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Soil Pollution Patterns in Terrestrial Ecosystems of the Kola Peninsula, Russia

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ABSTRACT

Soil chemistry is analysed in terrestrial ecosystems subjected to airborne pollution in the fragile boreal environment in the industrial part of the Kola Peninsula, northwestern Russia. The organic horizon of soils appeared to be the important accumulator of heavy metals and the barrier against transport of pollution to underlying mineral horizons. The concentrations of Ni and Cu in soils near the smelter are approximately one to two orders of magnitude higher than the background levels in the region. Based on pH values, air pollution has not resulted in a detectable topsoil acidification near the smelter. However, exchangeable K tends to be lower towards the smelter most likely due to replacement by air pollutants and leaching, thus confirming an early stage of ongoing acidification. Near the smelter heavy metals contribute significantly to cation exchange occupying up to ¼ fraction of exchangeable sites.

The survey of pollution and basic soil properties is presented as conjugated ordination diagrams that give a concise graphical rendition of soil chemistry state. Based only on analyses of spatial changes in soil properties, ordination revealed quite a natural, expected grouping of exchangeable cations as being divided into three groups: nutrients, heavy metals and acidity. Principal component analysis appeared to be a useful tool for evaluation of soil chemistry data in its unreduced, inherent uncertainty – natural spatial variation – and in its interrelations and changes under the influence of airborne pollution. Sensitivity analysis showed that the ordination was characteristic for the studied region, reflecting both natural and pollution induced soil variability.

INTRODUCTION

The areas surrounding the Pechenganikel smelter in northwestern Russia, close to Norwegian border, are heavily polluted from emissions of sulfur dioxide and heavy metals (HM) for several decades. Air pollution has caused severe damage to the terrestrial ecosystems (Aamlid and Venn, 1993; Lukina and Nikonov, 1996; Koptsik et al., 1998, 1999b). Conservation, management, and recovery of endangered and degraded terrestrial ecosystems require exhaustive knowledge of soil chemical state. Prevailing in the region poor thin sandy podzols form a convenient and promising natural-anthropogenic model object for understanding the combination of natural and pollution-induced processes. The release rate of base cations due to weathering, their only long-term source, range from 0.05 to 0.28 $\mathrm{kmol_c \cdot ha^{-1} \cdot yr^{-1}}$ in the 0-50 cm soil layer, thus demonstrating the high sensitivity of the coarse and thin podzols to acidification (Koptsik et al., 1999b). Soils and surface waters will acidify severely within the next 20-30 years according to calculations with the SMART model unless the SO_2 emissions from the "Pechenganikel" smelters are drastically reduced (Kämäri et al., 1995; Koptsik, 1997).

In boreal forests, soil organic horizons, or mor layers, are important in internal acidity generation and nutrient turnover. They contain a large body of fine roots and thus determine forest vital functions and productivity. At the same time surface organic horizons are to most extent subjected to air pollution impact. The scope of this study was to examine acidity and exchangeable cations, their spatial variability and relationships in soil organic horizons under the influence of air pollutants. Due to the large and complex set of observed data and to their high spatial variability multivariate analysis was used to identify and quantify most important relationships, and to present soil data in the concise graphical form.

MATERIALS AND METHODS

The study area is located around the nickel smelters in the northwestern part of the Kola Peninsula, Russia, close to the Norwegian border (Fig. 1). It is a hilly subarctic glaciated terrain covered by tills, glaciofluvial deposits, and open bedrock with coarse texture. The glacial till mineralogy of the study area is generally characterized by slowly weathered primary minerals, represented by mostly quartz and feldspars derived from gneisses and granites. The area is located at the polar tree line. Pine and birch forests are characterized by scarce tree stands and scarcely developed ground vegetation, dominated by crowberry, bilberry, mosses, and lichens. Podzol is the most common soil type; its thickness usually does not exceed 30-50 cm.

