	2550	2590	4570	1610	1120	912	6320	6710
3-CONTROL; UV; 150	99.3	55.9	168	568	564	149	237	551	499	592	54.8	194	61.7	325	1280
4-CONTROL; UV; 150	123	120	421	1040	1220	264	555	1090	928	1230	88.8	484	59.8	693	2020
1-CONTROL; V; 150	154	87.9	275	576	671	159	522	698	516	680	79.8	295	115	470	1420
2-CONTROL; V; 150	129	88.3	232	765	796	146	570	877	643	785	72.1	351	83.1	475	1790
3-CONTROL; V; 150	183	131	355	1040	1110	308	685	1220	891	1050	102	605	79.3	638	2470
4-CONTROL; V; 150	99.2	83.8	223	571	640	184	310	700	488	544	60.5	251	60.9	305	1270
1-CONTROL; UV; 327	108	64.5	252	493	666	203	502	641	434	634	67.8	373	98.6	355	950
2-CONTROL; UV; 327	102	55.4	146	415	575	249	347	566	406	563	59.3	265	85.6	311	902
3-CONTROL; UV; 327	115	75.5	178	463	598	270	495	624	449	603	65.0	374	98.2	334	934
4-CONTROL; UV; 327	173	87.4	334	676	1010	240	344	863	623	958	121	301	130	652	1410
1-CONTROL; V; 327	136	62.3	205	599	497	116	207	456	429	624	75.3	163	119	352	1170
2-CONTROL; V; 327	208	114	286	849	1070	287	437	973	717	910	129	316	141	634	2210
3-CONTROL; V; 327	151	91.5	608	736	842	218	334	853	652	980	110	265	164	515	1910
4-CONTROL; V; 327	123	65.9	149	487	605	155	254	572	400	544	69.0	205	108	348	1120
1-BIOSOLIDS; UV; 0	374	111	891	759	810	264	285	833	655	961	161	232	196	927	2130
2-BIOSOLIDS; UV; 0	420	124	734	837	912	366	297	947	685	1020	168	247	244	894	1990
1-BIOSOLIDS; V; 0	374	111	891	759	810	264	285	833	655	961	161	232	196	927	2130
2-BIOSOLIDS; V; 0	420	124	734	837	912	366	297	947	685	1020	168	247	244	894	1990
1-BIOSOLIDS; UV; 150	128	33.9	368	388	456	102	161	384	333	684	77.0	143	50.4	380	994
2-BIOSOLIDS; UV; 150	59.1	32.7	73.9	238	240	63.4	131	285	189	245	31.7	101	36.6	153	575
3-BIOSOLIDS; UV; 150	62.7	36.4	101	286	308	79.9	157	350	230	309	33.5	130	43.5	200	806
4-BIOSOLIDS; UV; 150	42.1	28.8	179	225	242	57.0	112	261	187	268	27.3	87.7	23.3	151	671
1-BIOSOLIDS; V; 150	93.4	60.5	122	388	534	126	252	555	343	395	48.2	176	73.8	246	928
2-BIOSOLIDS; V; 150	140	82.9	197	581	667	176	287	678	518	683	80.9	235	80.1	517	1340

*** Numerals represent replicates; UV = unvegetated; V = vegetated; 0, 150 & 327 = sample time in days. (Concentrations of Dibenz(a,h)anthracene and 2-Methylnaphthalene were below their detection limits.)**

Table C- 1 Continued.

