Technology for river protection against pollution from cultivated areas

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Abstract
The application of agrochemical and chemicals for plant protection, together with animal farming are main source of river pollution. Heavy rainfall and widespread use of irrigation and drainage can lead to leaching from 20% to 80% of nutrients and agrochemicals added from well-drained soils to river water. The application of Si soil amendments can reduce nutrients and pollutants leaching via increasing soil adsorption capacity, initiation of new mineral formation, optimization of microbial population and deactivation of toxic substances. During five years laboratory, greenhouse and field studies in Florida has demonstrated that application of the special Si soil amendments dramatically improved the quality of natural water. The leaching of nutrients was reduced from 40 to 80% for P, from 10 to 40% for K and from 25 to 60% for N. The leaching of heavy metals was reduced from 50 to 90% and heavy metals were transformed to passive forms. The leaching of manure was reduced from 20 to 50%. The mixing of Si-rich substance with fresh or composted manure reduced the P, N or organic substances leaching from 20 to 70% and kept nutrients in plant-available forms. The economical calculations showed that the application of active Si has high economical effect for farmers.

Keywords:
silicon soil amendment, nutrients, leaching, pollution, technology

INTRODUCTION

The role of agriculture in the pollution of water rarely has been clearly defined, largely because anthropogenic sources are often the major source of nutrient ions. Nutrients losses in land runoff are difficult to quantify due to their diffuse nature. These losses of nutrients emanate from a number of sources within the landscape and their amount, form, and timing are quite variable as a result of short-term and often unpredictable changes in hydrological conditions and farming practices. Sandy and deeply weathered soils usually have low nutrient retention and from 20 to 80% of applied nutrients or chemicals leach or runoff to the ground and surface waters (Campbell et. al., 1985; Sims et. al., 1998). A solution of the problem should be founded through an understanding of the chemical and chemical-physical processes in the soil-microorganism-plant system related with nutrients and pollutants behavior.

The movement of nutrients through soil is a complex process, controlled by biological, chemical, and physical soil conditions. Usually element chemical adsorption has priority in the studies devoted to reduction of nutrient leaching (He et al., 1999; Sims et al, 1998). For example, it is known that phosphorus reacts with Ca, Al, Fe, or Mn forming slightly soluble or plant-unavailable

compounds (Lindsay, 1979). Potassium and nitrogen can be adsorbing by secondary clay minerals, microorganisms and by plants (Orlov, 1985). The main part of Heavy Metals (HM) in soil immediately transferred to immobile or slightly soluble forms (Orlov, 1985). However, the mobile forms of HM in polluted soil also available and equilibrium between mobile and immobile forms of HM are depended on the soil properties (Ammosova and Matichenkov., 1989).

Besides element chemical adsorption, physical adsorption takes place in a soil. Negatively charged anions can interact with positively charged colloids or soil organic matter without formation of a strong chemical linkage (Orlov, 1985). Sandy soils and deeply weathered soils are characterised by low content of both colloids and organic matter (Kovda, 1973). It should be noted that physically adsorbed elements remains plant-available (Matichenkov and Ammosova, 1995).

The lack in phosphorus (P), nitrogen (N), and potassium (K) is a major factor limiting plant growth. Therefore successful agriculture require the application of mineral and organic fertilisers. But nutrients and pollutant leaching has negative influence on the environmental quality, include river water. This contradiction must be resolved. The simple reduction of mineral fertiliser rate reduces agricultural effectiveness. Using lime material for reduction of P mobility decreases both P leaching and P plant nutrition. Necessary new technology, which will allow optimizing plant nutrition and reducing the level on element leaching from cultivated soil to river. This is possible only by improvement of the soil matrix.

Silicon is one of the most widely distributed elements in the Earth's crust. Both inert and active Si compounds determine numerous physical and chemical properties of soil, including adsorption and exchange capacities (Matichenkov and Bocharnikova, 2000; Rochev et al., 1980). Si-rich biogeochemically active substances (Si fertilizers) usually exhibit very good adsorption properties (Rochev et al., 1980). The leaching of potassium and other mobile nutrients from the surface soil horizon is reduced by Si fertilization (Matichenkov, 1990; Tokunaga, 1991). Solid Si-rich substances, with high surface areas, adsorb mobile P, keeping them in a plant-available form (Matichenkov, 1990; Matichenkov et al, 1997; Olivera et al., 1986).

