Phytoremediation of dredged material from the San Pablo Bay, CA for heavy and transition metals with *Pelargonium crispum* and *Beta vulgaris*

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ABSTRACT

Phytoremediation by plant uptake reduces the concentrations of potentially toxic elements in soils. I grew *Beta vulgaris* (sugar beet) and *Pelargonium crispum* (lemon-scented geranium) in dredged material from the San Pablo Bay, CA known to contain elevated levels of arsenic, chromium, copper, lead, and nickel. I also attempted to grow *Brassica juncea* (Indian mustard) and *Helianthus annuus* (sunflower), but no individuals survived to the sampling date. Planting these species by direct seeding and transplanting at three different sizes suggest that transplanting after one month of growth in potting soil results in the highest survivorship. I sampled the roots, stems and leaves following 12 weeks of growth in the dredged material for *Beta vulgaris* and 22 weeks of growth for *Pelargonium crispum* and analyzed the tissue for concentrations of the elements of interest. Both species accumulated copper, lead, and nickel most, with accumulation favoring the stems and leaves rather than the roots.

KEYWORDS

Bioremediation, bioaccumulation, *Brassica juncea*, *Helianthus annuus,* San Francisco Bay

INTRODUCTION

The approximately four million cubic yards of dredged material collected annually from the San Francisco Bay (San Francisco Estuary Institute, 2009) is a significant volume of material to manage. Seen as a waste product, the material is traditionally disposed of near Alcatraz Island (U.S. Army Corps of Engineers, 2001). An alternative view sees the dredged material as a valuable resource with potential use in agriculture. Analysis of sediment dredged in 2005 indicates the presence of arsenic, chromium, copper, lead, and nickel (Azwell, unpublished data) at concentrations above average for U.S. agricultural soils (Schacklette & Boerngen, 1984). Because these elements may enter the edible portions of crop biomass and may cause adverse human health effects when ingested (Nordberg, 2002), the use of dredged material in agriculture requires their consideration and potential remediation of the soil to reduce concentrations.

Phytoremediation of metal-enriched soils reduces undesired metal concentrations by plant uptake, moving soluble metals from the soil solution to plant tissue, a process known as accumulation. Several species of plants have been identified as hyperaccumulators of transition and heavy metals, capable of sequestering at least 1000 mg of the metal per kg of aboveground tissue, and have been used to remediate soils (Reeves, 2006). Removal of the plant from the soil following accumulation effectively reduces the concentration of the undesired element.

Helianthus annuus (sunflower), *Brassica juncea* (Indian mustard), *Beta vulgaris* (sugar beet), and many species of *Pelargonium* (common geranium) are accumulators of arsenic, chromium, copper, lead and nickel, in addition to having other traits suitable for growth in the dredged material. *Helianthus annuus* and *Brassica juncea* exhibit drought tolerance, important in a Mediterranean climate, and the ability to accumulate copper (Salt et al, 1995; Salido, Hasty, Lim & Butcher, 2003). *Beta vulgaris* is known to be highly salt tolerant (Kaffka & Hembree, 2004), a desirable trait for the saltwater dredged material, and is able to uptake copper, chromium, nickel, and lead (Ciura, Poniedzialek, Sękara & Jędrszczyk, 2005). In addition, the sugar beet is easy to remove from the soil, in contrast to roots of the other three species. *Pelargonium* is also capable of accumulating chromium, copper, lead, and nickel (Dan, Krishnaraj & Saxena, 2002; Orroño & Lavado, 2009). These four species provide a potential means for reducing concentrations of the elements of interest in the dredged material.

In this study I will determine the method of planting which results in greatest survivorship of the four species in San Pablo Bay dredged material, and determine the extent of accumulation of arsenic, chromium, copper, lead, and nickel. The agricultural use of saltwater dredged material presents the additional challenge of high salinity compared with freshwater-derived dredged material (Darmody et al, 2004; Daniels, Whittecar & Carter III, 2007), which may adversely impact seed germination and plant growth and thus the potential for accumulation. Also, I will document any differential accumulation of the elements of interest in three plant tissues—roots, stems, and leaves. This information has practical implications because it is generally easier to remove aboveground portions of plants compared to belowground portions, with the sugar beet as an exception.

METHODS

Study site

My study was carried out in Petaluma, CA near the San Pablo Bay. The dredged material, moved onto the field site in December 2005, was aggregated and elevated in November 2008 because the surrounding land is at approximately sea level and floods in the winter. The elevation also allows salts in the dredged material to be washed away by rain, reducing salinity over time.

