# Technology for natural water protection against pollution from cultivated areas

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## Abstract

The application of agrochemicals for plant nutrition and protection, together with animal farming, are major sources of natural water pollution. Heavy rainfall and widespread use of irrigation and drainage can lead to leaching from well-drained soils to water of 20% to 80% of added nutrients and agrochemicals. Numerous agrochemicals contain heavy metals or organic toxins. On the other hand, minimising agrochemical application may have a negative impact on yield. Therefore, adoption of new technology which resolves both environmental and economic problems is necessary. The application of Si soil amendments can (i) reduce nutrient and pollutant leaching via increasing soil adsorption capacity, (ii) initiate new mineral formation in the soil, (iii) optimize soil microbial population, and (iv) deactivate pollutants: heavy metals, organic toxic substances. Laboratory and greenhouse studies demonstrated that application of specific Si-rich soil amendments significantly improved the quality of natural water. The reductions in leaching of nutrients composed of 40 to 80% for P, 10 to 60% for K, and 25 to 60% for N. The leaching of heavy metals (Cu, Pb, Cr, Ni, and Co) was reduced by 50 to 95% and heavy metals were transformed into passive forms.

## Key Words

Silicon fertilizer, nutrient leaching, heavy metals toxicity

## Introduction

The role of agriculture in the pollution of water has rarely been clearly quantified largely because anthropogenic sources are often the major source of nutrient ions (Arregui, Quemada, 2006; Ghiberto et al., 1990). Nutrients and heavy metals (HM) from pesticide losses in land runoff are difficult to quantify due to their diffuse nature. On the other hand, a reduction in agricultural productivity from reduced pesticide application may have negative influences on the economy and numerous social aspects. The movement of nutrients and pollutants through a soil is a complex process, influenced by biological, chemical, and physical soil conditions (Orlov, 1992). A solution to the problem should be founded through an understanding of the chemical and physical-chemical processes in the soil-microorganism-plant system, in association with the behavior of nutrients and pollutants, for development of new technologies and materials for agriculture.

During the last century, industry and agriculture have seriously disturbed the natural cycles of heavy metals in the soil-plant system (Adriano, 1986; Benavides et al., 2005). The abnormal concentrations of HM in polluted soils may lead to contamination of the entire ecosystem, and since soil is the basis for all living terrestrial organisms including plants, animals, and microorganisms, this is a problem that can no longer be taken lightly. HM are hazardous contaminants of food and through the food chains enter the human body as a cumulative poison (Benavides et al., 2005).

The rehabilitation of soil contaminated by HM presents some troublesome aspects, which don’t exist in other natural environments like water or air (Orlov, 1992), and the recovery of such soils is often characterized by high cost and low efficiency. Current and traditional methods used to regulate and manage HM mobility in the soil, such as changing pH or increasing soil adsorption capacity by adding amendments to the soil, may not be adequate in a dynamic soil matrix, influenced by the action of plants, microorganisms, and the inflow and outflow of water solutions (Orlov, 1992). Different integrated approaches are required in order to manage this complex issue.

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 (Snyder et al., 2006). Si-rich biogeochemically active substances (Si fertilizers) usually exhibit very good adsorption properties (Matichenkov, Bocharnikova, 2001; Chimney et al., 2006). The leaching of potassium, nitrogen, and other mobile nutrients from the surface soil horizon is reduced by Si fertilization (Matichenkov, 2008; Tokunaga, 1991). Previously, we suggested that the effect of soluble Si compounds on HM mobility depends on the concentration of monosilicic acid in the soil (Matichenkov, Bocharnikova, 2001; Matichenkov, 2008). Monosilicic acid and its anion exhibiting properties of weak acid can interact with many organic and inorganic compounds, including HM (Lindsay, 1979). If the concentration of monosilicic acid is low, the interaction with HM results in a soluble complex (Schindler et. al., 1976; Bocharnikova, Matichenkov, 2007). Monosilicic acid at high concentration may cause full precipitation of HM with formation of slightly soluble silicates (Lindsay, 1979; Matichenkov, 2008).

$$ZnSiO_4 + 4H^+ = 2Zn^{2+} + H_4SiO_4 \qquad \log Ko=13.15$$

$$PbSiO_4 + 4H^+ = 2Pb^{2+} + H_4SiO_4 \qquad \log Ko=18.45$$

The level of reduced HM mobility also depends on the adsorption properties of applied Si-rich minerals and properties of the HM (Bocharnikova et. al., 1999; Matichenkov, 2008). Therefore, it is important to investigate the interaction of the various heavy metals with various forms of Si.

The main aim of our study was to determine the effect of Si-rich substances on the leaching and mobility of nitrogen, phosphorus, potassium, cadmium, copper, nickel, and lead.

