Volume 5, Issue 1



Barr Report

# Barr Report

with Tom Barr, Greg Watson, and the Plant Guru Team

## ADA Aqua Soil™ and Power Sand™ Analysis

### Special points of interest:

- Many aquarists seem to focus on either the water column or the substrate for their dosing.
- Pre-mineralization of soil used for aquariums does not appear to offer an advantage when using ADA type of startup approach where water changes are done often for the first few weeks and then fish are added later.

### Inside this issue:



ADA Aqua Soil™ and Power Sand™ Analysis

**Introduction:**

Most aquarists only test the water column for nutrients for aquatic planted aquariums. Rarely, (if ever) do we look at testing the other half of the sources of nutrients for root submersed macrophytes, the sediment. This is not surprising as the hobby lacks a reasonably priced, commercially available, hobby test kit/s specifically for sediment analysis. By comparing various sediment types, their components from natural systems, and looking at a commercial brand and the same brand aged for 1.5 years, aquarist should be able to put together how, where and why plants grow in seemingly nutrient poor water columns. While it has long been shown in research in natural waters, that aquatic plants can obtain their nutrient demands for N and P, both from the water column and the sediment either partially or entirely (Cedergreen and Madsen, 2001; Barko et al, 1991, Cedergreen and Vindabaek, 2002). Many aquarist seem to focus on one location or the other for their dosing. In most aquariums where fish are present, some significant amount of N and P is added via fish waste to the water column. However, the fecal pellets may actually fall out of the water column and be engrained into the sediment for root uptake. Many aquarist have also noted that horticulture using enriched sediments with soil or various NPK mixtures, with some organic matter is sufficient to grow aquatic macrophytes without adding inorganic fertilizer to the water column over fairly long time frames of months; and in some cases years both with and without $CO_2$ gas enrichment. Therefore it is prudent to focus on both locations when applying a best management practice to adding nutrients, by fish, water column and the sediment. The goals of this research are to 1) help educate aquarist of what is involved in testing the sediment, 2) compare sediment fertility over time in a real practical planted aquarium, 3) compare various commercial products to natural clays found where submersed aquatic macrophytes are found in abundance, 4) compare subsediment amendments to the top layer sediments, 5) discuss dosing of the water column over time with the relative amount of loss of various nutrients in sediment types.

*"… it is prudent to focus on both locations when applying a best management practice to adding nutrients, by fish, water column, and the sediments."*

Table 1 is the raw data from several samples measured. The ADA aqua soil Amazonia I was tested and then the test repeated; the same method was used for used for the submersed clay sediment from Owl Harbor, in the California delta using repeated measure. ADA PS was also tested. NPK, Fe and Cu nutrients were tested, then physical chemical parameters Cation Exchange Capacity, Organic Matter % and organic Carbon

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... time effects on soil were tested ....

*" aquatic plants can obtain their nutrient demands for N and P from the water column, and the sediment, either partially or entirely..."*

... raw data from several samples were measured including ADA AquaSoil, wetlands sediments, and ADA Power Soil ....

# ADA Aqua Soil™ and Power Sand™ Analysis

%, and then particle size fractions. Each sample was dried for 48 Hours at 70C, then crushed into a power with a pestal. Methods for each test are described below in the reference section.

### Fertility parameters

| Sample Type: SOIL | | Date Sampled: Not Specified; Grower/Location/Project: Not Specified | | | | | |
|---|---|---|---|---|---|---|---|
| | | NH4-N | NO3-N | Olsen-P | X-K | Fe (DTPA) | Cu (DTPA) |
| SAMPLE # | DESC | [ SOP 312.02 ] ppm | [ SOP 312.02 ] ppm | [ SOP 340.02 ] ppm | [ SOP 360.03 ] ppm | [ SOP 380.02 ] ppm | [ SOP 380.02 ] ppm |
| 1 | ADAold | 15.19 | 28.03 | 155.4 | 554 | 216.8 | 1.7 |
| 2 | ADAnew | 262.89 | 9.19 | 111.3 | 390 | 324.9 | 1.2 |
| 3 | ADAps | 440.79 | 1616.02 | 160.0 | 1240 | 34.4 | 2.8 |
| 4 | Ohdelta | 15.66 | 2.20 | 18.7 | 127 | 174.4 | 9.4 |
| 5 | Luban pond | 8.03 | <0.10 | 5.2 | 41 | 190.9 | 6.7 |
| | | | | | | | |
| Analysis Date: | | 10/7/2009 | 10/12/2009 | 8/19/2009 | 8/25/2009 | 8/19/2009 | 8/19/2009 |
| Method Detection Limit: | | 0.10 | 0.10 | 1.0 | 1 | 0.1 | 0.1 |
| Blank Concentration: | | 0.00 | 0.00 | 0.0 | 0 | 0.0 | 0.0 |
| Standard Ref as Tested: | | 7.0 | 73 | 35.4 | 1049 | 54 | 1.72 |
| Standard Ref Acceptable: | | 6.3±1.0 | 68±6 | 39.1±8.0 | 1053±80 | 56±14 | 1.76±0.42 |
| Standard Reference: | | NORD | NORD | NORD | NORD | NORD | NORD |