At present, the smelter emits about 250,000 tons of sulfur dioxide annually and is the 4-th largest point SO_2 source in Europe (Barrett and Protheroe, 1995). The annual emissions from the smelters are about 140 tons of nickel, 90 tons of copper and 5 tons of cobalt according to data from the Laboratory for Observation of Environmental Pollution in Nikel. Total annual sulfur deposition significantly exceeds 2 $\mathrm{g \cdot m^{-2}}$ within the area of 20-40 $\mathrm{km^2}$ nearest to the nickel smelter, compared to about 0.1-0.2 $\mathrm{g \cdot m^{-2}}$ in background areas (Sivertsen et al., 1992). Total deposition of nickel and copper reaches 100 $\mathrm{mg \cdot m^{-2} \cdot y^{-1}}$ close to the smelter, decreasing significantly within the first 10 km. In background areas, it has been estimated to be about 1-3 $\mathrm{mg \cdot m^{-2} \cdot y^{-1}}$.

Soil samples were collected mainly from pine and birch

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forests typical for the region, at different distances and directions from the smelter (28 plots in total, Fig. 1). The surface soil organic horizon (Oi, Oe and Oa) was used for sampling. The samples were air dried at 20°C and ground to pass a 1 mm sieve. Chemical analysis of the soil included pH in H_2O and 0.01 M $CaCl_2$ suspensions. Exchangeable acidity (EA), exchangeable cations (Al, Ca, Mg, K, Na, Fe, Mn, Ni, Cu, Zn) and extractable sulfur were determined in the 1 M NH_4NO_3 extract by inductive coupled plasma atom emissionic spectroscopy (most elements) and atom absorption spectroscopy (Ni and Cu). Base saturation (BS) is defined as the sum of equivalents of the exchangeable pool of base cations (Ca^{2+}, Mg^{2+}, K^+, Na^+) calculated as the percentage of the cation exchange capacity (CEC). CEC was calculated as is the equivalent sum of exchangeable acidity (EA), base and HM cations. To get insight cation exchangeable properties in the studied polluted soils, we included also heavy metal saturation (HMS), defined as normalized to the CEC the sum of equivalents of the exchangeable pool of HM cations, Ni^{2+} and Cu^{2+} being the main pollutants: HMS = $(Ni^{2+} + Cu^{2+})$/CEC, %.

Correlation, linear and nonlinear regression analyses were used to study the current soil chemistry. The reason for applying principal component analysis (PCA) for characterization of the soil status is the complex character of pollution impact. This statistical method is convenient when it is unclear how to reduce the number of compatible variables so that only the most significant for the studied data are chosen (see, for example, ter Braak, 1987). Conjugated graphical ordination diagrams, that are a useful approximate method of projection of large dimensional space, can be treated as concise visualizations multidimensional matrices with soil data onto two-of the soil state as a whole.

The procedure of singular value decomposition of the standardized data matrix with concentrations of chemical elements for the studied sites was used. Covariance scaling was chosen for graphical presentation of results. In this scaling the angle between lines representing chemical elements provides approximation to their pair-wise correlation. External environmental variables (hatched lines) are presented in the same diagram as directions that have maximum correlations with the studied variables. Each of these directions was determined by multiple least-squares regression of the variable on the site scores.

Figure 1. Plot locations.

RESULTS AND DISCUSSION

The upper organic horizons of the studied podzols had the highest acidity within the profiles and were often extremely acid ($pH_{H2O}<4.0$). Exchangeable acidity varied from 80 to 230 mmol·kg^{-1}, with the mean value being about 142 mmol·kg^{-1}. General information about variation in exchangeable cations is summarized in Fig. 2a. Sides of rectangles mark for each property lower and higher quartiles, cutting off lower and higher 25% of observed values; bars, shrinking the rectangles, mark medians. Dotted lines denote one and a half expanded interquartile ranges of the corresponding values; outliers are shown with crosses. Absolute maximal values of properties are given in the figure to simplify comparison of results. Both H^+ and Al^{3+} contributed considerably to exchangeable acidity. However, large amounts of exchangeable H^+ were usually present due to abundance of organic functional groups and limited available aluminum sources. CEC was dominated by both the H^+ ions and the sum of exchangeable bases, mainly Ca^{2+}. BS ranged from 17 to 72%, with a mean value of 50%. No significant difference was observed for the studied variables between the organic horizons of pine and birch forests.

