Climatically driven loss of calcium in steppe soil as a sink for atmospheric carbon

A. G. Lapenis,[1] G. B. Lawrence,[2] S. W. Bailey,[3] B. F. Aparin,[4] A. I. Shiklomanov,[5] N. A. Speranskaya,[6] M. S. Torn,[7] and M. Calef[1]

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[1] During the last several thousand years the semi-arid, cold climate of the Russian steppe formed highly fertile soils rich in organic carbon and calcium (classified as Chernozems in the Russian system). Analysis of archived soil samples collected in Kemannaya Steppe Preserve in 1920, 1947, 1970, and fresh samples collected in 1998 indicated that the native steppe Chernozems, however, lost 17–28 kg m^{-2} of calcium in the form of carbonates in 1970–1998. Here we demonstrate that the loss of calcium was caused by fundamental shift in the steppe hydrologic balance. Previously unleached soils where precipitation was less than potential evapotranspiration are now being leached due to increased precipitation and, possibly, due to decreased actual evapotranspiration. Because this region receives low levels of acidic deposition, the dissolution of carbonates involves the consumption of atmospheric CO_2. Our estimates indicate that this climatically driven terrestrial sink of atmospheric CO_2 is ~2.1–7.4 g C m^{-2} a^{-1}. In addition to the net sink of atmospheric carbon, leaching of pedogenic carbonates significantly amplified seasonal amplitude of CO_2 exchange between atmosphere and steppe soil.

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1. Introduction

[2] In soil, inorganic carbon can be found in the form of lithogenic carbon as fragments of parent rock and as pedogenic carbon, formed through weathering and reprecipitation. In this text we use soil inorganic carbon (SIC) as a synonym for pedogenic carbon. The global pool of SIC is comparable in size to the global pool of soil organic carbon (SOC) and contains between 900 and 1700 Pg of carbon [*Schlesinger*, 2002; *Eswaran et al.*, 1995]. Most pedogenic carbonates are found in semi-arid landscapes such as steppe, prairie, and semi-deserts [*Lal and Kimble*, 1999]. In the steppe of Eastern and Central Europe, pedogenic carbonates are formed from calcareous eolian loess, a common parent rock of steppe soils [*Scharpenseel et al.*, 1999; *Altermann et al.*, 2005].

[3] In the steppe, mean annual precipitation is less than potential evapotranspiration [*Budyko*, 1971]. Therefore the leaching of pedogenic carbonates from the downward movement of water is minimal or nonexistent [*Afanas'eva*, 1966]. In the absence of leaching there is no mechanism for net storage or the release of atmospheric CO_2 through changes in the pool of pedogenic carbonates [*Schlesinger*, 1985, 1997; *Nordt et al.*, 1999].

[4] During the last 30 to 40 years, the climate of the Russian steppe has become warmer and wetter. The direction of these changes is consistent with some scenarios of global warming due to the anthropogenic enhancement of the greenhouse effect. The forecast for the steppe region is similar for 80% of the global climate models, and at the time of CO_2 doubling, predicts summer temperature increases of 2 to 3°C along with an increase in mean annual precipitation of 30 to 60 mm a^{-1} [*IPCC*, 2007].

[5] How the pool of pedogenic carbonates in the steppe is responding to this changing climate is not well understood. We address this issue through study of archived steppe soil profiles from the Central Dokuchaev Soil Museum in St. Petersburg, Russia.

2. Site Description and Archived Samples

[6] During the last several thousand years the semi-arid, cold climate of the Russian steppe formed highly fertile soils rich in organic carbon and calcium (classified as

[1]University at Albany, Department of Geography and Planning, Albany, New York, USA.
[2]USGS, Troy, New York, USA.
[3]USDA Forest Service, Northeastern Forest Experiment Station, Durham, New Hampshire, USA.
[4]Central Dokuchaev's Soil Museum, St. Petersburg, Russia.
[5]University of New Hampshire, Complex Systems Research Center, New Hampshire, USA.
[6]State Hydrologic Institute, St. Petersburg, Russia.
[7]Lawrence Berkeley National Laboratory, California, USA.

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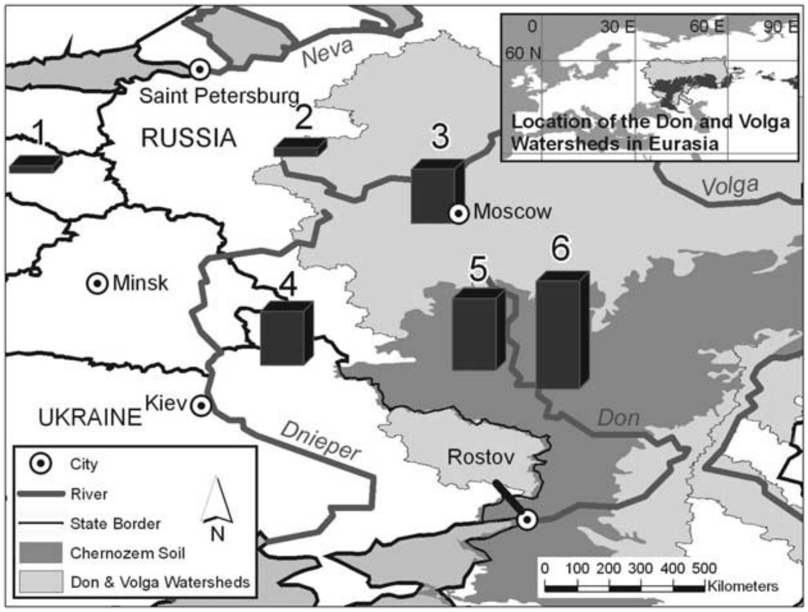

Figure 1. Map of Russian Chernozem soil and watersheds of rivers Volga and Don. The same map demonstrate 1960–1996 rise of the groundwater level at 6 regional watersheds with long-term hydrologic records (the size of the bar at Kamennaya Steppe (6) corresponds to 4 m rise of water table) [*Georgievsky et al.*, 1996]: (1) Pribaltiyskaya, (2) Valdai, (3) Podmoskovnaya, (4) Pridesnyanskaya, (5) Niznedevickaya, (6) Kamennaya Steppe.