It is known that monosilicic acid has double influence on the HM mobility (Bocharnikova et al., 1999; Lindsay, 1979; Schindler et. al., 1976). High concentration of monosilicic acid in the water solution precipitate soluble HM with formation the HM-silicates. On the other hand the slight increasing of monosilicic acid concentration in the system, which has equilibrium between mobile and immobile HM result increasing the concentration of mobile forms of HM (Bocharnikova et. al. 1995; Schindler et. al., 1976). By this means the mobility of HM can be managed or controlled by application of the various rates of active Si.

The preliminary investigations demonstrated significant effects of Si fertilizers on both the environment and the economy (Matichenkov et al., 1997; Matichenkov et al., 1999, Matichenkov et al., 2000b; Matichenkov et al., 2001). The Si-rich materials have demonstrated significant adsorption capacity for P. The sandy soils and sand treated with Si soil amendments increased the soil adsorption capacity for P, K, NO_3^-, and NH_4^+ from 20 to 70% (Matichenkov et al. 1999). These effects may have been caused by the action of several mechanisms, include increasing soil exchange capacity, formation of the soil secondary minerals, increasing of soil microbial population and increasing of the root mass of cultivated plants.

In 2000 the special project "Minimizing nutrient and pollutants leaching from sandy agricultural soils and optimization of plant nutrition" was initiated in the University of the Florida and supported by Florida Department of Environmental Protection. During four years the laboratory, greenhouse and field demonstrations have shown that application of commercial Si-rich soil

amendments had the following effects on the soil-plant system under observation (Matichenkov et al., 2001; 2002 a; 2002 b):

1. The application of Si-rich materials as soil amendments has both economical and ecological benefits and can be recommended as a Best Management Practice.
2. Si-rich soil amendments can reduce leaching of P by 20 to 80%, K by 10 to 40%, and N by 5 to 40% from cultivated areas treated by inorganic and organic fertilizers.
3. The data developed in the demonstrations allow us to calculate the positive effects of Si-rich soil amendments on the P balance in the soil-plant system. The effects range from 3609 to 58 pounds of P per acre.
4. The largest effect of Si-rich soil amendments was observed for soil treated manure. The leaching of organic substances (manure) was reduced from 20 to 50%. The mixing of Si-rich substance with fresh or composted manure reduced the P, N or organic substances leaching from 20 to 70% and kept nutrients in plant-available forms.
5. Si-rich soil amendments not only reduce P leaching, but also maintained P in plant available form. The content of P in plant tissue was increased under application of active Si from 20 to 40%.
6. Si-rich soil amendments dramatically reduced mobility of HM in the cultivated soil and transformed HM from active to passive forms (HM silicateas). The leaching of HM (Cu, Pb, Cr, Ni, Co) was reduced from 50 to 90%.
7. The application of Si-rich soil amendments also increased the quality and quantity of crop production (rice, grass, citrus, tomato and corn). In the average the crop production under Si fertilization was increased from 15 to 30%. The content of sugar, vitamins in the fruits and vegetables were increased from 5 to 15%. The quality of grain for rice and fodder unit for grass and corn was increased as well.
8. Si-rich amendments or Si fertilizers were recommended for reduction of P as well as other nutrients leaching from sandy soils.

In this project only Si-rich industrial by-products were tested as Si-rich soil amendmets. But using of industrial by-product can provide the risk for secondary pollution of soil and natural water. It is necessary to find more safety material for widely practical implication. Probably some natural materials, like Diatomaceous Earth, zeolites can be used for optimization of the soil matrix properties and for plant nutrition. The objective of this paper is study of the effect some natural and environmental friendly Si-rich substances on the P, N, K, Cu, Pb, Cr, Ni and Co leaching in the sandy soils.

METHODS

Pure quartz sand (40-100 mesh) was used as basic matrix for all experiments. This sand has pH = 6.5. Before experiments sand was washed in the 0.1 n HCl and then washed in the bi-distilled water and dried at 65^{o}C.

Amorphous fine silica (FSS) (S-153, Fisher Scientific, Fair Lawn, NJ), calcium silicate ($CaSiO_3$, wollastonite, Aldrich Chemical Co., Inc., Milwaukee, WI), Pro-Sil (product from steel production, PRO-CHEM Chemical Company, FL), Silica Plus (Natural Agricultural Solution, Pallkarra (Australia). Selected properties of these materials are presented in the Table 1.