Planting

Various planting methods were carried out in four trials, detailed in Table 1. In my first trial I transplanted *Beta vulgaris*, *Brassica juncea*, and *Helianthus annuus* after growing them from seed in potting mix to approximately three inches height. I purchased *Pelargonium crispum* from local nurseries and transplanted at about one foot height. I did not grow this species from seed because the necessary growth period is too long for the study's timeframe. In my second trial, I direct seeded the former three species. Third, I grew new seedlings in potting mix to a height of five inches and protected them from rabbit predation with metal baskets following transplant. In my fourth trial, I grew additional seeds in potting mix and let them reach approximately one foot height for *Helianthus annuus*, following the successful example of the geraniums, and six inches leaf length for *Beta vulgaris* and *Brassica juncea*. These individuals were also protected from predation by metal baskets.

Table 1. Planting Trials

Trial	Species	Number of Individuals/Seeds	Planting Method
1	*Pelargonium crispum*	18	transplant one foot plant
	Brassica juncea	25	transplant three inch seedlings
	Beta vulgaris	25	
	Helianthus annuus	25	
2	*Brassica juncea*	25	direct seed
	Beta vulgaris	25	
	Helianthus annuus	25	
3	*Brassica juncea*	10	transplant five inch seedlings with metal baskets
	Beta vulgaris	10	
	Helianthus annuus	10	
4	*Brassica juncea*	3	transplant at six inch leaf length with metal basket
	Beta vulgaris	4	
	Helianthus annuus	2	transplant at one foot height with metal basket

Sampling and Analysis

To measure differential accumulation I sampled root, stem, and leaf tissue from *Beta vulgaris* and *Pelargonium crispum*. I first washed the samples with deionized water to remove adhered soil and extraneous particles. I dried all collected tissue at 110^{0}C for 24 hours. I sent the samples to the University of California, Davis Analytical Lab where the dried material was ground, homogenized and sampled for analysis.

RESULTS

Survivorship

Survivorship varied across the four species and four planting trials, detailed in Table 2. *Pelargonium crispum* was only transplanted at one foot height and showed 100% survivorship. No seeds of *Beta vulgaris*, *Helianthus annuus*, or *Brassica juncea* germinated in the dredged material. In addition, no *Helianthus annuus* or *Brassica juncea* survived 12 weeks from transplant to the time of sampling. The adult transplanted *Beta vulgaris* showed 67% survivorship.

Table 2. Survivorship with Different Planting Methods

Species	Planting Method	Number Planted	Survivorship (%)
Beta vulgaris	seed	25	0
	seedling	37	0
	adult	3	67
Helianthus annuus	seed	50	0
	seedling	37	0
	adult	3	0
Brassica juncea	seed	50	0
	seedling	37	0
	adult	3	0
Pelargonium crispum	adult	18	100

Accumulation

Beta vulgaris and *Pelargonium crispum* accumulated arsenic, chromium, copper, lead, and nickel to varying degrees, as detailed in Table 3. The greatest accumulation for *Beta vulgaris* was of copper and the least was of arsenic. The greatest accumulation in *Beta vulgaris* relative to the concentration present in the dredged material was of copper, and the least was of chromium. The greatest accumulation in *Pelargonium crispum* was of nickel and the least was of arsenic. The greatest accumulation in *Pelargonium crispum* relative to the concentration present in the dredged material was of lead, and the least was of chromium. Hyperaccumulation was not achieved in either species because no element reached 1000 ppm in the aboveground tissue.

Table 3. Metal Accumulation by Tissue Type and in Dredged Material (dry weight, in ppm)

Species	Element	Roots	Stems	Leaves	Total	$\frac{[plant]}{[soil]}$	Dredged Material
Beta vulgaris	As	0.01	0.02	0.04	0.07	0.007	10
	Cr	<0.1	0.2	0.3	<0.6	<0.007	90
	Cu	8.3	8.1	19.7	36	0.73	49
	Pb	<0.5	13.8	1.9	<16	~0.70	23
	Ni	2	18	11	31	0.32	96
Pelargonium crispum	As	0.09	0.09	0.20	0.4	0.04	10
	Cr	0.8	0.9	1.4	3	0.03	90
	Cu	9.1	11.5	9.1	30	0.61	49
	Pb	34.3	20.7	21.3	76.3	3.3	23
	Ni	35	8	122	165	1.7	96

DISCUSSION

Survivorship from seed, seedling, and adult

The low survivorship of young *Beta vulgaris*, *Brassica juncea*, and *Helianthus annuus* transplants can be attributed to the physical and chemical properties of the dredged material. The soil has a high clay content, causing it to form large aggregates when dry and a thick mass when wet. It is difficult for the plant roots to penetrate such dense soil, especially a young seedling whose roots are not well established (Håkansson, Henriksson & Blomquist, 2006). In addition, there was some rabbit predation of the seedlings, common for *Helianthus annuus* until the plant reaches about 25 cm (Blamey, Zollinger & Schneiter, 1997), evidenced by rabbit droppings found adjacent to the absent seedlings. Thus, future planting in the dredged material should use transplants of at least 25 cm height for *Helianthus annuus* and a comparable growth for the other species, in addition to protecting younger transplants with metal baskets.