	ACN	ACL	ANT	BAA	BBF	BKF	BPR	BAP	CHR	FLR	FLU	INP	NAP	PHE	PYR
Sample*	(*µg kg*$^{-1}$)														
3-BIOSOLIDS; V; 150	176	90.5	740	712	806	193	355	768	660	856	105	264	90.8	709	1770
4-BIOSOLIDS; V; 150	317	78.9	572	1740	2090	669	1050	1880	1570	1830	140	913	68.8	1020	3620
1-BIOSOLIDS; UV; 327	140	71.8	383	854	812	184	262	697	776	743	86.7	192	147	456	1840
2-BIOSOLIDS; UV; 327	240	121	304	1450	1250	489	360	1090	1320	1390	129	324	119	823	2940
3-BIOSOLIDS; UV; 327	146	70.2	326	919	842	309	254	777	790	910	85.3	201	113	539	2120
4-BIOSOLIDS; UV; 327	105	67.1	342	945	735	272	185	636	821	926	67.1	171	81.6	467	2070
1-BIOSOLIDS; V; 327	201	172	1110	1110	1240	360	757	1200	949	1090	129	599	216	765	2050
2-BIOSOLIDS; V; 327	203	161	256	911	1370	360	943	1330	853	785	86.3	717	125	510	2060
3-BIOSOLIDS; V; 327	178	165	324	1160	1530	374	844	1500	924	947	91.7	647	154	549	2260
4-BIOSOLIDS; V; 327	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.
1-COMPOST; UV; 0	136	49.9	526	335	396	95.4	147	384	261	372	82.9	123	91.7	393	1100
2-COMPOST; UV; 0	387	140	1020	905	1040	315	361	999	774	1180	219	297	267	1210	2560
1-COMPOST; V; 0	136	49.9	526	335	396	95.4	147	384	261	372	82.9	123	91.7	393	1100
2-COMPOST; V; 0	387	140	1020	905	1040	315	361	999	774	1180	219	297	267	1210	2560
1-COMPOST; UV; 150	88.2	42.8	110	329	397	123	186	427	277	351	43.6	177	63.4	236	890
2-COMPOST; UV; 150	82.3	49.1	111	294	343	113	159	422	254	313	37.2	142	59	201	830
3-COMPOST; UV; 150	58.1	34.6	131	233	279	80.2	136	298	196	241	34	116	48.2	172	676
4-COMPOST; UV; 150	84.1	54.5	171	332	448	135	171	461	292	326	44.3	156	64.9	242	971
1-COMPOST; V; 150	128	78.8	443	493	635	186	322	676	448	640	74.1	248	99.7	380	1180
2-COMPOST; V; 150	166	64.7	280	527	650	185	272	680	452	677	88.7	255	95.7	539	1370
3-COMPOST; V; 150	91.4	51	160	354	506	129	188	496	298	480	43	168	55.1	227	918
4-COMPOST; V; 150	90.8	47.5	196	336	461	123	180	470	294	461	49.3	161	53.6	273	951
1-COMPOST; UV; 327	131	99.3	194	555	670	210	397	732	466	660	65.3	334	105	356	1540
2-COMPOST; UV; 327	72.4	66.5	86.8	336	544	141	319	516	343	317	37.1	268	83	231	809
3-COMPOST; UV; 327	184	263	359	2130	2340	1000	828	1850	1890	2430	131	792	122	1540	3430
4-COMPOST; UV; 327	78.8	59.8	108	346	424	157	265	449	322	469	41.2	207	65.1	281	1020
1-COMPOST; V; 327	115	107	304	570	828	261	418	848	526	589	69.1	363	95.4	366	1320
2-COMPOST; V; 327	152	125	315	756	862	274	451	930	673	808	85.6	405	87.2	585	1870
3-COMPOST; V; 327	129	80.2	145	527	635	211	346	706	449	547	66.1	302	101	360	1350
4-COMPOST; V; 327	194	169	477	958	1110	271	463	1110	799	1120	114	394	94.4	737	2330
1-STRAW; UV; 0	331	118	710	1150	1260	398	502	1230	1050	1050	170	465	224	1120	2610
2-STRAW; UV; 0	395	133	1070	956	955	304	382	1040	772	1330	211	326	267	1090	2770
1-STRAW; V; 0	331	118	710	1150	1260	398	502	1230	1050	1050	170	465	224	1120	2610
2-STRAW; V; 0	395	133	1070	956	955	304	382	1040	772	1330	211	326	267	1090	2770

*** Numerals represent replicates; UV = unvegetated; V = vegetated; 0, 150 & 327 = sample time in days. (4-Biosolids; V; 327 sample was damaged. Concentrations of Dibenz(a,h)anthracene and 2-Methylnaphthalene were below their detection limits.)**

Table C- 1 Continued.