### Physical/chemical parameters

| Sample Type: SOIL | | | | | | |
|---|---|---|---|---|---|---|
| | | CEC | OM | Sand | Silt | Clay |
| SAMPLE # | DESC | [ SOP 430.02 ] meq/100g | [ SOP 410.03 ] % | [ SOP 470.03 ] % | [ SOP 470.03 ] % | [ SOP 470.03 ] % |
| 1 | ADAold | 27.4 | 4.74 | 22 | 36 | 42 |
| 2 | ADAnew | 24.7 | 6.17 | 20 | 38 | 42 |
| 3 | ADAps | 8.4 | 2.37 | 69 | 25 | 6 |
| 4 | Ohdelta | 26.5 | 2.33 | 11 | 68 | 21 |
| 5 | Luban pond | 15.2 | 1.22 | 63 | 25 | 12 |
| | | | | | | |
| Analysis Date: | | 10/27/2009 | 8/26/2009 | 9/24/2009 | 9/24/2009 | 9/24/2009 |
| Method Detection Limit: | | 2.0 | 0.10 | 1 | 1 | 1 |
| Blank Concentration: | | - | - | - | - | - |
| Standard Ref as Tested: | | 30.5 | 2.52 | 25 | 53 | 22 |
| Standard Ref Acceptable: | | 31.0±2.0 | 2.47±0.20 | 24±3 | 54±5 | 23±3 |
| Standard Reference: | | NORD | NORD | TEHEMA | TEHEMA | TEHEMA |



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# ADA Aqua Soil™ and Power Sand™ Analysis

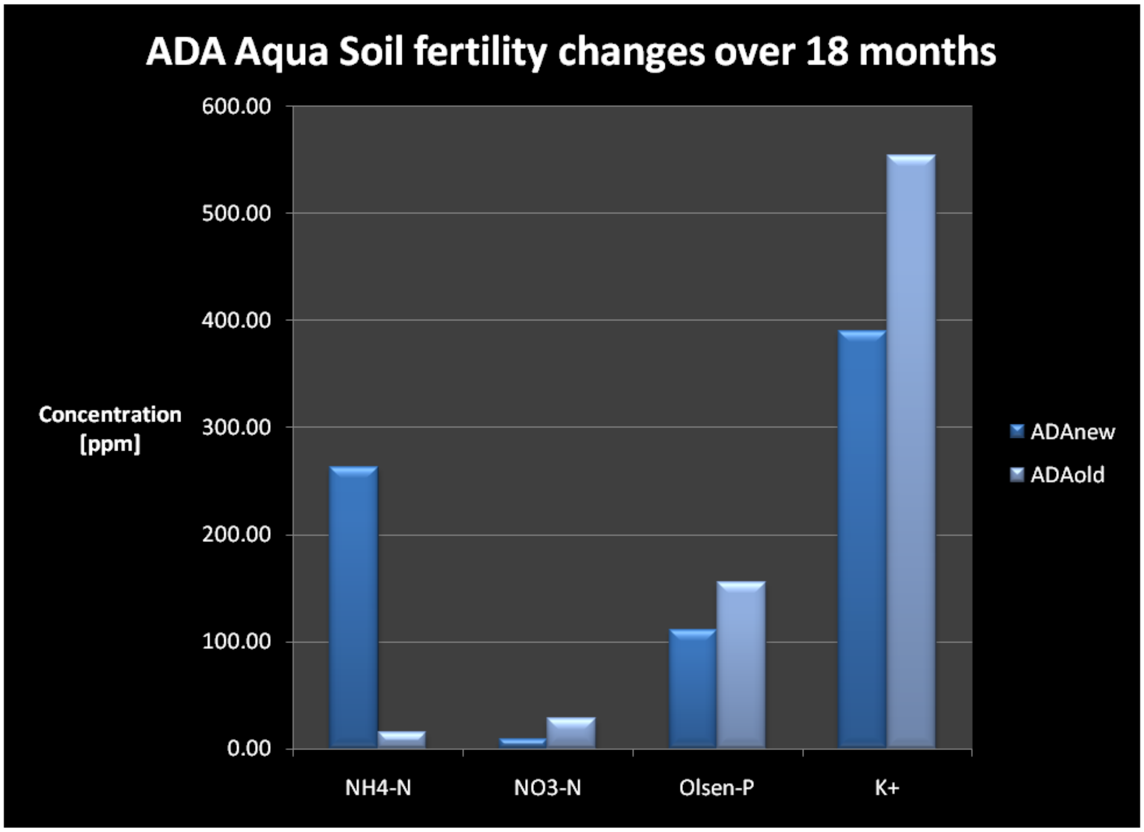


Figure 1. The effects of time on ADA aqua soil use on my aquarium. 1st column is the new, second is the old. EI dosing was done over 18 months. This theoretically would reduce the amount of N, P and K+ removal and re enrich with the CEC as roots removed these nutrients. Initial NH4-N concentrations are extremely high. This is correlated well with the observation of high NH4-N levels in new aquariums due to leaching from new ADA aqua soil into the water column. Over time, this NH4 is taken up by plants, removed via water changes or is oxidized to NO3 by bacteria. NO3-N is low initially and increased slightly over time, perhaps some of the remaining NH4-N was oxidized prior to analysis and drying (Old sediment was sitting for 1 month after wards in a bucket drying). The clay also seemed to bind some more PO4 more likely due to high KH2PO4 over the last 18 months. Perhaps less was used compared to foliar uptake thus reducing draw from the soil as well. Potassium also increased over time likely due to a similar factor like that of PO4. As we can see from this analysis, ADA As really only declines significantly over time with respect to Nitrogen. This will allow us to modify dosing to allow for more KNO3 addition after a several months, feed the fish more or a time frame to replace the ADA AS. Oscillitoria blooms are often common with older ADA AS sediment, this correlates well with the observation shown above with greatly reduced Nitrogen. Note, this is with non limiting nutrients to the water column, therefore the ratios and perhaps other nutrients would/may be much more depleted. However, the lighting was roughly 2x that of a typical ADA light system on a similar sized aquarium. Perhaps these balance out, but I would suggest that the levels left in the sediments with leaner dosing would be greatly reduced over time comparatively. Still, the high NH4 clearly helps grow plants effectively in the initial stages and this might have application when applying the traditional ADA method to using mineralized soil, in other words, it might be much better to not mineralize the soil initially, and do water changes and allow the sediment mineralize with the plants in the tank instead of doing before placing the mineralized sediment inside the aquarium. It would take the same time frame and the plants would have access to the NH4 for their initial growth phase. Fish would be added after 4-6 weeks later. Water changes would be done 30-50% 2x a week during that period.