The lack of germination is also likely due to the dredged material's properties, because sufficient water was applied via a drip irrigation system and seeds from the same package germinated well in the potting soil. *Helianthus annuus* is regularly grown in high-clay soils but is sensitive to pH and soil salinity, measured as electrical conductivity (EC). An EC greater than 0.2 – 0.4 S/m or a pH less than about 5.7 is detrimental to *Helianthus annuus* growth (Blamey et al, 1997). The dredged material has an EC of 0.67 ± 0.23 S/m and a pH of 6.4 ± 0.9 (Azwell, unpublished data), which may explain the lack of seed germination. *Beta vulgaris* is also sensitive to acidity, growing best at circumneutral pH and poorly at pH 5.5 (Morillo-Velarde & Ober, 2006).

Differential accumulation in roots, stems, and leaves

The findings of no seed germination and differential accumulation in the plant tissues, detailed in Table 4, are significant for the phytoremediation of Petaluma dredged material on a larger scale. The most economically-viable method of phytoremediation, in terms of materials and labor, is to directly plant seeds and then remove the harvestable portions (e.g. stems, leaves, flowers, fruits, etc.) following some growth period. Because the roots are generally not considered harvestable (Wang, 2004), species accumulating elements of interest more in aboveground tissues are preferred. It should be noted that *Beta vulgaris* is an exception because the sugar beet, which constitutes nearly all the root mass, is easily pulled from the soil.

Table 4. Accumulation by Tissue Type (dry weight, in ppm)

Species	Element	Belowground Tissue	Aboveground Tissue
Beta vulgaris	As	0.01	0.06
	Cr	<0.1	0.5
	Cu	8.3	27.8
	Pb	<0.5	15.7
	Ni	2	29
Pelargonium crispum	As	0.09	0.29
	Cr	0.8	2.3
	Cu	9.1	20.6
	Pb	34.3	42
	Ni	35	130

Toxicity and Solubility of Metals in Soil

Metal elements in soils such as chromium, copper, nickel and lead are of concern because they may end up in food crops, leading to adverse human health effects when ingested (Song et al, 2009). It is important to understand the toxicity of a metal element, which can be predicted using two descriptors—its ionic potential and classification as a class A, B, or borderline metal (Sposito, 2008). Ionic potential (IP) is a quantity defined as the ratio of an element’s valence to its ionic radius in units of nanometers (Sposito, 2008). For example, the IP of Cr(III) can be calculated as shown in equation 1:

$$IP_{Cr(III)} = \frac{3}{0.062\ nm} \approx 48\ nm^{-1} \qquad \boxed{1}$$

Ionic potential predicts the solubility and, to some extent, the reactivity of a metal. When IP is less than 30 nm^{-1} a metal is generally found as a cation in solution, for example $Ca^{2+}_{(aq)}$. When IP is between 30 and 100 nm^{-1} the species tends to hydrolyze and precipitate, and when IP is greater than 100 nm^{-1} the species tends to form a soluble oxyanion, such as $Cr_2O_7^{2-}$.

The class A and B categories are distinguished based on polarizability and preferred ligand—those elements which do not fall strictly under either class are defined as borderline. The class A metals include sodium and calcium, the class B metals include lead and mercury, and the borderline metals include chromium, copper, and nickel. Table 5 (Sposito, 2008) summarizes the predicted toxicity of a metal in soil solution at neutral pH based on the two criteria described above.