Table 1. Selected properties of investigated materials.

Material	pH (H_2O)	Ca,%	Fe, %	Al,%	Si, %
FSS	7.0	-	-	-	46.5
$CaSiO_3$	8.0	34.5	-	-	24.1
Pro-Sil	8.6	27-31	0.08-0.4	0.2-0.3	13-14
Silica Plus	7.0	0.2-0.3	1-2	-	34-36

One rate of Si-rich materials was used in the experiment: 10 g of materials per 1 kilo of sand for solid materials, which approximately equal to 10 ton per hectare. The sand was mixed with Si-rich materials.

The column experiment was to model elements leaching using the various Si-rich substances. The plastic column had a volume 60 cm^3 and a diameter of 2.5 cm. The various test solutions were added to the column at 6-8 ml h^{-1} using a peristaltic pump. The percolate was collected at 40 mL intervals. A drop of chloroform was added to the collected solution, which was then stored in a refrigerator at 4^{o}C. A total of 280 mL solution was applied to each column. Each column was replicated three times and triplicate analyses of each liquid sample were conducted. The following solutions were used for imitation of the element leaching:

solution 1- 40 ppm of P (as Na_2HPO_4), 40 ppm of K as KCl and 40 ppm of N as $NaNO_3$);

solution 3 – waste water from milk farm (MacArthur Farm, Florida) with 32 ppm of P, 5 ppm of K and 20 ppm of N (NO_3^-);

solution 2 - 25 ppm of Cd as $CdCl_2$; 25 ppm of Cr as CrO_3; 25 ppm of Cu as $CuSO_4$; 25 mg/kg of Ni as $NiSO_2$ and 25 ppm of Pb as $Pb(NO_3)_2$).

The concentration of the K, Cd, Cr, Cu, Ni and Pb in percolated solution was tested by atomic-adsorption methods in the Gainesville soil lab, University of Florida. The concentration of P in percolated solution was tested by standard colorimetric method and N was as tested by ion-metric method in the Soil Water Laboratory, Silicon section in the Indian River Research and Education Center, University of Florida. Three replications were conducted for each treatment. All data were subjected to a statistical analysis based on comparative methods using Duncan's multiple range tests for mean separation at the 5% level of significance.

RESULT AND DISCUSSION

The obtained results are present in the tables 2, 3 and 4. The experiment with first solution has demonstrated that all tested material dramatically reduced the leaching on the nutrients (Table 2). However, the results also allow determining that each substance has some specific properties. For example, Pro-Sil has highest adsorption capacity for P and reduces P leaching more then on 90%. Our previous publication intimated such specification for Pro-Sil (Matichenkov et al., 2001; 2002 a). We suggested that high influence of Pro-Sil on P behavior is determined by unique chemical composition. Probably not only Si-rich surface adsorbed P, but Ca has influence of the P mobility as well. Pro-Sil was tested in the field experiments (Florida Department of Environment Protection project 2000-2004), which has demonstrated that Pro-Sil not only dramatically from 40 to 80% reduced P leaching from sandy cultivated soils, but also kept P in plant available forms. The maximum effect for potassium was determined for FSS. Silica Plus showed the best result for nitrate adsorption.

Table 2. The content of the tested elements in the percolated solution (first solution)

Treatment	Percolated solution, ml						
	40	80	120	160	200	240	280
	P, ppm						
Control	12.3	25.2	34.2	38.5	40.4	41.7	40.3
FSS	5.6	8.9	12.5	17.5	22.6	32.1	38.5
$CaSiO_3$	4.5	7.8	17.5	22.8	28.5	35.4	39.5
Pro-Sil	0.1	0.3	0.3	0.2	0.5	0.6	0.6
Silica Plus	3.5	6.5	8.8	12.2	16.7	18.4	20.4
LSD_{05}	0.3	0.3	0.4	0.4	0.4	0.3	0.4
	K, ppm						
Control	34.5	38.7	40.2	40.2	39.2	41.3	40.2
FSS	3.2	5.8	9.6	10.2	13.2	18.4	22.3
$CaSiO_3$	14.3	18.7	25.4	28.7	33.5	38.4	39.2
Pro-Sil	14,5	18.6	19.4	20.4	28.5	35.6	35.9
Silica Plus	8.3	10.4	12.5	17.5	23.4	28.5	30.2
LSD_{05}	1.1	1.1	1.0	1.0	1.1	1.0	1.0
	N, ppm						
Control	15.3	19.6	25.4	29.5	34.2	38.8	40.1
FSS	4.6	12.4	16.5	21.3	27.4	33.4	38.4
$CaSiO_3$	11.3	17.3	22.6	27.3	30.2	34.5	37.7
Pro-Sil	3.4	5.8	10.2	14.3	18.2	22.1	24.5
Silica Plus	2.1	4.3	8.2	11.3	15.3	16.3	17.2
LSD_{05}	1.2	1.3	1.3	1.3	1.2	1.3	1.4