	ACN	ACL	ANT	BAA	BBF	BKF	BPR	BAP	CHR	FLR	FLU	INP	NAP	PHE	PYR
Sample*	*($\mu g\ kg^{-1}$)*														
1-STRAW; UV; 150	115	74.1	240	626	605	135	277	581	523	666	64.1	225	55.2	340	1570
2-STRAW; UV; 150	477	48.6	886	2160	2750	830	1150	1940	2000	3260	346	1080	252	2620	3730
3-STRAW; UV; 150	72.5	47.1	100	292	323	120	171	352	237	332	37.5	147	54.6	193	842
4-STRAW; UV; 150	85.7	60.5	142	383	513	105	217	524	322	507	48.7	179	42.1	265	1180
1-STRAW; V; 150	120	59.9	195	708	808	184	335	677	670	1050	69.8	277	77.6	882	1510
2-STRAW; V; 150	75.2	55.5	159	363	526	113	237	507	314	486	43.9	192	63.6	238	978
3-STRAW; V; 150	81.2	47.8	130	351	436	92.8	215	479	289	497	43.5	172	54.4	256	1010
4-STRAW; V; 150	76.6	44.9	108	337	422	92.4	184	386	282	560	43.8	154	46.9	285	1000
1-STRAW; UV; 327	136	92.1	414	714	661	217	322	654	592	859	96.2	255	96.2	498	1880
2-STRAW; UV; 327	201	118	344	842	841	221	280	677	725	1020	128	210	126	641	2300
3-STRAW; UV; 327	87.3	47.5	450	371	384	22.9	137	348	310	462	66.8	22.9	80.9	280	1210
4-STRAW; UV; 327	156	93.3	290	652	799	169	333	808	552	1120	104	251	104	607	1600
1-STRAW; V; 327	192	130	388	528	739	249	319	735	452	923	130	274	177	624	1280
2-STRAW; V; 327	273	173	794	1230	1430	404	415	1290	1030	2020	238	402	107	1390	2140
3-STRAW; V; 327	118	52.9	405	698	447	143	182	447	624	676	75.8	150	126	428	1360
4-STRAW; V; 327	179	51	249	791	767	172	254	637	717	784	85.6	220	98.7	430	1670
1-CONTROL; HG; 150	82.5	59.6	772	496	497	162	230	574	324	476	71.4	186	53.3	322	1210
1-CONTROL; HG; 327	215	136	345	813	1020	176	426	1010	638	890	109	362	144	637	2140
1-BIOSOLIDS; HG; 150	41.2	28.6	189	200	249	59.3	116	251	167	218	27.2	103	39	127	558
1-BIOSOLIDS; HG; 327	175	90	381	1170	1540	536	421	1280	1120	1640	106	393	91.2	1040	2260
1-COMPOST; HG; 150	125	56.9	750	451	536	161	178	566	346	655	104	168	69.3	648	1420
1-COMPOST; HG; 327	106	87.3	286	494	682	198	407	717	470	595	56.4	314	93.1	349	1310
1-STRAW; HG; 150	144	57	253	605	641	145	249	609	506	696	73.2	233	50.6	365	1470
1-STRAW; HG; 327	137	136	256	756	997	366	365	912	594	853	74.3	317	114	496	1770

*** Numerals represent replicates; UV = unvegetated; V = vegetated; HG = mercury treatment; 0, 150 & 327 = sample time in days. (Concentrations of Dibenz(a,h)anthracene and 2-Methylnaphthalene were below their detection limits)**