Atmospheric deposition of Ni and Cu from the nickel processing industry has lead to the severe contamination of surrounding soils within 20-30 km from the pollution source. Heavy metals were concentrated in the surface organic horizons. The mobility of Ni and Cu in the soils was limited, as shown by a sharp reduction in their concentrations with depth (Koptsik et al., 1998). Close to the smelter soils contained elevated concentrations of total and exchangeable Ni^{2+} (25-35 and 15-25 mmol·kg^{-1}) and Cu^{2+} (25-40 and 8-15 mmol·kg^{-1}) in organic horizons comparing to remote sites (<1-2 mmol·kg^{-1}, Fig. 2b). In heavily polluted soils HM reach 17-24% of the soil CEC. Thus, surface organic horizons can be used as indicator of HM pollution of forest soils.

Results of correlation and regression analyses showed that air pollution has not resulted in topsoil acidification that is detected in the form of unusually low pH values or especially high exchangeable Al near the smelter. Contrary, pH in water and $CaCl_2$ suspensions increased and exchangeable acidity decreased towards the smelter. This was probably due to the high Ca and Mg deposition near the pollution source, the decreased input of protons as a result of organic matter transformation and plant uptake in destroyed ecosystems, and more basic lithology. However, exchangeable K, the most mobile base cation, decreased

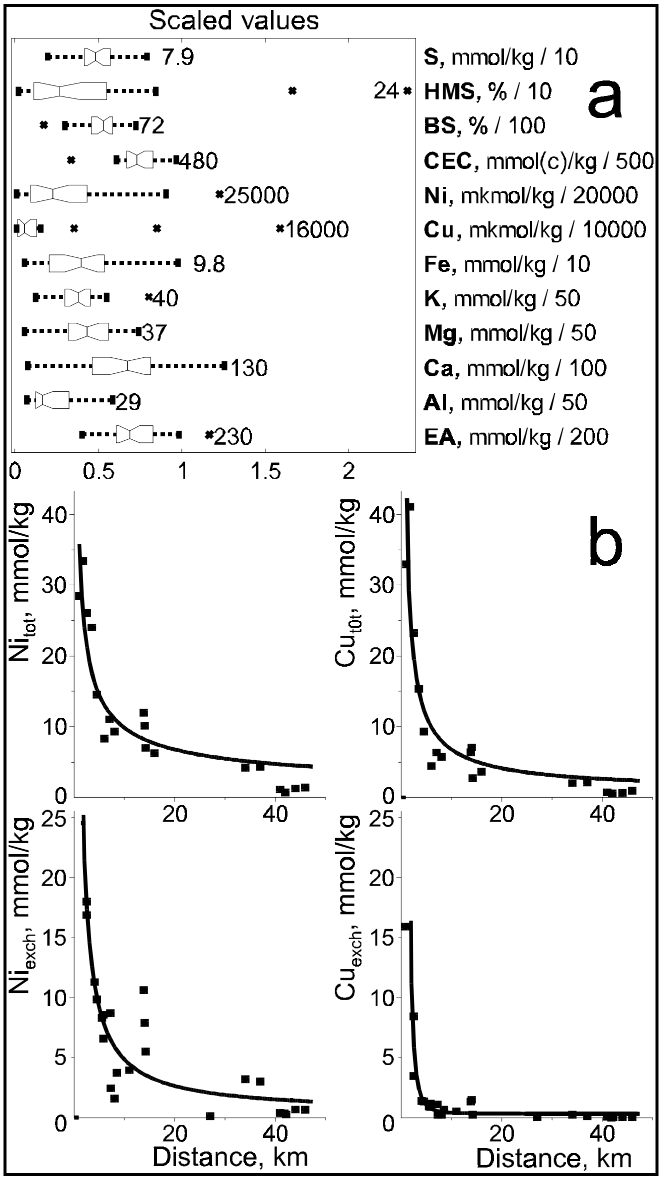

Figure 2. Acidity and exchangeable cations (a) and dependencies of total and exchangeable Ni and Cu (b) on distance from the smelter for soil organic horizons. EA - exchangeable acidity, BS - base saturation, HMS - heavy metal saturation, CEC - cation exchange capacity.