The using of wastewater from dairy farm as solution in the column experiment also has shown high effect of Si-rich substance on the nutrient leaching (Table 3). The obtained result was similar, as in first test with using solution 1 (Table 2). The maximum effect for P was obtained for Pro-Sil. The maximum adsorption capacity for potassium was determined for FSS and Silica Plus was best for nitrogen adsorption.

The summarizing of the both experiments data allow to conclude that application of Si-rich substances can dramatically reduce the leaching of P, K and N. The leaching of nutrients was reduced from 40 to 80% for P, from 10 to 40% for K and from 25 to 60% for N. Practically the application of FSS or $CaSiO_3$ are difficult, because both substances are very expensive. The application of Pro-Sil has positive influence on the soil adsorption properties. But using of this materials on the practice has risk for secondary pollution by HM. The best way is using of natural products. Silica Plus is natural material produced from Diatomaceous Earth and don't content any pollutants. By this means the using of this material will protect soil matrix and river water against chemical pollution.

Table 3. The content of the tested elements in the percolated solution (second solution)

Treatment	Percolated solution, ml						
	40	80	120	160	200	240	280
	P, ppm						
Control	9.3	18.3	23.7	28.6	30.2	32.1	32.2
FSS	4.3	6.5	8.3	12.3	15.6	20.1	24.3
$CaSiO_3$	5.4	10.2	14.3	20.3	22.8	26.4	28.1
Pro-Sil	0.2	0.2	0.4	0.4	0.5	0.7	0.9
Silica Plus	3.7	3.9	4.8	5.9	9.3	12.3	17.3
LSD_{05}	0.3	0.4	0.3	0.4	0.5	0.5	0.5
	K, ppm						
Control	1.2	3.4	4.3	5.1	5.0	4.9	5.1
FSS	0.2	0.6	0.7	1.4	1.6	2.3	2.5
$CaSiO_3$	1.0	2.4	4.1	4.7	5.2	5.1	4.9
Pro-Sil	0.6	0.8	1.5	2.4	2.7	3.1	3.5
Silica Plus	0.3	0.7	1.5	1.8	2.3	2.8	3.2
LSD_{05}	1.2	1.2	1.1	1.1	1.3	1.3	1.3
	N, ppm						
Control	8.3	12.5	18.5	21.1	20.3	20.1	20.2
FSS	4.5	6.4	10.2	12.4	15.4	18.4	20.1
$CaSiO_3$	3.2	4.3	6.3	7.2	7.8	8.4	9.3
Pro-Sil	2.6	3.7	4.3	5.6	6.5	8.3	10.2
Silica Plus	2.1	2.7	3.2	3.6	4.2	4.8	5.3
LSD_{05}	1.1	1.0	1.2	1.2	1.3	1.2	1.3

The final part of the experiment was conducted with solution contains HM. Heavy metals exist in numerous agrochemicals, such as fertilizers (phosphates), insecticides, fungicide et al. Some heavy metals occasional arrived to the soil. These substances have extremely negative influence on the natural water, drinking water and living organisms include humans. The application of the tested Si-rich materials dramatically reduced HM leaching (Table 3).

The maximum effect of Si-rich material for mobility of Cu, Cd, Ni, Cr and Pb was determined for Pro-Sil and Silica Plus. These substances reduced HM leaching up to 50-90%. For various HM the effect of Si-rich substance application was different. Probably this is related with specific properties of each element. This data linkage with other our previous experiments and investigations (Bocharnikova et al. 1999). Using of chemical pure FSS has demonstrated that silicon has direct influence on the mobility of the HM in the soil and consequently the application of Si-rich substances can control movement of HM to river waters.