*Copper levels appear to be decreasing over time, suggesting that copper dosing might be insufficient in the water column (**However [emphasis added],** it would be years before it was exhausted). ...*



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# ADA Aqua Soil™ and Power Sand™ Analysis

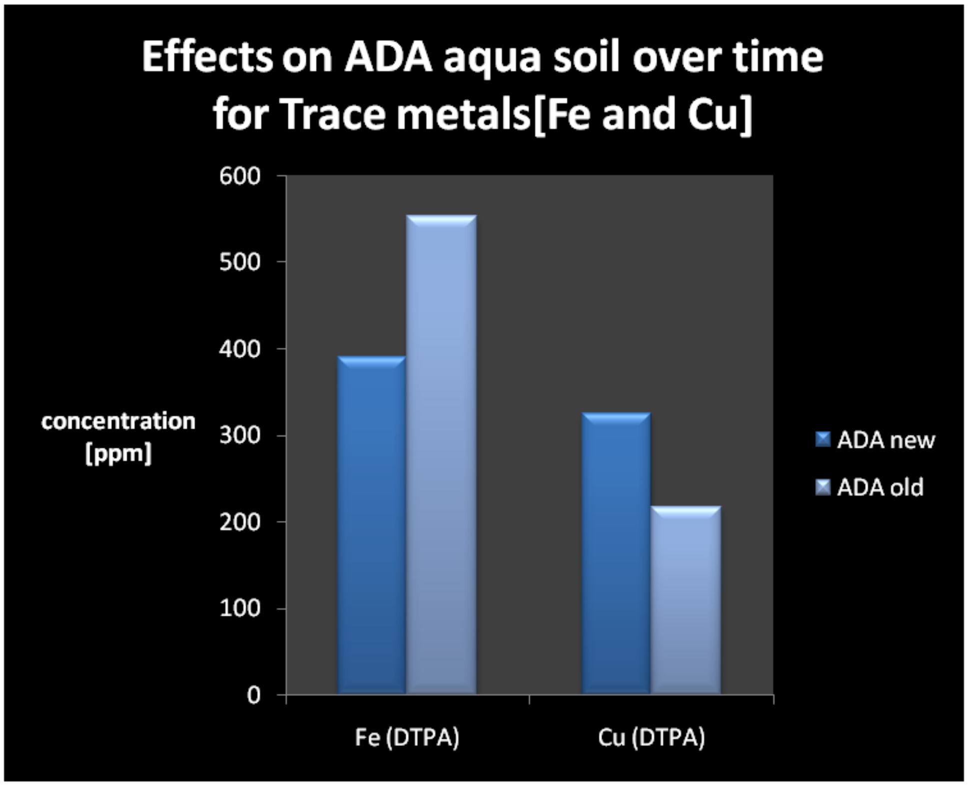


Figure 2. Surprisingly, the amount of iron (Fe) actually increased over the 18 month time frame. This may be due to precipitation of liquid chelated Fe and binding by the clay ADA aqua soil's cation exchange capacity as other trace metals where removed by plants and where replaced by Fe. Copper levels appear to be quite high and decreased over time, suggesting that copper dosing might be insufficient in the water column leading to depletion over time (however, it would be a few years before it was exhausted).

*"... Power Sand appears to provide an initial burst of NPK relative to [alternate sediments or substrates] ..."*