Chernozems in the Russian system). Chernozems or Mollisoils in the US classification are the 8th most common soil order and are estimated to cover 900 million ha or approximately 7% of the ice-free land area on Earth [*Bell and McDaniel*, 2000]. In the United States, Mollisols make up approximately 25% of the land area, most of which was converted to cropping [*Bell and McDaniel*, 2000]. Similar to the U.S., nearly all of the 117 million ha of Chernozems in the Russian steppe and 12 million ha of Chernozems in the Ukrainian steppe are used for agriculture [*Stolbovoi and McCallum*, 2002].

[7] Native Chernozems can be found only in a few preserves, including the Kamennaya Steppe. This preserve in the central part of the Russian steppe (Figure 1) was established in 1892 by Dokuchaev as a sanctuary of zonal Chernozem soil, typical of the steppe and forest steppe region [*Dokuchaev*, 1893; *Sherbakov and Vassenev*, 1996]. The Kamennaya Steppe is an approximately 5000 ha watershed that is drained by the Chigla and Talovaya Rivers, which are tributaries of the Don River (Figure 1). According to our GIS analysis of digital soil maps produced by *Stolbovoi and McCallum* [2002], River Don drains ~28.4 million ha of Chernozem soils from 42.5 million ha of its total watershed area. The average height of Kamennaya Steppe plateau is 200 m above sea level. The groundwater in the Kamennaya Steppe is represented by an unconfined aquifer located within Quaternary deposits that exhibits seasonal changes in the water table depth. The geologic deposits of the unconfined aquifer are loess and clays with rare inclusions of boulders. The typical thickness of unconfined aquifer is ~14 m [*Ivanov*, 1991].

[8] The Central Dokuchaev Soil Museum in St. Petersburg has archived soil samples collected from the Kamennaya Steppe in 1920, 1947, 1970, and 1998 (Figure 2). The last set was taken by authors of this paper. Soil samples represent three plots: Native steppe, windbreak or forest plantation, and agricultural field. Prior to planting the windbreak and plowing for the agricultural field, the region of the Kamennaya Steppe was covered with native steppe vegetation such as feather grass and sage, and was used for grazing domestic animals [*Shapovalov*, 1969; *Sherbakov and Vassenev*, 1996]. Now the Kamennaya Steppe is one of ten largest Federal Nature Preserves in Russia.

3. Regional Climate Change

[9] The mean annual surface air temperature in the Russian steppe region has increased by 1 to 3°C over the last century. This increase was stronger in the winter months (~4–5°C) and somewhat weaker during the summer months (~1°C) according to the *NOAA National Climatic Data Center* [2007]. In Kamennaya Steppe the mean annual temperature was 5.3°C from 1893 to 1950 but increased to 6.6°C from 1989 to 1998. This increase occurred mostly during the winter months [*Sentsova*, 2002].

[10] Statistical analysis of long-term climate records for the Northern Hemisphere indicates a 7 to 12% increase in the annual precipitation over the 30–85°N latitudes during the last century [*IPCC*, 2001]. However, the spatial patterns of trends in precipitation are less uniform than the temperature change. There are a number of stations in the steppe region that have detected a decline in precipitation [*NOAA National*

Figure 2. Soil monoliths from Kamennaya Steppe (Central Dokuchaev's Soil Museum, St. Petersburg): CDSM1006, pristine steppe sampled in 1920; CDSM 1289, pristine steppe sampled in 1970; CDSM 1214, windbreak sampled in 1947. The scale on the right side of soil monoliths is in decimeters.

Climatic Data Center, 2007]. Overall, the increase in precipitation in the Russian steppe region was statistically significant for the winter and fall months, increasing by 10 to 20% over 100 years [*IPCC*, 2001]. The mean annual precipitation in Kamennaya Steppe (average of 2 weather stations) was 439 mm a^{-1} in the early 20th century and 507 mm a^{-1} from 1989 to 1998 [*Setntsova*, 2000].

[11] Along with increased precipitation, soil moisture, river runoff, and groundwater levels have also increased (Figures 1 and 3). From the 1960s through the 1990s, the annual mean soil moisture of the top 1 m of soil in the Kamennaya Steppe increased by 20 to 30% and, in some years, reached field capacity [*Robock et al.*, 2000]. River runoff from the Kamennaya Steppe watershed increased by 30% (~29 to 38 mm a^{-1}) from 1970 to 1998 [*Sentsova*, 2002]. As shown in Figures 1 and 3, the average annual groundwater level for the Kamennaya Steppe Preserve and for the entire region, including the forest steppe, has been rising since the end of the 1960s [*Ivanov*, 1991; *Georgievsky et al.*, 1996; *Sentsova*, 2002].

[12] Increases in summer soil moisture, groundwater levels, and river runoff have also been detected in the steppe regions of Southern Russia and Ukraine [*Georgievsky et al.*, 1996; *Robock et al.*, 2000]. Discharge data from the Volga River, the largest river in the steppe region, indicate an increase in flow to the extent that the decreasing trend in water level of the Caspian Sea has reversed [*Shiklomanov and Georgievsky*, 2003]. The annual discharge of Don River, which is an order of magnitude lower than discharge of River Volga, slightly declined over the last century. This decline might be a result of natural as well as anthropogenic factors such as construction of dams and increase in water demand for irrigation [*Georgievsky et al.*, 1996].

[13] In addition to the increase in precipitation, pan evaporimeters in Southern Russia show pronounced decreases in evaporation rates over the last few decades [*Peterson et al.*, 1995; *Golubev et al.*, 2001; *Roderick and Farquhar*, 2002]. The decreasing rate of evaporation off the water surface, however, may not be fully representative of trends in actual evapotranspiration from soil and vegetation [*Golubev et al.*, 2001]. Nevertheless, there is additional evidence that transpiration by plants during the period of 1970 to 1998 may have been suppressed by rising levels of atmospheric carbon dioxide. This decline in the plant transpiration caused decrease in the actual evapotranspiration and increase in the discharge of many European rivers [*Gedney et al.*, 2006]. Whatever the primary cause, the large increase in groundwater levels and soil moisture from 1960 to 1990 strongly suggest an increased downward flux of soil water and an associated increase in the leaching of pedogenic carbonates in the Russian steppe.