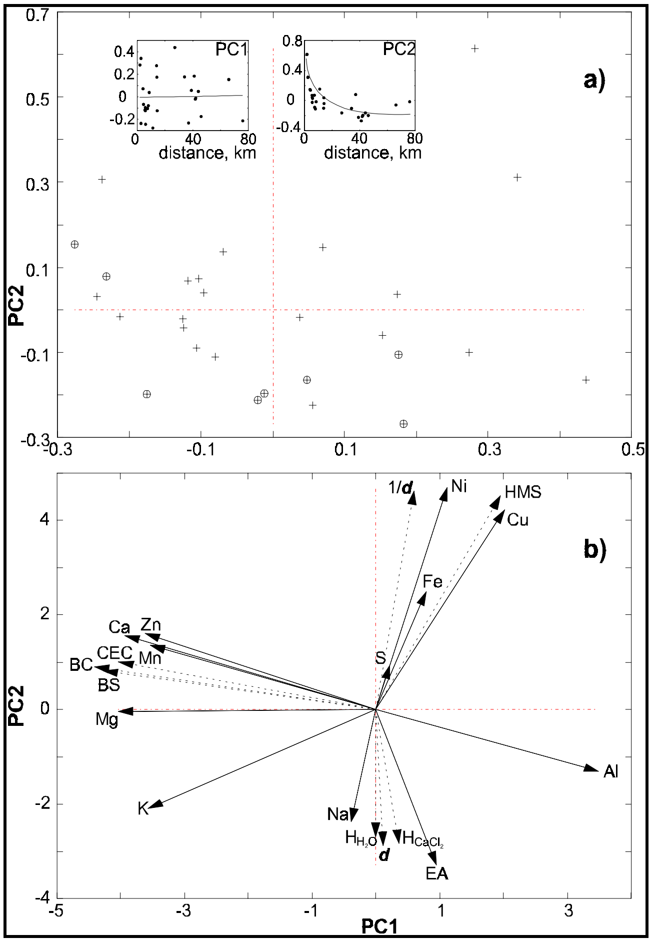

Figure 3. Ordination plot of sites (a) and exchangeable cations (b). BC - sum of base cations, other notations as in Fig. 2a.

towards the pollution source. The decrease of K^+ seems to be the first sign of started acidification. This tendency may be caused by replacement of K^+ with pollutant cations, which is evidenced by negative correlations with Al^{3+}, Ni^{2+}, and Cu^{2+}. As was shown previously (Koptsik et al., 1999a), despite increase of exchangeable Ca, Mg and base saturation towards the smelter in lower mineral horizons due to geological inheritance, they did not show the same trends in upper horizons. This fact is surprising as the anthropogenic dust input of Ca and Mg near the smelter is easily available. The deep penetration of acidity, peculiarities of spatial distribution of base cations and their losses from the topsoil revealed an early stage of ongoing soil acidification. Thus, both natural and anthropogenic factors affected the chemistry of surface organic horizons in acid sandy podzols in the study area. Complex interaction between amount and composition of organic matter and removal and addition of other cations, that occurs in processes of deposition, leaching and biocycling, determined acidity and exchangeable cations in soil organic horizons.

In order to get somewhat more abstracted view of the observed data, to get insight into its general picture, we applied PCA. Exchangeable cations (H, Al, Ca, Mg, K, Na, Fe, Mn, Cu, Ni and Zn) and extractable S in organic horizons were chosen as 12 independent variables for PCA. The first two principal components (PC) accounted for 28 and 24% of total variation. The sites (Fig. 3a) were distributed mainly as a cloud in the second and forth quadrants. Two sites in the first quadrant, that fell outside of the general tendency, were close to the smelter and were highly contaminated. These are the barren industrial land at 1.8 km from the smelter and the heavily damaged sparse pine forest at 2.5 km from the smelter. Crosses within circles mark those sites that lie to the south of the smelter. Excluding those sites that lie on this transect reduced the variation in site positions markedly and made the cloud appear somewhat closer to a dependent relationship. This graphical reduction of uncertainty pictorially shows the importance of natural spatial variability.

While the first PC did not depend on the distance from the smelter, the dependence of second PC was significant. Moreover, the increase of second PC with decrease of distance was nonlinear; it qualitatively repeated the dependence of exchangeable Ni and Cu on distance. Exchangeable Mg, Ca, Zn and K were the main elements contributing to the first PC; Ni, Cu, acidity and Fe to the second; S and acidity to the third. Thus, we came to the conclusion that the first PC represented mainly natural soil nutrients (exchangeable base cations, Mn and Zn), and the second and third PCs mainly the airborne pollution induced properties (exchangeable HM and acidity).