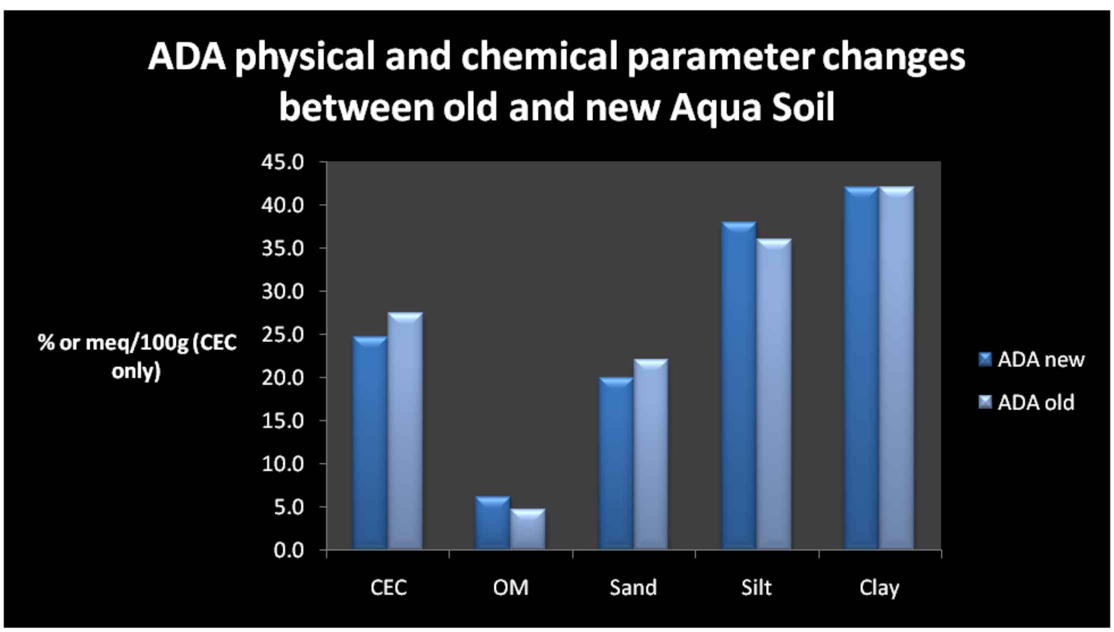


Figure 3. Less surprisingly, this figure shows that the particle sizes did not change significantly over time, nor CEC and a slight change in the % organic matter. CEC is about comparative to most products such as other soil types and aquarium sediment products. See : http://www.thekrib.com/Plants/Fertilizer/substrate-jamie.html And http://home.infinet.net/teban/jamie.htm



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Seems that some CEC is useful, but it is not really a primary parameter given that nutrients are coming in from fish and the water column (thus replaced routinely) in this example above. The main difference is really the dramatic decrease of NH4 and the less dramatic, but significant increase of the other nutrients (other than copper). Seems that based on the sediment, perhaps the copper dosing and the N dosing should have been higher over this time period. With less K+, Fe, NO3, and PO4 dosing, perhaps this would balance out.

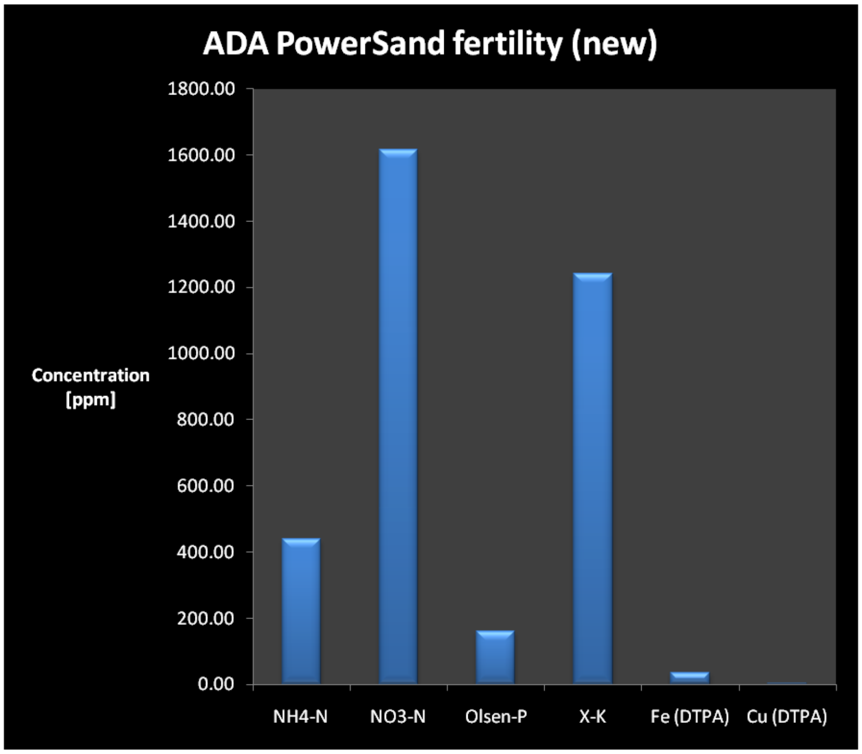
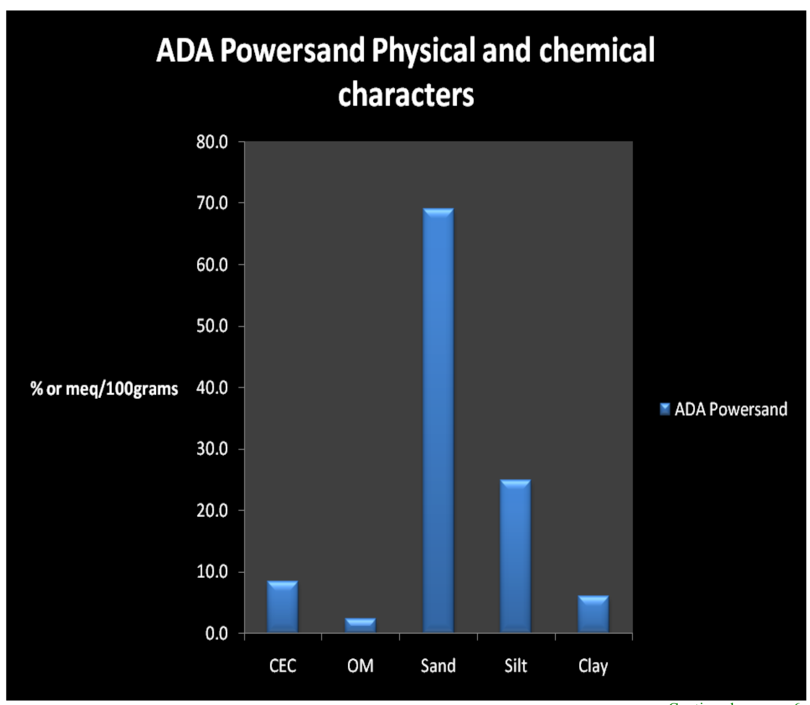