4. Methods

[14] We analyzed soil archives collected in the Kamennaya Steppe Preserve in 1920, 1947, 1970, and 1998. All samples were collected in late July to mid August. Soil samples represent 3 plots: Native steppe (~4 ha established in 1893, and sampled in 1920, 1970, and 1998), windbreak or forest plantation (~7 ha, planted in 1906 and sampled in 1947 and in 1998), and agricultural field (100 ha, first tilled in 1921, and sampled only in 1998). We followed the sampling protocol for archived soil samples [*Torn et al.*, 2002; *Lapenis et al.*, 2004]. This protocol suggests the first pit should be the most probable location of archived profile. If the exact location of the archived profile is known (e.g., 1970 soil pit in native steppe plot), we moved pits a few meters from the original location to avoid disturbed soil profiles. We place the second and third pits approximately 100 m from the first pit to evaluate the spatial variability of the soil. Soil samples were collected from the frontal wall of pits starting from the bottom and sampling in a channel with 10 cm increments. Because the Chernozem is a relatively homogeneous soil (no coarse fragments, flat topography), the single pits sampled in 1920, 1947, and 1970 were considered representative of soil conditions for the specific land-use at the time of sampling. The latter assumption is supported by our estimates of spatial variability in 1998 soils. These estimates are based on multiple pits taken from the plots with the same land-use, but located in a few hundred meters from each other (Figure 4).

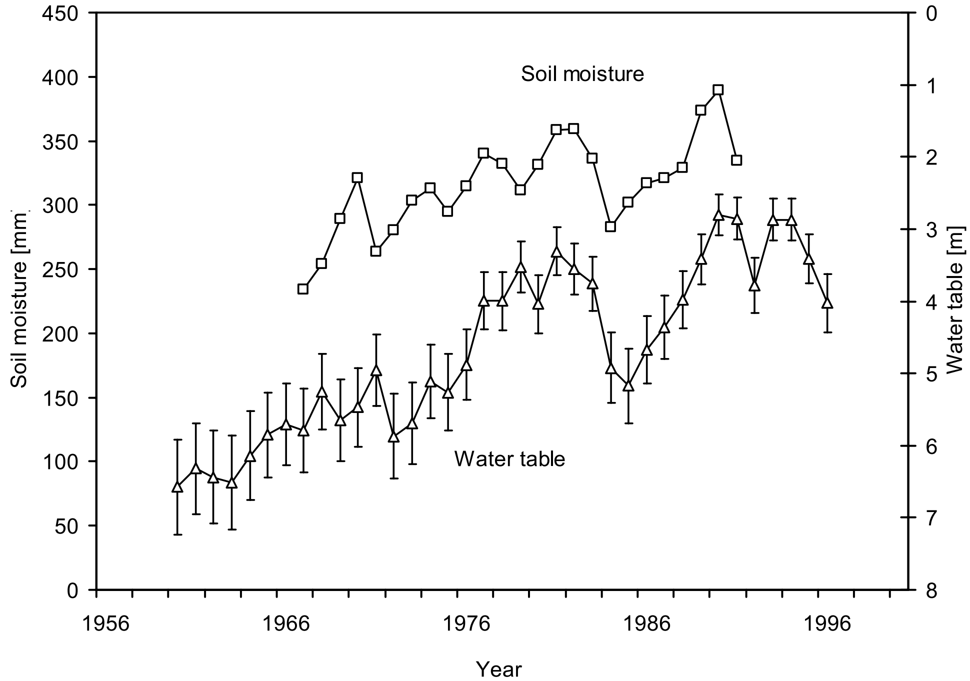

Figure 3. Available data on the water table, and moisture of the first 1 m of soil in Kamennaya Steppe. [*Sentsova*, 2002; *Robock et al.*, 2000]. Error bars indicate range of seasonal variations in the water table. After ~1970, soil moisture approached its field capacity, which is 350–400 mm in Chernozem of tall grass steppe [*Zubenok*, 1976].

[15] All soil samples (modern and archived) were passed through a 2 mm sieve and dried at 100°C to determine moisture content. Soil samples were analyzed for soil pH, exchangeable acidity and Al [*Thomas*, 1982], exchangeable base cations [*Blume et al.*, 1990]. Total concentrations of Ca and Mg were estimated by the method of microwave digestion with HF, followed by ICP analysis (EPA method 3052). Total concentrations of C and N were estimated by a Carlo Erba CHN analyzer.

[16] Changes in the mass of SIC within the top 1 m of soil were calculated through changes in the mass of calcium carbonate in individual layers. Total calcium in Kamennaya Steppe soil consists of two pools: carbonates and exchangeable calcium. Therefore the mass (M) of carbonate carbon in layer (i) at year (t) can be calculated through the difference of total pool of calcium and exchangeable calcium:

$$M_i(t) = K \times \left\{[Ca]_{Total} - [Ca]_{Exchangeable}\right\} \times D_{bi} \qquad (1)$$

[17] Where $[Ca]_{Total,Exchangeable}$ are concentrations [mg/kg] of total, and exchangeable forms of calcium in the layer (i), K – is a coefficient used to convert concentration of calcium into the carbonate carbon ($K = \frac{12}{40}$). Also, D_{bi} - is the bulk density of the layer (i) [Mg/m^3].

[18] The bulk density of 1998 soils was measured (Figure 5). For 1920, 1947, and 1970 soils we assumed that the bulk density of these soils was the same as in 1998 soils of the same land use.