Table 5. Metal Toxicity Based on IP and Class

Class	**Ionic Potential (IP)**	**Toxicity**	**Example in Dredged Material**
A	$IP < 30\ nm^{-1}$ $30\ nm^{-1} < IP < 100\ nm^{-1}$ $IP > 100\ nm^{-1}$	Not toxic Toxic Possibly Toxic	
B	$IP < 30\ nm^{-1}$ $30\ nm^{-1} < IP < 100\ nm^{-1}$ $IP > 100\ nm^{-1}$	Toxic Toxic Possibly Toxic	Pb
Borderline	$IP < 30\ nm^{-1}$ $30\ nm^{-1} < IP < 100\ nm^{-1}$ $IP > 100\ nm^{-1}$	Possibly Toxic Toxic Possibly Toxic	Ni, Cu, Zn Cr

Heavy metal toxicity is related to solubility because it is generally the soluble species which is bioavailable. There are reservoirs other than the soil solution where metals may be found, one of the largest being particle surfaces. Metals considered toxic in solution may be harmless if adsorbed to a surface at a non-exchangeable site. Thus, the adsorption of transition and heavy metals generally decreases metal uptake in a soil.

A soil's cation exchange capacity (CEC), its ability to bind positive charge, is mostly the result of a structural charge imbalance in minerals and humus creating negatively-charged sites that attract positively-charged cations. There is competition for the negatively-charged binding sites in a soil, with an equilibrium forming under fixed conditions. With increasing competition from other cations, most importantly H^+ (Welp & Brümmer, 1999), a metal will occupy a smaller fraction of total CEC if its concentration remains fixed. Thus, pH is a factor affecting the bioavailability of metal cations (Kabata-Pendias, 2004). Because the San Pablo Bay dredged material has a large fraction of clay minerals and a large CEC (Azwell, unpublished data), it is possible that much of the total arsenic, chromium, copper, lead, and nickel will be adsorbed.

Limitations

It is unlikely that hyperaccumulation, defined as 1000 ppm dry weight, would be achieved for any element at the concentrations present in the dredged material. For example, arsenic has a total concentration of about 10 mg/kg in the dredged material. To reach 1000 mg/kg in the plant tissue, assuming an average dry total plant weight of 1 kg, the roots must extract all the arsenic from 100 kg of soil, at minimum. The conditions necessary for this to occur are: (1) the roots are exposed to 100 kg of soil, (2) all 10 mg/kg of arsenic are bioavailable, either in solution or adsorbed to exchangeable sites (Abdullah & Sarem, 2010), and (3) the roots actually uptake and store all the arsenic. These three conditions can be generalized for any element and at any soil concentration, but it is unlikely for all three conditions to be met. First, the roots may not grow large enough to span the necessary volume of soil, due to the relatively short 12 week growth period allotted in this study and the high clay content of the soil that would impede root expansion. Second, the total soil concentration of an element is not necessarily equal to its bioavailable concentration. Some fraction of the total concentration may be adsorbed to non-exchangeable sites or precipitated. Third, the roots will not uptake all the bioavailable elements they are exposed to, some will be passed over. In some studies where hyperaccumulation is achieved, the soil is artificially contaminated with large concentrations of the elements of interest to increase the potential for plant uptake (Abdullah & Sarem, 2010).

Future Research

The results of this study may guide future research for the phytoremediation of dredged material, which competes with other technologies in soil remediation. First, the most economically-viable method of remediation should be determined. Transplanting is a considerable increase in labor and material costs when compared to direct seeding. In addition, phytoremediation studies may focus more on soils with several elements of interest at moderate to low total concentrations. Much information on metal-accumulating species focuses on a single or relatively small number of elements. It is often not known which species or combination of species will best accumulate several elements simultaneously.

Broader Implications

Many phytoremediation studies focus on a single species accumulating a single element present in very high total concentration, often above 1000 ppm, in the starting soil. In soils with several toxic elements present in moderate concentrations, such as the dredged material from the San Pablo Bay, phytoremediation requires selection of an optimal species or combination of species. A general method will be described for a single species which can be repeated for several species. First, the relative need of removal for each toxic element should be weighted for the particular study soil. These weights may be denoted $x_1 \ldots x_n$, where the subscript is unique to each element of interest. Next, the plant species should be assigned an accumulation potential for each element in the soil, a measure of how effective the species is at accumulating that element. This variable may be denoted $P_1 \ldots P_n$, where the subscripts have the same meaning as for the weights. The optimal species for phytoremediation can be found by summing the product of the weight and accumulation potential of each element, as in equation 2:

$$S = \sum_{i=1}^{n} x_i P_i \qquad (2)$$

If m species are to be used for phytoremediation ($m > 1$) from a pool of q potential species ($q > m$), the optimal combination of species is determined by the greatest sum of m terms in $S_1 \ldots S_q$. In relation to the current study, the total accumulation of *Beta vulgaris* and *Pelargonium crispum* is used as a measure of phytoremediation. The species capable of accumulating the greatest total concentration of arsenic, chromium, copper, lead, and nickel is the most suitable for large-scale phytoremediation of the dredged material.