Figure 4. ADA Powersand has a pretty common ratio for terrestrial plants, roughly a 13:1:8 by mass ratio.
1:3.7 for NH4: NO3. There was not much else in the powersand other than some macro nutrients. At 1610 ppm of NO3-N (4.4 x more if you want NO3ppm). A simple jar test with powersand and DI water also showed very high source of NO3's some years back. This confirms that ADA powersand is mostly a NPK terrestrial type fertilizer on pumice with a little peat for organic matter. This also shows why there's little need to add NO3 at the first initial stage. The total amount of NO3 is still several orders of magnitude higher than say EI. However, NO3 is highly mobile, leaching and low CEC of ADA Powersand seems unlikely that the NO3 would stay put for long.

Figure 5. Physical and chemical parameters show little CEC, % OM. Most of the silt and clay fraction is from the crushing or the pumice done in order to process the material. So it's mostly just pumice sand in this figure. Therefore, overall, based on these measurements, powersand is more or less just a source of NPK under the power sand with a high fraction of NO3 relative to ADA aqua soil. This supports my contention some years ago that simply adding KNO3 in place of powersand would be adequate for plant health and growth when using ADA Aqua soil alone. As the NO3 leaches and the NH4 is removed or oxidized, these are removed rather quickly over time. This leads to a low N state for the ADA methods. BGA issues seem common in such tanks, thus adding more KNO3 might be a wise solution. Adding KNO3 is certainly cheaper than powersand over time and would not lose potency. Since Step 1 or 2 are still added daily, the fact that you do not have to dose KNO3 when using ADA powersand does not save the aquarist time or effort (or money or aesthetics).

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# ADA Aqua Soil™ and Power Sand™ Analysis