## Methods

Two experiments were conducted at the Institute Physical-Chemical and Biological Problems in Soil Science Russian Academy of Sciences: 1) greenhouse test with barley and 2) column investigation with heavy metals. Two types of Si-rich substances were used in both studies:

1) Amorphous silicon dioxide (chemically pure $SiO_2$, Fisher) (ASD) with surface area 30 $m^2$/g;

2) Diatomaceous earth (Natural Silica, Synergy Fertilizers Pty Ltd, North Queensland, Australia) (DE).

### *Test with fertilizers*

The greenhouse experiment with Grey Forest Soil (45% of sand, $pH_{H2O}$= 6.8, $C_{org}$=2.71) was conducted in 1L volume plastic pots using barley (*Hordeum vulgare* L) as the tested plant. The traditional mineral fertilizers (mix of urea with triplesuperphosphate and potassium chloride with N:P:K proportion as 20:20:20) was used at the rate 100 and 500 kg $ha^{-1}$ (NPK100 and NPK500). The effect of DE was studied in comparison with that of ASD as the compound to be high in plant-available Si. There were the following treatments: control, NPK100, NPK500, NPK100+ASD, NPK500+ASD, NPK100+DE, and NPK500+DE. Each treatment was replicated three times. All fertilizer treatments were applied before planting. One hundred mL of distilled water was added to each pot daily, percolated solutions were collected on 5th and 25th days of the experiment and analysed for soluble N, P, and K by standard methods. The biomass of barley was measured after 1 month of growth.

### *Test with heavy metals*

Dry soil (1 kg of the upper horizon of Gray Forest Soil) was mixed with either ASD (10 g), DE (10 g), or no additive for the control treatment, and then placed in plastic tubes of 10 cm diameter and 20 cm height. All columns were irrigated with 100 mL of water for equilibrating the moisture level prior to application of the heavy metal treatments. One hundred mL of solution containing 250 mg of Cd as $CdCl_2$, 200 mg Cu as $CuSO_4$, 100 mg Ni as $NiSO_2$ and 150 mg Pb as $Pb(NO_3)_2$ was then added to each column. Each treatment was replicated 3 times. An additional 200 ml of distilled water was added to each column and the percolated solutions collected, daily over 1 week. The average concentrations of HM were then determined. The soils from the columns were dried at $65^oC$ and tested for $MgCl_2$-extractable (mobile) and 0.1N HCl-extractable (potentially mobile) forms of Cd, Cu, Ni, and Pb and 0.1N HCl–extractable Si. The contents of Cd, Cu, Ni, and Pb in the percolated solutions and soil extracts were measured by the atomic-adsorption method (AAS Hitachi 170-50A). Statistical significance of the means of three replicates was compared at 0.05 probability level using analysis of variance (ANOVA).

## Results and Discussion

The addition of the Si fertilizers resulted in a reduction in the amount of leached nutrients compared to the traditional fertilizer treatment (Table 1). There was a 25% reduction in the amount of leached nitrates for the NPK500+ASD on the 5th day, up to a 60% reduction for the NPK500+DE treatment on the 25th day.

**Table 1. The content of nitrates, phosphorus and potassium in the percolated waters and reduction of the nutrient leaching**

| Traditional Fertiliser Treatment | Nitrogen in percolated water, ppm $NO_3^-$ | | Phosphorus in percolated water, ppm P | | Potassium in percolated water, ppm K | |
|---|---|---|---|---|---|---|
| | 5th day | 25th day | 5th day | 25th day | 5th day | 25th day |
| Control | 0.4 | 0.1 | 0.5 | 0.4 | 0.2 | 0.2 |
| NPK | | | | | | |
| 100 kg/ha | 8.4 | 2.4 | 3.6 | 0.8 | 10.3 | 5.3 |
| 500 kg/ha | 15.4 | 8.3 | 7.4 | 1.7 | 18.2 | 8.3 |
| NPK+ASD | | | | | | |
| 100 kg/ha | 5.4 (35.7%) | 1.3(45.8%) | 2.2(38.8%) | 0.2(75.0%) | 7.5(27.2%) | 4.7(11.3%) |
| 500 kg/ha | 11.5(25.0%) | 4.7(43.4%) | 4.3(41.8%) | 0.3(82.3%) | 11.2(38.4%) | 4.4(46.9%) |
| NPK+DE | | | | | | |
| 100 kg/ha | 4.7(44.0%) | 1.1(54.4%) | 1.6(55.5%) | 0.3(62.5%) | 4.2(59.2%) | 3.2(39.6%) |
| 500 kg/ha | 10.4(32.4%) | 3.2(60.0%) | 2.4(67.6%) | 0.7(58.8%) | 7.8(57.1%) | 4.2(49.4%) |