[19] We calculated available space (pore space) in soil through the bulk density by the formula [*Brady and Weil*, 1999]:

$$V\% = 100 - \left[\frac{D_b}{D_p} \times 100\right] \qquad (2)$$

Where D_b and D_p are bulk density of soil and particle density respectively. Here we used particle density of common silicate minerals: 2.65 (Mg/m^3) [*Brady and Weil*, 1999]. The bulk density of lower soil horizons

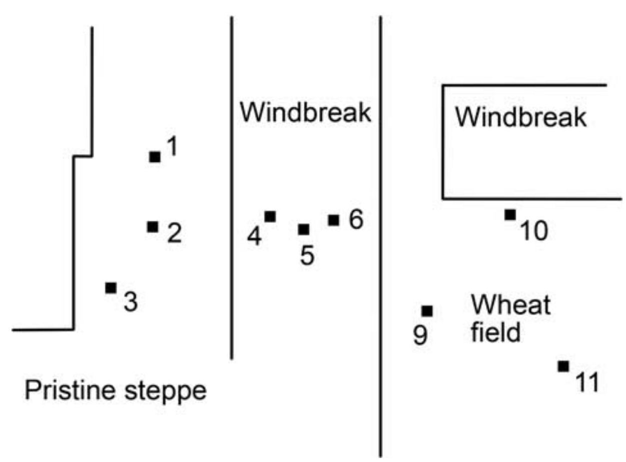

Figure 4. The scheme of 1998 soil sampling in Kamennaya Steppe.

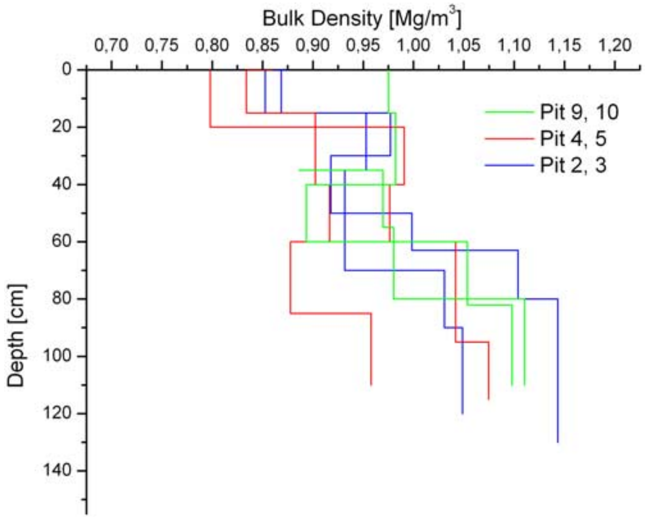

Figure 5. Bulk density of 1998 soil profiles. Position of pits is shown in Figure 4.

(Figure 5) is smaller than 1.20 Mg/m^3, thus the pore space in this layer is more than ~54%. The space available for water storage in loess deposits (specific retention) is ~18% [*Bowen*, 1986].

5. Results and Discussion

5.1. Loss of Calcium Carbonate From the Soil Profile

[20] The stock of organic carbon and concentrations of organic carbon and ^{13}C throughout the vertical profile were found to be approximately the same in 1900 and 1997–1998, in a previous study of soils in the Kamennaya Preserve [*Torn et al.*, 2002]. The profile of soil pH and exchangeable Ca concentrations also did not change appreciably from 1920 to 1998 (Figures 6a and 6b). The average position of the uppermost depth where carbonates (UDC) occur in the profile, however, was 20–25 cm deeper in 1998 than in 1970 (Figure 7). Concentrations of total Ca (and associated carbonate) also decreased substantially from the 50 to 100 cm depths between 1970 and 1998. This pronounced decrease represents the loss of 17.1–28.3 kg m^{-2} of calcium and 5.0–8.5 kg m^{-2} of inorganic carbon in the form of carbonates from the upper 1 m of soil equation (1). Thus the average rate of this loss from 1970 to 1998 in the native steppe plot was ~810 ± 200 g Ca m^{-2} a^{-1}, and 240 ± 62 g C m^{-2} a^{-1}. These numbers are two orders of magnitude greater than typical rates of soil leaching in the Russian steppe for the last thousand years [*Ryskov et al.*, 1999]. The depletion of total calcium was accompanied by loss of total magnesium (Figure 8). During 1970–1998 period native soils of Kamennaya Steppe lost 1.2–2.3 kg m^{-2} of magnesium. The ratio of magnesium to calcium loss (~1:10) reflects on chemical composition of parent material: Carbonate loess with high content (10–20%) of magnesium (see below).

[21] Changes in land use might have affected the position of carbonates in soil profiles. The transition from native steppe to agricultural field, for example, suggests a dramatic change in the typical depth of the rooting zone. The roots of native steppe vegetation such as tall grass might be 50 to 100 cm deeper than the roots of crops [*Canadell et al.*, 1996]. The rooting depth is the principal factor along with soil texture that defines soil field capacity and therefore the ability to store moisture [*Zubenok*, 1976; *Lapenis and Shabalova*, 1994]. Thus one might argue that the transition from native steppe to agricultural vegetation should reduce soil field capacity and increase the depth of water infiltration, leading to carbonate dissolution. Reduction of rooting depth might also reduce the concentration of carbon dioxide in soil air, which can lead to carbonate preservation and a rise in the UDC [*Mikhailova and Post*, 2006]. However, despite the possible variations in leaching associated with different land uses, a comparable loss of calcium was found in each of the 3 land-uses in the study. Because all these plots lost similar amounts of calcium (Figure 7) and magnesium (Figure 8) in comparison to the 1970 native steppe soil samples, we conclude that the principle mechanism of carbonates loss in Kamennaya Steppe was not related to the specific land-use history.

[22] Other factors that might affect the position of the UDC are the acidity of soil solution and the effects of irrigation. The acidity of the soil solution depends on a number of factors, including the acidity of atmospheric precipitation and the concentration of CO_2 in soil air. During the last century, the Kamennaya Steppe and the Southern Russian plain were not subjected to significant levels of acidic deposition. The typical rate of sulfur deposition in this predominantly agricultural region is 20 times lower than in the industrial northwest of Russia and only slightly exceeds the pre-industrial levels of 1906 [*Lapenis et al.*, 2004]. Therefore acidic deposition is not the likely cause of the high rate of calcium loss between 1970 and 1998 (Figure 7).