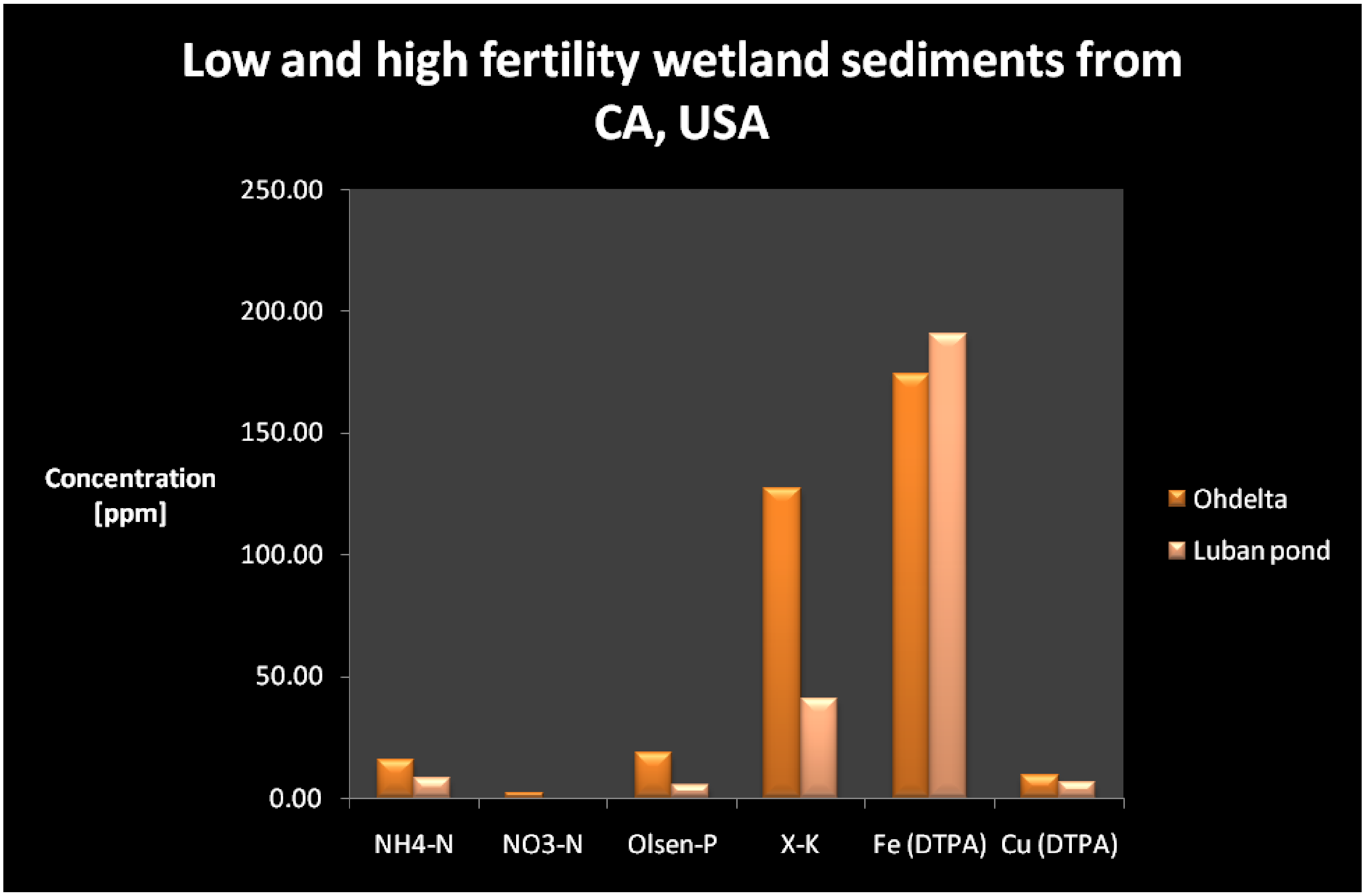


Figure 6. Fertility of mineralized wetland sediments are compared where aquatic plants have been found in rich clay sediments. Ohdelta is from the California delta region where there have been ongoing aquatic weed eradication and control programs for several years close by but have not treated this site. They tend to be rich in P, Fe and K and low in N, thus the sediments are predicted to be N limiting sediments naturally. This is the case for most wetland sediments in California, thus adding P, Fe or K+ will not increase aquatic weed growth here. Many clay soils exhibit this downward trend in N loss and sequester P and Fe effectively. This is due in large part to NO3=> N2 denitrification in wetlands and perhaps some as export of plant biomass from intensive farming. Adding extra K+ to wetland sediments does not appear to be harmful, but does not appear to be "required" when using mineralized sediments for aquariums. A survey I did some years ago for class also showed a similar trend on a much wider range of California sediments. Regular top soils used for making a DIY mineralized soil for aquatic plants will vary greatly I'd suspect. Various studies for the NPK are often shown on the bag or available from the suppliers for those products. Soil samples over say 3-6-9-12-18-24 months can be saved and frozen and sent to an agriculture service for analysis if the aquarist using those sediments wishes to have them tested. While a great deal of emphasis is often placed on sediments that are enriched and have NPK, it is important to bear in mind that the water column can greatly influence the growth of aquatic macrophytes. Thus the combined effects of the various concentrations of these nutrients in each location must be considered prior to making any conclusion. Aquarists have often over looked these location issues and made poor conclusions about the water column as well as the sediment nutrients. Only by looking at both, can aquarist find some sense of understanding for whole plant growth.



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# ADA Aqua Soil™ and Power Sand™ Analysis