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WORKS CITED

Blamey, F. P. C., Zollinger, R. K., & Schneiter, A. A. (1997). Sunflower Production and Culture. In A. A. Schneiter (Ed.), *Sunflower Technology and Production*. Madison, WI: American Society of Agronomy, Inc., Crop Science Society of America, Inc., Soil Science Society of America, Inc.

Ciura, J., Poniedzialek, M., Sękara, A., & Jędrszczyk, E. (2005). The Possibility of Using Crops as Metal Phytoremediants. *Polish Journal of Environmental Studies, 14*(1), 17-22.

Dan, T. V., Krishnaraj, S., & Saxena, P. K. (2002). Cadmium and nickel uptake and accumulation in scented geranium (*Pelargonium* sp. *'frensham'*). *Water, Air, and Soil Pollution, 137*, 355-364.

Daniels, W. L., Whittecar, G. R., & Carter III, C. H. (2007). *Conversion of Potomac River Dredge Sediments to Productive Agricultural Soils*. Paper presented at the National Meeting of the American Society of Surface Mining and Reclamation, Gillette, WY.

Darmody, R. G., Marlin, J. C., Talbott, J., Green, R. A., Brewer, E. F., & Stohr, C. (2004). Dredged Illinois River Sediments: Plant Growth and Metal Uptake. *Journal of Environmental Quality, 33*, 458-464.

Håkansson, I., Henriksson, L., & Blomquist, J. E. (2006). Soil Tillage and Crop Establishment. In A. P. Draycott (Ed.), *Sugar Beet*: Blackwell Publishing.

Kabata-Pendias, A. (2004). Soil-plant transfer of trace elements-an environmental issue. *Geoderma*, *122*, 143-149.

Kaffka, S., & Hembree, K. (2004). The effects of saline soil, irrigation, and seed treatments on sugarbeet stand establishment. *Journal of Sugar Beet Research, 41*, 61-72.

Morillo-Velarde, R., & Ober, E. S. (2006). Water Use and Irrigation. In A. P. Draycott (Ed.), *Sugar Beet*: Blackwell Publishing.

Nordberg, G. F., Sandström, B., Becking, G., & Goyer, R. (2002). Essentiality and Toxicity of Metals. In B. Sarkar (Ed.), *Heavy Metals in the Environment* (pp. 1-33). New York, New York, U.S.A.: Marcel Dekker, Inc.

Orroño, D. I., & Lavado, R. S. (2009). Heavy metal accumulation in *Pelargonium hortorum*: Effects on growth and development. *International Journal of Experimental Botany, 78*, 75-82.

Reeves, R. D. (2006). Hyperaccumulation of trace elements by plants. In J. Morel, G. Echevarria & N. Goncharova (Eds.), *Phytoremediation of metal-contaminated soils*: Springer Netherlands.

Salido, A. L., Hasty, K. L., Lim, J. M., & Butcher, D. J. (2003). Phytoremediation of arsenic and lead in contaminated soil using Chinese brake ferns (*Pteris vittata*) and Indian mustard (*Brassica juncea*). *International Journal of Phytoremediation, 5*, 89-103.

Salt, D. E., Blaylock, M., Kumar, P. B. A. N., Dushenkov, V., Ensley, B. D., Chet, I., et al. (1995). Phytoremediation: a novel strategy for the removal of toxic metals from the environment using plants. *Bio/Technology*, *13*, 468-478.

San Francisco Estuary Institute (2009). The Pulse of the Estuary: Monitoring and Managing Water Quality in the San Francisco Estuary. San Francisco Estuary Institute, Oakland, CA.

Song, B., Lei, M., Chen, T., Zheng, Y., Xie, Y., Li, X., et al. (2009). Assessing the health risk of heavy metals in vegetables to the general population in Beijing, China. *Journal of Environmental Sciences, 21*, 1702-1709.

Sposito, G. (2008). *The Chemistry of Soils*. New York, New York, U.S.A.: Oxford University Press.

U.S. Army Corps of Engineers, U.S. Environmental Protection Agency, San Francisco Bay Conservation and Development Commission, and San Francisco Bay Regional Water Quality Control Board (2001). *Long-term Management Strategy for the Placement of Dredged Material in the San Francisco Bay Region*.

Welp, G., & Brummer, G. W. (1999). Adsorption and solubility of ten metals in soil samples of different composition. *Journal of Plant Nutrition and Soil Science, 162,* 155-161.