| | | | | | | |
|---|---|---|---|---|---|---|
| LSD$_{05}$ | 0.10 | 0.20 | 0.10 | 0.20 | 0.10 | 0.15 |

All fertilizer treatments increased barley biomass compared to the control treatment, with the addition of the Si treatments resulting in higher barley biomass, compared with traditional NPK fertilizer only (Table 2). This effect may be attributed to firstly the optimization of plant silicon nutrition usually increases the bioproductivity of the cultivated plants (Snyder et al., 2006). Secondly, the reduction of NPK leaching reinforced the plant nutrition by macronutrients. Consequently, the amendment of traditional NPK fertilizers by Si-rich materials can improve the availability of these nutrients, possibly leading to a reduction in the rate of their application.

**Table 2. The dry weight of barley (g) for different fertilizer treatments**

| Fertilizer treatment | NPK rate, kg ha$^{-1}$ | |
|---|---|---|
| | 100 | 500 |
| Control (0 kg ha$^{-1}$) | 0.16 | - |
| NPK | 0.25 | 0.29 |
| NPK+ASD | 0.28 | 0.30 |
| NPK+DE | 0.30 | 0.34 |
| LSD$_{05}$ | 0.02 | 0.03 |

The column test simulated the behavior of HM as influenced by Si-rich substances. Results showed that Si substances provided the reductions in the leaching of HM (Cu, Pb, Cr, Ni, and Co) by 18% to 94% and the transformation of HM into passive forms (Table 3). The tested forms of Cd in the soil were decreased by 65 to 90% and 37 to 96%, accordingly for mobile and potentially mobile forms. The maximum reducing effect was received from DE. Mobile Cu in the soil was reduced by 18 to 53%. The tested forms of Ni in the soil were reduced by 44 to 79% and 74 to 94%, accordingly for mobile and potentially mobile forms. Mobile Pb was reduced by 43 to 65% and potentially mobile Pb by 54 to 65%.

The reduction in the leaching of HM may be explained by the interaction between HM and Si-rich substances. Several mechanisms of this interaction may occur, including weak physical adsorption, strong chemical adsorption of HM on the surface of Si-rich minerals, and the reaction between monosilicic acid and HM (Bocharnikova et al., 1999; Bocharnikova & Matichenkov, 2007; Orlov, 1992).

The application of Si fertilizers can increase crop production through improved plant Si nutrition (Snyder et al., 2006), with the additional benefit of reducing nutrient leaching and deactivating HM in the soil, effectively providing a multifunction in the soil-plant system. This presents the basis for Best Management Practice for fertilizer application, encompassing improved economics of agricultural productivity and a reduction in the negative influence on the environment.

**Table 3. HM in the soil after column test.**

| HM | Treatment | Aver. content of HM in percolated solution | | Mobile HM ($MgCl_2$-extractable) | | Potentially mobile HM (0.1 n HCl-extractable) | |
|---|---|---|---|---|---|---|---|
| | | mg $L^{-1}$ | reduction, % | mg $kg^{-1}$ | reduction, % | mg $kg^{-1}$ | reduction, % |
| Cd | Control | 5.0 | | 28.5 | | 58.6 | |
| | ASD | 3.0 | 40.0 | 9.9 | 65.3 | 36.9 | 37.0 |
| | DE | 1.8 | 64.0 | 2.6 | 90.8 | 1.9 | 96.7 |
| Cu | Control | 7.7 | | 24.2 | | 163.4 | |
| | ASD | 4.0 | 48.0 | 19.8 | 18.2 | 103.4 | 36.7 |
| | DE | 2.6 | 66.2 | 11.2 | 53.7 | 114.2 | 30.1 |
| Ni | Control | 3.3 | | 13.4 | | 21.9 | |
| | ASD | 2.2 | 33.3 | 7.4 | 44.8 | 5.6 | 74.4 |
| | DE | 1.4 | 57.6 | 2.8 | 79.1 | 1.3 | 94.0 |
| Pb | Control | 1.7 | | 3.2 | | 24.4 | |
| | ASD | 0.7 | 58.8 | 1.1 | 65.6 | 8.3 | 65.9 |
| | DE | 0.4 | 76.5 | 1.8 | 43.8 | 11.2 | 54.1 |
| | $LSD_{05}$ | 0.1 | | 0.2 | | 0.4 | |

## Conclusion

Results showed that application of Si-rich materials, especially Natural Silica, as amendments to traditional fertilizers, can significantly reduce the leaching of nutrients and heavy metals from cultivated areas, plus potentially increase crop productivity. This could lead to a reduction in traditional fertilizer rate application, deactivation of heavy metals which may be present in the soil or traditional fertilizers, with ultimate benefits to the environment.

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