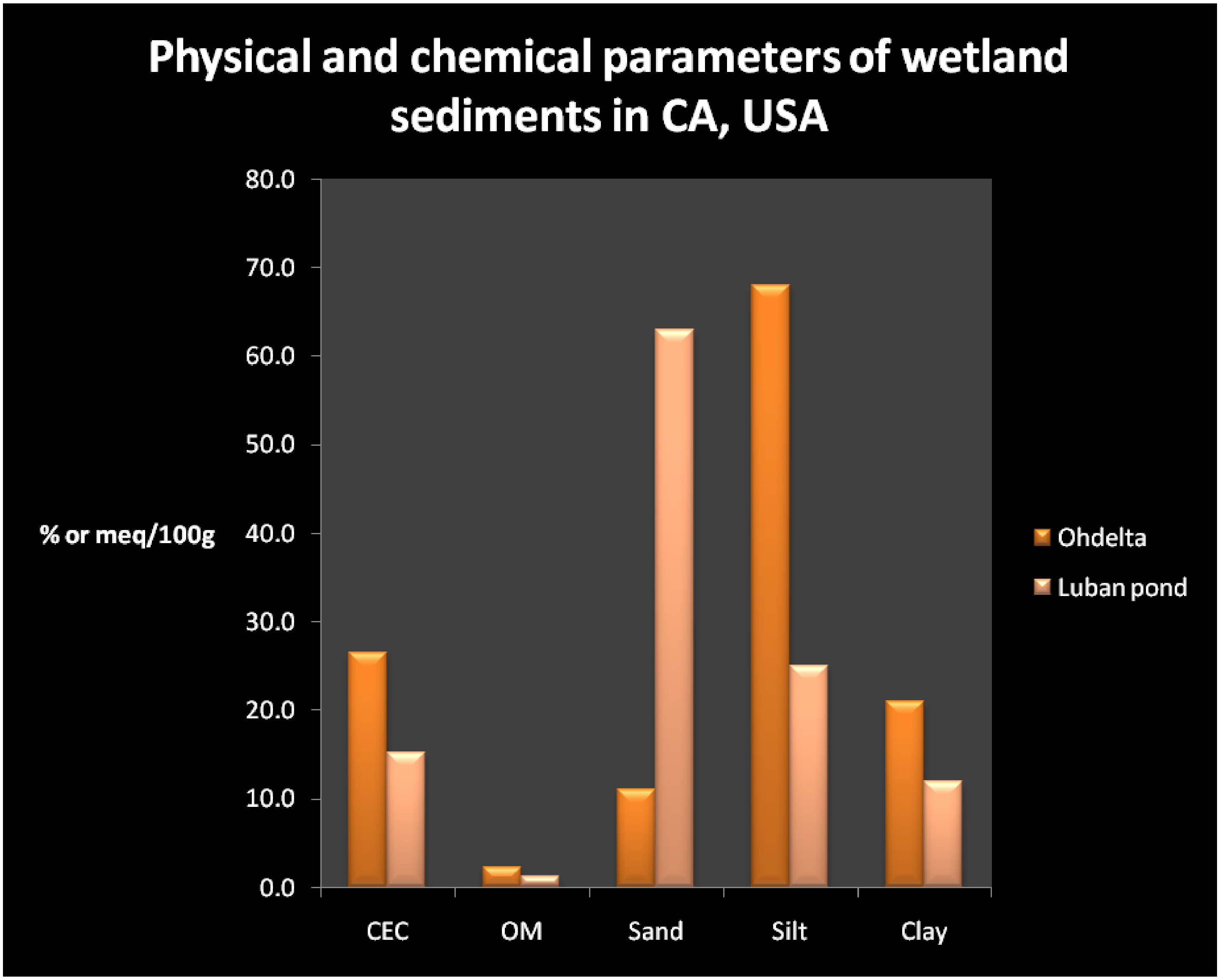


Figure 7. Physical and chemical parameters are listed for two sediment types. The high CEC found in the delta sediment is typical for many wetland sediment types. The lower CEC and higher sand % fraction for Luban pond is typical of more oiligotrophic waters/ sediments where aquatic plants are found. The productivity is higher in the richer sediments; however, there are very high levels of aquatic plants found in Luban pond as well. This shows that aquatic plants can and do grow in both richer and leaner situations. The rates of growth are different, but they do still grow and often grow fairly well even in seemingly limited water/sediments.

**Concluding remarks:**

If KNO3 is used in addition, the delta sediment appears to be as good as the ADA aqua soil in many respects. Thus adding more KNO3 seems to be a good idea for both MS and for ADA sediments over time and should yield better plant health and growth. For most other nutrients, it appears like the sediments could yield good growth without large additions for several years. Powersand appears to provide an initial burst of NPK, mostly NO3 relative to other nutrients already found in ADA aqua soil Amazonia(Type 1), thus additions of KNO3 to the water column would also negate the use of ADA powersand for most aquarist when used with mineralized soils or ADA aqua soil. Pre mineralization of soil used for aquariums does not appear to offer an advantage when using an



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ADA type of startup approach where water changes are done often for the first few weeks and then fish are added later. Additionally, the need to add Fe and K+ to sediments may offer little advantage over time. Rates of leaching will vary greatly over time. The % nutrient drawn from the sediment by plants is dependent on the water column dosing. It seems adding nutrients to both locations seems to be the best overall management plan for aquarist. However, for those curious about how the ADA system or other systems might work, this will give some insight and also provide a model for adding leaner dosing to such systems without limiting plant growth too much.

**References:**

Cedergreen, N. y R. Vindbaek. 2002. Nitrogen uptake by the floating macrophyte Lemna minor. New Phytol., 155: 285-292

Madsen, T. V., and N. Cedergreen. 2002. Sources of nutrients to rooted submerged macrophytes growing in a nutrient rich stream. Freshwater Biology 42:283–291.

**Method references:**

Specific method analysis and references are listed below for each parameter.
NOTE: The SOP # (Standard Operating Procedure number) is a reference to the laboratory method used.
The SOP heading in this Excel file is linked to the method summary at the end of this article.

NOTE: No result within this report is accurate to more than 3 significant figures. More figures may be present due to software rounding rules.

**Methods used for analysis:**

**Fertility: NO3-N, NH4-N**
Equilibrium extraction of soil for nitrate and ammonium with potassium chloride and subsequent determination by flow-injection analyzer.
**Summary:** This method involves the quantitative extraction of nitrate (NO3-N) from soils using an equilibrium extraction with 2.0 N KCl solution. Nitrate is determined by reduction to nitrite via a copperized cadmium column. The nitrite is then determined by diazotizing with sulfanilamide followed by coupling with N-(1-naphthyl)ethlyenediaminie dihydrochloride. The absorbance of the product is measured at 520 nm. This method is also semi-quantitative for ammonium (NH4-N) in soils. Ammonia is heated with salicylate and hypochlorite in an alkaline phosphate buffer. The presence of EDTA prevents precipitation of calcium and magnesium and sodium nitroprusside is added to enhance sensitivity. The absorbance of the reaction product is measured at 660 nm and is directly proportional to the original ammonia concentration. Extracts can be stored for up to three weeks at low temperature (<4°C). For long term storage, toluene or thymol may be added to the sample to prevent microbial growth. The method has detection limit of approximately 0.1 mg/kg (on a soil basis) and is generally reproducible within 7%.
Hofer, S. 2003. Determination of Ammonia (Salicylate) in 2M KCl soil extracts by Flow Injection Analysis. QuikChem Method 12-107-06-2-A. Lachat Instruments, Loveland, CO.o:p>
Knepel, K. 2003. Determination of Nitrate in 2M KCl soil extracts by Flow Injection Analysis. QuikChem Method 12-107-04-1-B. Lachat Instruments, Loveland, CO.

**Fertility: Olsen-P**
Extractable phosphate based on alkaline extraction by 0.5 Normal NaHC03. Plant available phosphate for soils with pH greater than 6.5 by ascorbic acid reduction of phosphomolybdate complex and measurement by flow injection analysis.
**Summary:** This method estimates the relative bioavailability of inorganic ortho-phosphate (PO4-P) in soils with neutral to alkaline pH. It is not appropriate for soils which are mild to strongly acidic (pH <6.5). The method is based on the extraction of phosphate from the soil by 0.5 N sodium bicarbonate solution adjusted to pH 8.5. In the process of extraction, hydroxide and bicarbonate competitively desorb phosphate from soil particles and secondary absorption is minimized because of high pH. The orthophosphate ion reacts with ammonium molybdate and antimony potassium tartrate under acidic conditions to form a complex. This complex is reduced with abscorbic acid to form a blue complex which absorbs light at 880 nm. The absorbance is proportional to the concentra-


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# ADA Aqua Soil™ and Power Sand™ Analysis

tion of orthophosphate in the sample. The method has shown to be well correlated to crop response to phosphorus fertilization on neutral to alkaline soils. The method has a detection limit of 1.0 mg/kg (soil basis) and is generally reproducible within 8%.