The obtained result has shown that using of natural sources of active Si, such as FSS, calcium silicate or Natural Silica can improve the quality of the soil matrix and we can suggest that these substances will has high influence on the element leaching from cultivated area to river water. The special methodology for determination of the technological parameters (best rate, time and type for application) was elaborated and tested in the Florida. Now it is possible to move the elaborated technology to other regions in the World.

Table 4. The content of the tested elements in the percolated solution (third solution).

Treatment	Percolated solution, ml						
	40	80	120	160	200	240	280
	Cu, ppm						
Control	15.3	20.8	25.4	25.2	24.3	25.1	25.0
FSS	1.1	2.8	6.4	16.3	19.3	20.3	24.3
$CaSiO_3$	2.3	14.3	18.5	20.3	22.3	25.4	25.0
Pro-Sil	0.9	1.3	2.4	4.4	8.2	9.3	12.3
Silica Plus	0.8	2.4	5.8	9.2	14.4	16.3	18.3
LSD_{05}	0.2	0.3	0.3	0.4	0.4	0.4	0.5
	Cd, ppm						
Control	3.4	7.9	12.4	18.9	20.2	24.1	24.3
FSS	0.3	0.5	0.6	0.9	1.5	2.3	3.6
$CaSiO_3$	1.1	2.2	2.7	3.5	5.8	10.2	15.2
Pro-Sil	0.1	0.2	0.2	0.5	0.6	0.6	0.7
Silica Plus	0.5	1.2	1.7	2.4	5.8	5.9	8.6
LSD_{05}	0.2	0.2	0.3	0.4	0.3	0.3	0.4
	Ni, ppm						
Control	8.6	10.2	15.6	19.3	23.4	25.1	25.1
FSS	2.2	6.2	8.3	10.2	15.4	20.3	22.1
$CaSiO_3$	6.4	10.2	13.3	18.2	22.3	23.4	24.3
Pro-Sil	0.6	0.9	1.4	1.6	2.3	3.4	3.9
Silica Plus	0.9	1.4	2.8	4.3	7.1	10.2	13.2
LSD_{05}	0.3	0.3	0.2	0.3	0.3	0.2	0.2
	Cr, ppm						
Control	3.2	6.4	10.2	14.5	19.3	23.4	25.1
FSS	1.2	2.1	2.7	3.5	7.4	9.2	14.2
$CaSiO_3$	2.5	3.4	6.4	10.2	14.3	17.3	20.3
Pro-Sil	0.2	0.1	0.6	0.4	0.7	0.9	1.2
Silica Plus	0.9	1.4	1.9	2.4	3.5	5.2	8.2
LSD_{05}	0.3	0.3	0.3	0.3	0.3	0.2	0.3
	Pb, ppm						
Control	1.2	3.5	9.2	13.2	18.5	20.3	22.3
FSS	1.1	2.1	2.7	5.3	8.2	15.4	20.3
$CaSiO_3$	1.3	2.5	4.3	6.3	12.3	17.3	20.5
Pro-Sil	0.1	0.2	0.2	0.3	0.5	0.7	1.2
Silica Plus	0.6	0.9	1.3	2.6	3.8	5.2	9.2
LSD_{05}	0.1	0.1	0.2	0.3	0.3	0.3	0.3

CONCLUSIONS

The application of Si soil amendments, with active forms of Si can reduce nutrients and pollutants leaching via increasing soil adsorption capacity, initiation of new mineral formation in the soil, optimization of soil microbial population and deactivation of such pollutants as HM or organic toxic substances.

During five years laboratory, greenhouse and field studies in the Central and North Florida has demonstrated that application of the special Si-rich soil amendments dramatically improved the quality of natural water. The leaching of nutrients were reduced from 40 to 80% for P, from 10 to

40% for K and from 25 to 60% for N. The leaching of heavy metals (Cu, Pb, Cr, Ni, Co) was reduced from 50 to 90% and heavy metals were transformed to passive forms. The leaching of organic substances (manure) was reduced from 20 to 50%.

The application of Si-rich soil amendments also increased the quality and quantity of crop production (rice, grass, citrus, tomato and corn). The active Si also can be used for optimization of manure utilization. The mixing of Si-rich substance with fresh or composted manure reduced the P, N or organic substances leaching from 20 to 70% and kept nutrients in plant-available forms. The economical calculations showed that the application of active Si has high economical effect for farmers also.

The methodology for adaptation of elaborated technology was elaborated. The best sources for Si soil amendment are natural Si-rich materials, which will be totally environmental friendly and has agricultural benefits.

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