The first two PCs of element scores are shown in ordination plot (Fig. 3b) with solid lines, external variables (distance and inverse distance from the smelter, CEC, sum of base cations and BS) – with hatching lines. Whereas Fig. 2a gives only cursory outlook on the underlying database, Fig. 3b enable one to assess correlations between different properties and thus to consider the background processes. PCA divide exchangeable cations into three natural groups. The nutrient group – exchangeable base cations (Mg, Ca, K), Mn and Zn – lie compactly around the negative direction of the first PC axis. This fact confirmed the suggestion that the first PC represented natural soil properties. The angles between these elements and CEC, the sum of base cations and BS were small due to strong correlation, and simply reflect that these external properties are just the derivatives of exchangeable base cations. Exchangeable Ni, Cu, Fe and extractable S, the concentration of which are directly linked with deposition of airborne pollutants, lie in the first quadrant close to the second PC axis, thus confirming the conclusion that the second PC reflected the industrial impact. The diagram clearly showed strong dependence of exchangeable HM on the distance from the smelter. Even stronger correlations with the inverse distance simply reflected that this parameter is a natural external variable for studying the problem of the influence of a point emission source on the environment. Exchangeable acidity and Al, activities of H^+ in water and salt suspensions lie in fourth quadrant and formed a third group. The diagram emphasizes their different nature compared with base cations and exchangeable forms originating from deposited pollutants. Exchangeable acidity and activity of H^+ in water and salt suspensions were correlated with distance from the smelter. Exchangeable Na lies separately from the main base cations, almost orthonormal to them. The isolated role of exchangeable Na is probably due to marine origin.

The intuitive division of soil chemical properties into three groups was confirmed by strict mathematical treatment. In cluster analysis we considered the whole set of soil variables, main and external, as being equal. Inverse square distance between element scores and centers of clusters was chosen as the measure of similarity. The PCs values were scaled with weights equal to the fraction of total variation that they account. The results of fuzzy ***c***-mean clustering of element scores for acidity and cation exchangeable properties into three groups are shown in Fig. 4a by different symbols; the points corresponding to clusters are surrounded by dashed curves. As the norm of distance between elements, the simple Euclidean distance in the first two PCs of element score space was chosen; the exponent for the partition matrix equaled 2. Three half-tone trajectories showed successive iterations starting from some arbitrary, random division of data into three clusters. Subdivision of the element arrow fan into three natural groups – nutrients, heavy metals and acidity – gave a pictorial rendition of the different origin and relative independence of these groups of cation exchange properties in the O horizon. The only difference from an intuitive division is that Na is included in the acidity group. Ordination revealed quite a natural, "expected" grouping of properties. This result, however, was not trivial and could not be expected beforehand since analysis was based only on variation in properties. It showed that the nature of soil properties is hidden in the patterns of variation of these properties. On the other hand, it confirmed the objective character of conclusions based on traditional statistical analysis, demonstrated the objective and quite natural character of ordination.

Another problem that should be considered in connection with PCA ordination is how typical the obtained structure of elements is for the studied region. To put this question more strictly, how sensitive the obtained element arrow fan is to random changes in input data? This question is especially interesting taking into account the uncertain, cloud-like nature of environmental data.

To assess distribution of element coordinates in ordination diagrams we calculated their two-dimensional histograms for 2,000 simulated ordination structures. Data were randomly scattered round the reflected in Fig. 3 data matrix, using normal distribution with standard deviations of concentrations of chemical elements being equal for all sites. As the standard deviation for each site cannot be assessed on the available data, we assumed it to be 25% of the standard deviation within the whole territory for most of the independent properties. For heavy metal concentrations, which changed widely due to the influence of the smelter, the same assessment was based on the background regions. Smoothed 2D-histograms for acidity and main exchangeable cations are shown in Fig. 4b. To make overlapping distributions distinguishable, they were placed in two subplots. All distributions were characterized by larger angle spread than radius spread. Ni and Cu were characterized by sharp distributions, especially in radius; exchangeable acidity, Al, S and Fe were characterized by spread distributions. Analysis of these distributions clearly showed that PCA ordination diagrams are robust enough to cope with random scattering of input data. Thus, the ordination diagram (Fig. 3b) was characteristic for the studied region, reflecting both natural geochemical and pollution-induced variability.