[23] Irrigation water from rivers or groundwater reservoirs is usually saturated with carbonates and has relatively high concentrations of calcium and carbonate alkalinity ($2 \times CO_3^{2-} + HCO_3^-$). On a global scale, irrigation increases precipitation of pedogenic carbonates and causes the release of about 30 Tg of C a^{-1} back into the atmosphere [*Suarez*, 1999]. In the former USSR, however, only 17.7 million ha were irrigated, which is less than 14% of the Chernozem soil region in Russia and Ukraine [*Suarez*, 1999]. The native steppe and windbreak plots studied in the Kamennaya Steppe were never irrigated. The plot in the agricultural field, however, was subjected to regular irrigation by water pumped from a nearby pond. Despite this practice, the agricultural field showed changes in carbonate concentrations that were essentially the same as those seen in the native steppe and windbreak plots (Figures 7 and 8). Therefore we conclude that irrigation had a minimal role in the changes measured in SIC concentrations in Kamennaya Steppe soils.

[24] In the absence of land use changes or acidic deposition, the distribution of pedogenic carbonates in the soil profile is regulated by the amount of available water and the concentration of carbon dioxide in soil air [*Nordt et al.*, 1999] as follows:

$$CO_2 \downarrow + H_2O + CaCO_3 \Rightarrow 2HCO_3^- + Ca^{2+} \quad (3)$$

$$2HCO_3^- + Ca^{2+} \Rightarrow CaCO_3 + H_2O + CO_2 \uparrow \quad (4)$$

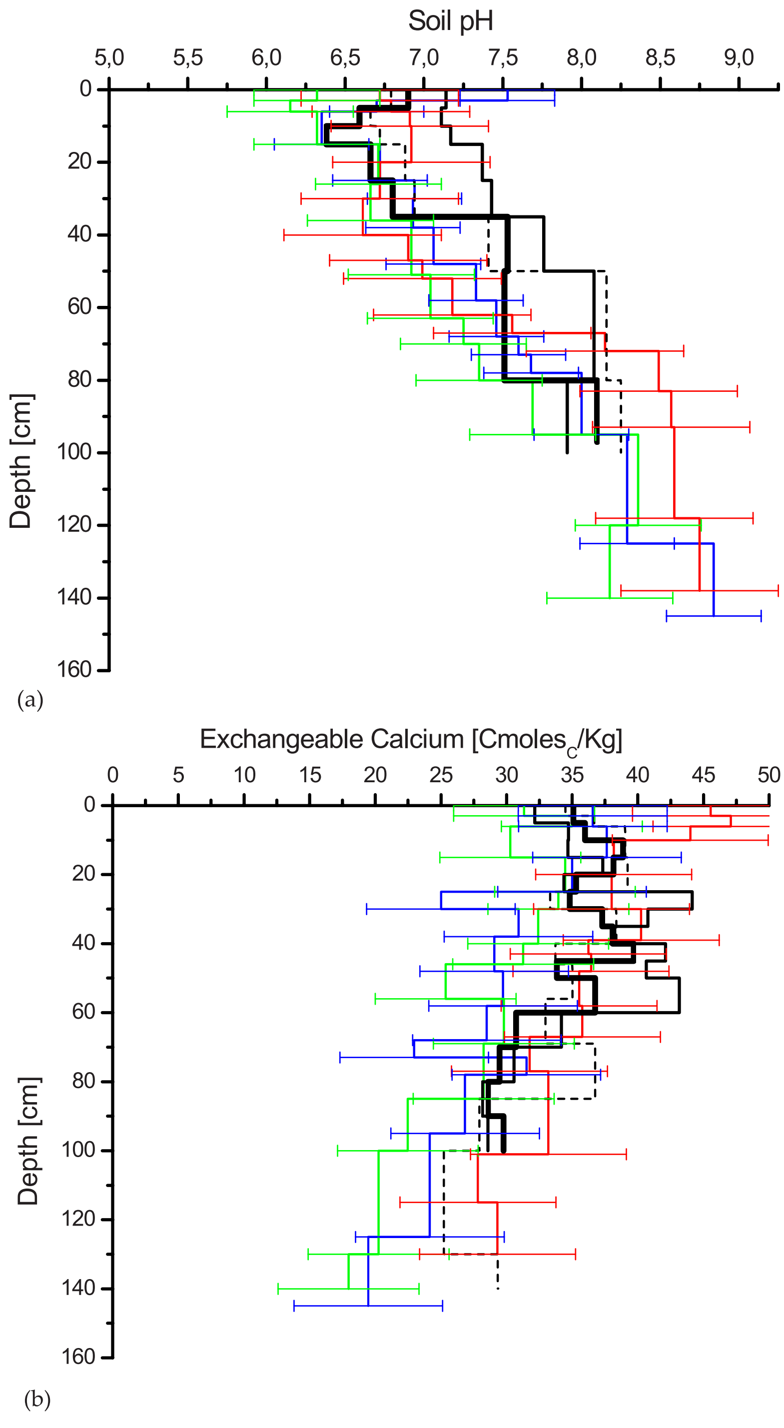

Figure 6. (a) Changes in the measured in water solution soil pH, and (b) exchangeable calcium concentration of soil. The thick solid black line represents data for 1920 (native steppe); the thin solid black line, 1947 (windbreak); the dashed black line, 1970 (native steppe). The colored lines represent average data for 1998 soils (blue, native steppe; green, windbreak; red, agricultural field). The error bars represents 3 sigma intervals of variations in 1998 soil parameters.