Olsen, S. R. and Sommers, L. E. 1982. Phosphorus. p. 403-430. In: A. L. Page, et al. (eds.) Methods of soil analysis: Part 2. Chemical and microbiological properties. Agron. Mongr. 9. 2nd ed. ASA and SSSA, Madison, WI.

Prokopy, W. R. 1995. Phosphorus in 0.5 M sodium bicarbonate soil extracts. QuikChem Method 12-115-01-1-B. Lachat Instruments, Milwaukee, WI.

**Fertility: X-K+**

Equilibrium extraction of soil for plant available exchangeable potassium, sodium, calcium and magnesium using 1 Normal ammonium acetate (pH 7.0) and subsequent determination by atomic absorption/emission spectrometry.

**Summary:** This method is semi-quantitative and determines the amount of soil exchangeable K, Ca, Mg, and Na residing on the soil colloid exchange sites by displacement with ammonium acetate solution buffered to pH 7.0. Generally, these cations are associated with the exchange capacity of the soil. The method does not correct for calcium and magnesium extracted as free carbonates or gypsum. The method has a detection limit approximately of 1 ppm or 0.01 meq/100g.

Sample amount requested: 10 g (for one or up to all four elements)

Questions concerning limited sample size can be answered by the DANR Analytical Laboratory.

Thomas, G. W. 1982. Exchangeable cations. pp 159-165. In: A.L. Page et al. (ed.) Methods of soil analysis: Part 2. Chemical and microbiological properties. ASA Monograph Number 9.

**Fertility: Zn, Mn, Cu, Fe**

Equilibrium extraction of soil using DTPA and subsequent determination by atomic absorption spectrometry.

**Summary:** The DTPA (diethylenetriaminepentaacetic acid) micronutrient extraction method is a non-equilibrium extraction for estimating the potential soil availability of Zn, Cu, Mn, and Fe. It has been used for cadmium, nickel and lead in soils. The method has shown to be well correlated to crop response to fertilizer for zinc and copper. The amount of micronutrients and trace metals extracted are affected by solution pH, temperature, soil extraction ratio, shaking time, extraction time, and extractant concentration. Extracts are analyzed by ICP-AES or Flame AA. The method has a detection limit of approximately 0.1 mg/kg for Zn, Cu, Mn, and Fe and is generally reproducible within 10% for Cu and Zn and 15% for Fe and Mn. The method is not well characterized for other elements.

Lindsay, W. L. and Norvell, W. A. 1978. Development of a DTPA soil test for zinc, iron, manganese, and copper. Soil Sci. Soc. Amer. J. 42:421-428.

**Physio Chem: CEC**

Cation Exchange Capacity by barium acetate saturation and calcium replacement.

**Summary:** The method determines the cation exchange capacity (CEC) of soil. The soil is quantitatively displaced of all exchangeable cations with barium, followed by four deionized water rinses to remove excess barium. A known quantity of calcium is then exchanged for barium and excess solution calcium is measured. CEC is determined by the difference in the quantity of the calcium added and the amount found in the resulting solution. The method has a detection limit of approximately 2.0 meq/100g.

Rible, J. M. and Quick, J. 1960. Method S-19.0. In: Water soil plant tissue. Tentative methods of analysis for diagnostic purposes. Davis, University of California Agricultural Experiment Service. Mimeographed Report.

**Physio Chem: OM, Org C**

Organic Matter by potassium dichromate reduction of organic carbon and subsequent spectrophotometric measurement (modified Walkley-Black).

**Summary:** This method quantifies the amount of oxidizable organic matter in which OM is oxidized with a known amount of chromate in the presence of sulfuric acid. The remaining chromate is determined spectrophotometrically at 600nm wavelength. The calculation of organic carbon is based on organic matter containing 58% carbon. The method has a detection limit of approximately 0.10% and, on homogeneous sample material, is generally reproducible within 8%.

The method requires 2 g sample, but 10 g is requested to allow for quality control.  Samples with concentrations greater than 80% OM are best tested by the Loss-on-Ignition (OM-LOI) method.

Nelson, D. W. and Sommers, L. E. 1982. Total carbon, organic carbon and organic matter. p. 539-579. In: A. L. Page et al. (ed.) Methods of soil analysis: Part 2. Chemical and microbiological properties. ASA Monograph Number 9.



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# ADA Aqua Soil™ and Power Sand™ Analysis

**Particle Size Analysis (Sand/Silt/Clay)**

Particle Size Analysis of sand, silt and clay in soil suspension by hydrometer.
**Summary:** This method quantitatively determines the physical proportions of three sizes of primary soil particles as determined by their settling rates in an aqueous solution using a hydrometer. The hydrometer method of estimating particle size analysis (sand, silt and clay content) is based on the dispersion of soil aggregates using a sodium hexametaphosphate solution and subsequent measurement based on changes in suspension density. The method has a detection limit of 1% sand, silt and clay (dry soil basis).
Sample amount required: 50 g is required but 100 g is requested to allow for quality control.
Sheldrick, B. H. and Wang, C. 1993. Particle-size Distribution. pp. 499-511. In: Carter, M. R. (ed), Soil Sampling and Methods of Analysis, Canadian Society of Soil Science, Lewis Publishers, Ann Arbor, MI.



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