CONCLUSIONS

Multivariate analysis of spatial variability of acidity and exchangeable cations showed that both natural and anthropogenic factors affected the chemistry of surface organic horizons in acid sandy podzols near the Pechenganikel smelter. While soil pH in organic horizons increased, exchangeable acidity decreased towards the smelter mainly due to combined effects of deposited base cations, vegetation disturbance, and geology. However,

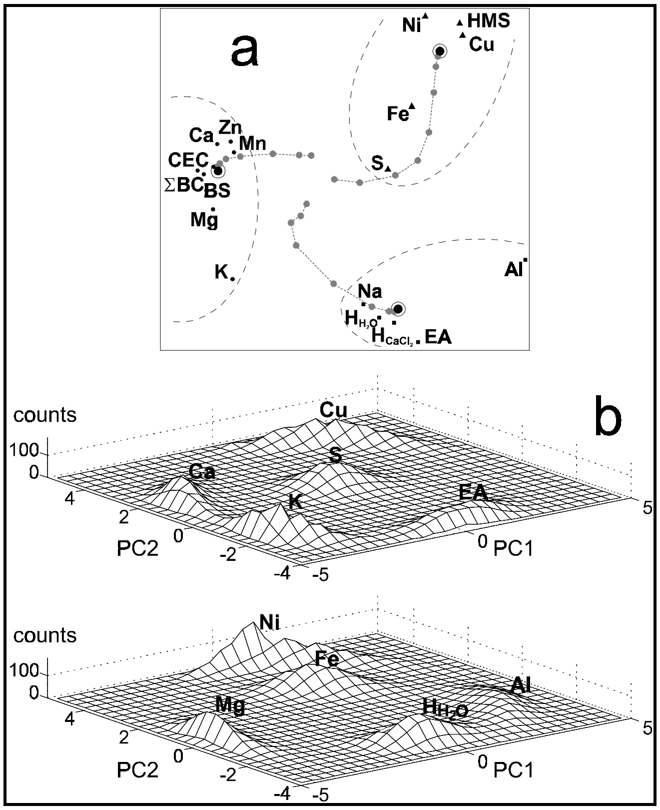

Figure 4. Clustering of properties loadings (a) and their 2-D distributions (b) for soil organic horizons. Coordinate axes and notations as in Fig. 2a.

decreased concentrations of exchangeable K towards the smelter revealed an early stage of acidification. This decrease reflected replacement of K^+ in exchange complex and leaching out of organic horizons, caused by increased input of pollutants (Ni, Cu, Al). The concentrations of exchangeable Ni and Cu in soils near the smelter were approximately one to two orders of magnitude higher compared to background regional levels. The organic horizon of podzols appeared to be the important accumulator of heavy metals and the barrier against transport of pollution to underlying mineral horizons.

Principal component analysis appeared to be a useful tool for graphical rendition and for evaluation of soil chemistry data in its inherent uncertainty – natural spatial variation. It helps to establish natural for the system inner structures in soil properties and to analyze interrelations and changes in data under the influence of airborne pollution. Natural sources of variation were the most significant. Exchangeable Ca, Mg, K, Mn and Zn, the soil fertility forming nutrients that determined the first principal component, formed an isolated group in the ordination plot. The first component correlated highly with these cations and with the sum of base cations, cation exchange capacity and base saturation; it did not depend on the distance from the smelter. Variation of exchangeable Ni, Cu and Fe, caused by heavy metal deposition from the nickel smelter, was very high; these variables were the main factors contributing to the second component and formed another second ordination group. Like the forming the second principal component heavy metals, it nonlinearly depended on the distance from the smelter. Sulfur and exchangeable acidity, that is determined by pollution induced H^+ input as well as by highly varied Al, were the main factors contributing to the third PC; they lie isolated and formed a third group in the ordination plot. These results, that showed a natural, intuitive grouping of elements, were confirmed by cluster analysis. Sensitivity analysis showed that the ordination diagram obtained was characteristic for the studied region, reflecting both natural and pollution induced soil variability. Evaluation of regional problems gives a light footpath for a better understanding of the theoretical basis and practicable needs of soil conservation and management within the paradigm of viably and sustainably developed systems in our global environment.

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