[25] The first reaction reflects the absorption of carbon dioxide by carbonate dissolution, whereas the second equation describes the release of carbon dioxide due to the precipitation of pedogenic carbonates. These two reactions have prominent seasonal lags. In Chernozems of tall grass steppe, seasonal variations in the upward and downward movement of soil water have been shown to cause 1 to 2 cm variations in the UDC position [*Afanas'eva*, 1966]. During the early spring of wet years, dissolved carbonate migrates downward with the surplus of water caused by melting

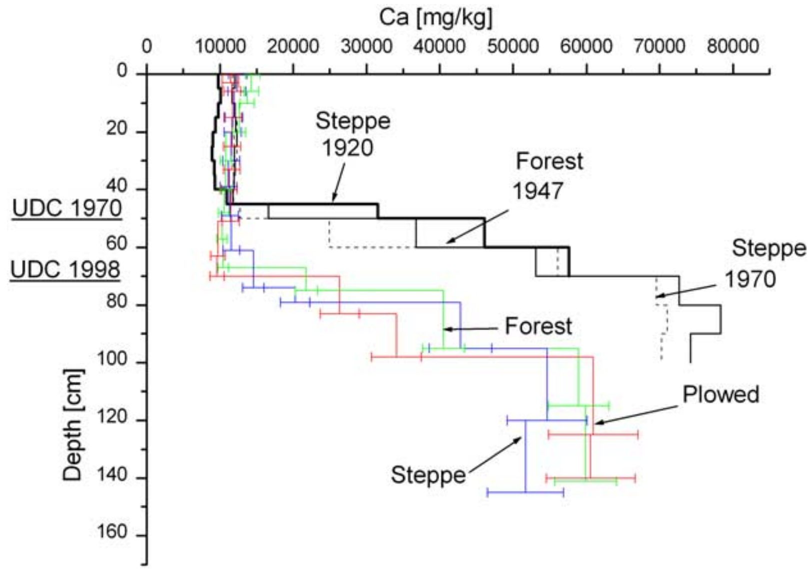

Figure 7. Modern and archived profiles of total calcium in soil of Kamennaya Steppe (mg kg^{-1}). Legend is the same as for the Figure 6. The average position of Uppermost Depth of Carbonates (UDC) for 1970 and 1998 is shown on vertical axis.

snow and spring precipitation equation (3). During the summer, an increase in temperature supports higher microbiological activity and increases root respiration. The relatively high summer CO_2 concentrations in the soil trigger carbonate dissolution and lead to the saturation of soil water with carbonate and bicarbonate ions. High summer temperatures and high biological activity in the rooting zone near the soil surface increase evapotranspiration, which stimulates the upward capillary movement of water. As the soil solution moves upward, the dissolved carbon dioxide escapes into the atmosphere, and carbonate precipitates as shown in equation (4) [*Marion et al.*, 1985; *Sobecki and Wilding*, 1983]. This seasonal pattern of the UDC occurs, however, only during wet years with a sufficient amount of available moisture in soil profile [*Afanas'eva*, 1966].

[26] Thus the lack of change in the UDC from 1920 to 1970 (Figure 7) indicates that the steppe climate for this period resulted in little, if any, net retention of carbon dioxide, whereas the significant lowering of the UDC from 1970 to 1998 reflects a wet period when dissolution of carbonates was greater than carbonate precipitation. On the basis that each mole of dissolved calcium carbonate consumes one mole of atmospheric CO_2 equation (3), we estimated that soils in Kamennaya Steppe consumed about $\sim$240 g C m^{-2} a^{-1} from 1970 to 1998 during the spring and early summer months (810 g Ca m^{-2} a^{-1} $\times \frac{12}{40} =$ 243 g C m^{-2} a^{-1}). The soil water, however, received twice as much dissolved carbon due to another $\sim$240 g C m^{-2} a^{-1} added from leached calcium carbonate (see above).

[27] From the $\sim$240 g m^{-2} of atmospheric carbon absorbed every year in Kamennaya Steppe through the increased leaching of pedogenic carbonates a significant amount could be returned to the atmosphere upon precipitation of $CaCO_3$. The balance of carbon dioxide in the soil-groundwater-river system depends on the fate of dissolved carbonates, which can remain dissolved in groundwater, discharge in solution into rivers, or redeposit deeper in the profile as the pH rises (Figure 6a) or within river channels as the water equilibrates with atmospheric CO_2. The precipitation of carbonates at deeper parts of soil profile releases CO_2 back into the atmosphere, whereas carbonates remaining in solution in groundwater and rivers represent a net sink for atmospheric CO_2 [*Sundquist*, 1991; *Raymond and Cole*, 2003].

5.2. Estimate of the Net Transport of Dissolved Calcium From Soil Profile

[28] The transport of carbonates into rivers and groundwater can be traced through the transport of dissolved carbon in the form of carbonate alkalinity or through the transport of dissolved calcium. Here we used the concentration of calcium, thus, the ratio between the moles of total calcium removed from Kamennaya Steppe watershed and the moles of absorbed atmospheric carbon should be 1:1. The steppe loess has carbonate with a high ($\sim$10–20%) magnesium content [*Altermann et al.*, 2005]. For calculations of carbon sequestration we will use the simple formula of calcium carbonate: $CaCO_3$, keeping in mind, however, that the resulting estimate should be at least $\sim$10% higher due to presence of magnesium in typical steppe carbonate.

5.3. Sequestration of Atmospheric Carbon Through Export of Dissolved Carbonates by River Runoff

[29] The flux of calcium in river runoff ($F(t)$) at any year can be estimated as a product of annual water discharge and average concentration of calcium in the water:

$$F(t) = r \times \left[Ca^{2+}\right] \quad (5)$$

[30] Where r is the annual river runoff per unit of surface area of watershed (l m^{-2} a^{-1}), (Ca^{2+}) is the average concen-

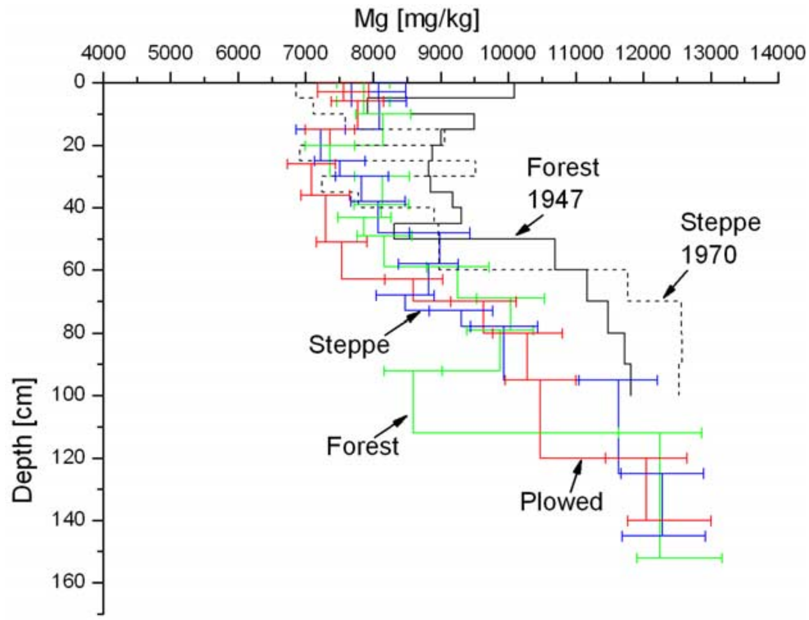

Figure 8. Modern and archived profiles of total magnesium in soil of Kamennaya Steppe (mg kg^{-1}). Legend is the same as for the Figures 6 and 7.

tration of dissolved calcium (g l^{-1}), and t is the time. River runoff from Kamennya Steppe watershed increased from 29 mm a^{-1}, (29 l m^{-2} a^{-1}) in 1970 to 38 mm a^{-1} (38 l m^{-2} a^{-1}) in 1998 [*Sentsova*, 2002]. Unfortunately, we did not have data on changes in the water chemistry of the Chigla and Talovaya Rivers. Therefore we made two estimates of the transport of dissolved *Ca* from Kamennaya Steppe; each based on different assumptions. The first estimate assumes that the concentration of dissolved calcium in river water equaled the concentration in the unconfined aquifer. This assumption should lead to some degree of overestimation of the export of dissolved calcium from Kamennaya Steppe because the equilibrium concentration of dissolved calcium in groundwater would be expected to be higher than in the river as a result of higher CO_2 concentrations. The second estimate is based on the assumption that the export of carbonates from Kamennaya Steppe watershed is the same as the average export of carbonates from the watershed of the River Don. This assumption should lead to an underestimation of the export of carbonates from Kamennaya Steppe, because Chernozems on loess deposits occupy only ~67% of the Rivers Don watershed (see above) whereas the entire Kamennaya Steppe watershed is composed of this landscape. The remainder of the River Don watershed is covered by relatively acidic soils that are not a significant source of carbonates. Thus the true rate of carbonates export from Kamennaya Steppe should be in between of these two estimates.

5.4. Assumption 1: The Concentration of Dissolved Calcium in River Water Equaled the Concentration in the Unconfined Aquifer

[31] Detailed measurements of the chemical composition of groundwater in the Kamennaya Steppe were taken in 1956 and in 1991 [*Ivanov*, 1991]. According to these data, the carbonate alkalinity and concentrations of dissolved calcium and magnesium in groundwater increased by a factor of 3 from 1956 to 1991 (Table 1). The chemical equilibrium model SPECIES [*Barak*, 1990] was used to evaluate mineral control of carbonate species in solution. Results indicated that groundwater in 1956 (Table 2) was close to equilibrium with pure calcite, whereas groundwater in 1991 was close to equilibrium with magnesium carbonate, which is approximately 9 times more soluble [*Barak*, 1990]. The calcite occurs at the bottom of unconfined aquifer in Cretaceous limestone deposits 15–19 m below soil surface [*Ivanov*, 1991]. During the last 30 to 40 years, however, the increase in the water table level has brought groundwater in direct contact with the parent material of the

Table 1. Chemical Composition of Groundwater of Kamennaya Steppe Unconfined Aquifer in 1956 and 1991[a]

		Cations, mg l^{-1}			Anions, mg l^{-1}					
Year	N of Wells	Na^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	NO_3^-	CO_3^{2-}	HCO_3^-	Total Dissolved Solids, mg l^{-1}
1956	50	101/375	3/94	3/89	17/59	3/412	1/117	1/88	229/688	210/1188
1991	43	45/895	8/412	10/137	19/194	51/1275	1/464	1/842	127/2355	413/2909

[a]The minimum/maximum concentrations are averaged over several wells [*Ivanov*, 1991].

Table 2. Chemical Composition of Groundwater in Chemical Equilibrium With Calcite (a) and Magnesium Carbonate (b)[a]

		Cations, mg l^{-1}			Anions, mg l^{-1}					
	pH	Na^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	NO_3^-	CO_3^{2-}	HCO_3^-	Total Dissolved Solids, mg l^{-1}
a	8.0	200	45	33	30	200	50	40	450	1060
b	8.0	450	210	149	100	600	200	400	1300	3360

[a]These calculations were done by SPECIES model [*Barak*, 1990] under assumption of no changes in groundwater pH. This assumption is consistent with data on pH in soil solution during 1920–1998 (Figure 6a).

Chernozems; loess with high content of magnesium carbonate. As a result, the composition of groundwater in 1991 had shifted toward equilibrium with a more soluble type of carbonate (Table 2).

[32] We suggest that the concentration of dissolved calcium in the Kamennaya Steppe's rivers in 1970 was in equilibrium with calcium carbonate, but in 1998 in equilibrium with magnesium carbonate. Taking into account data on the changes in the river runoff by *Sentsova* [2002] and our estimates of the concentration of dissolved calcium (Table 2), we can calculate the flux of dissolved calcium from the watershed of Kamennaya Steppe in 1970:

$$F(1970) = 29\,\mathrm{l\,m^{-2}\,a^{-1}} \times 0.045\,\mathrm{g\,l^{-1}} = 1.3\,\mathrm{g\,Ca\,m^{-2}\,a^{-1}},$$

and in 1998:

$$\mathrm{F}(1998) = 38\,\mathrm{l\,m^{-2}\,a^{-1}} \times 0.21\,\mathrm{g\,l^{-1}} = 8.0\,\mathrm{g\,Ca\,m^{-2}\,a^{-1}}.$$

[33] Thus in 1998, the rate of Ca loss in the Kamennaya Steppe watershed was 6.7 g Ca m^{-2} a^{-1} more than in 1970. We can employ the 1:1 molar ratio (C:Ca) to calculate the increase in the amount of atmospheric carbon sequestrated through increased dissolution of pedogenic

$$\text{carbonates:}\ 6.7\,\mathrm{g\,Ca\,m^{-2}\,a^{-1}} \times \frac{12}{40} = 2.0\,\mathrm{g\,C\,m^{-2}\,a^{-1}}.$$

5.5. Assumption 2: The Export of Carbonates From Kamennaya Steppe is Equal to the Average Rate of Carbonate Weathering in the Entire River Don Watershed

[34] The annual reports by the Federal Service for Hydrometeorology and Environmental Monitoring (FSHEM) provide information on the chemical composition and discharge of all major rivers in Russia. We used daily data on the chemical composition and discharge of water in the mouth of the Don River (FSHEM station Razdorskaya, near the city of Rostov). During 1960–1997, 207 measurements of Ca and HCO_3 concentrations were reported [FSHEM Annual Reports, 1960–1997], averaging by 7.6 measurements per year, with some bias toward 1983–1997. These data were used in a similar manner to that of *Raymond and Cole* [2003], who estimated the export of carbonate alkalinity in the Mississippi River. According to our estimates

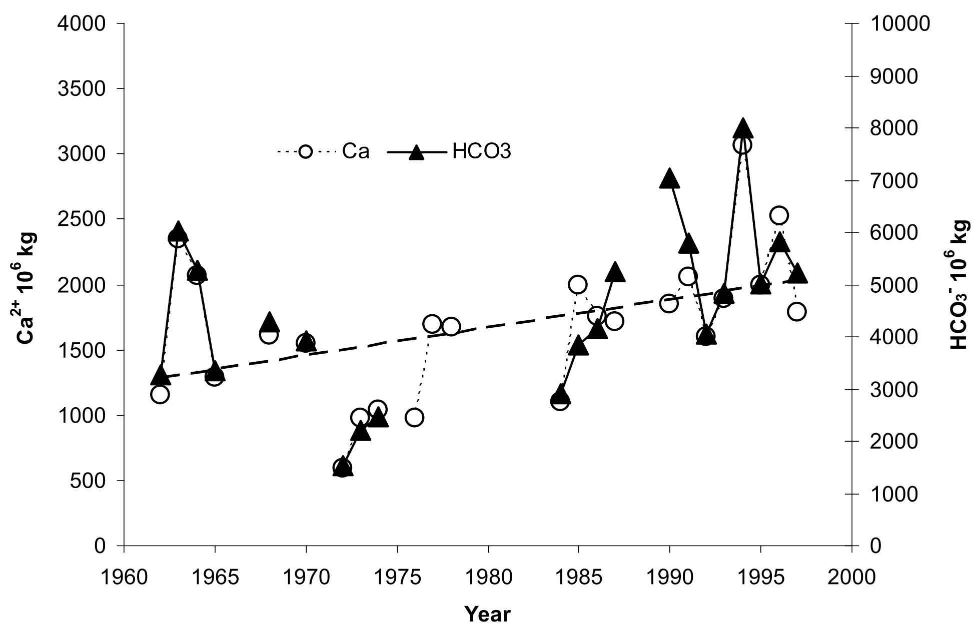

Figure 9. Annual flux of dissolved calcium and bicarbonate ions in the mouth of the Don River. The data represent a product of mean annual concentration of ions and annual discharge of the river (FSHEM Annual Reports, 1960–1997).

(Figure 9), the export of dissolved calcium and bicarbonate ions by the Don River significantly increased despite some decline in Don River discharge, due to significant increases in Ca and HCO_3 concentrations during the summer and fall months (FSHEM Annual Reports, 1960–1997). This increase was from $\sim$15 10^{11} g Ca a^{-1} in 1970 to $\sim$20 10^{11} g Ca a^{-1} in 1997 (Figure 9). By dividing these numbers on the total area of River Don watershed (42.5 10^{10} m^2, see above), we estimate annual export of dissolved calcium per unit of area of River Don watershed in 1970: $\sim$3.5 g Ca m^{-2} a^{-1}, and in 1997: 4.7 g Ca m^{-2} a^{-1}. The net increase in the export of dissolved calcium was $\sim$1.2 g Ca m^{-2} a^{-1}, which corresponds to the net increase of $\sim$0.4 g C m^{-2} a^{-1} in the sequestration of atmospheric carbon (1.2 g Ca m^{-2} a^{-1} $\times \frac{12}{40} =$ 0.4 g C m^{-2} a^{-1}). Thus the entire range of two estimates of the sequestration of atmospheric carbon through the export of dissolved carbonates by river runoff made under these two assumptions is 0.4–2.0 g C m^{-2} a^{-1}.

5.6. Calculations of Atmospheric Carbon Sequestration Through Accumulation of Dissolved Carbonates in Groundwater

[35] Groundwater monitoring in the Kamennya Steppe indicated an increase in the water table level (Δh) of about 4 m (Figure 3) or 0.14 m a^{-1} (140 l m^{-2} a^{-1}) during 1970–1998, [*Ivanov*, 1991]. Because this increase occurred in a close proximity to lower soil horizons, one can assume that the percentage of the space available for the water storage (V%) should not be more than in soil and not less than in the parent rock of loess deposits. The available space of loess deposits is $\sim$ 18%, and of lower soil horizons is $\sim$54% (see Methods). The amount of dissolved calcium accumulated every year during 1970–1998 ($M(t)$) can be calculated by multiplying water equivalent of groundwater rise ($V\%\ \Delta h$) by the concentration of dissolved calcium:

$$M(t) = V\% \times \Delta h \times \left[Ca^{2+}\right] \qquad (6)$$

[36] We can use the range of free space estimates with Ca^{2+} concentrations estimated from equilibrium modeling (Table 2) to calculate the lowest and the highest rates at which dissolved calcium was accumulated as the groundwater volume increased. We estimated this rate to be from 5.3 to 15.8 g Ca m^{-2} a^{-1}:

$$\begin{aligned} M(1998)_{Lowest} &= 0.18 \times 0.21\,\mathrm{g\,l^{-1}} \times 140\,\mathrm{l\,m^{-2}\,a^{-1}} \\ &= 5.3\,\mathrm{g\,Ca\,m^{-2}\,a^{-1}}, \end{aligned}$$

$$\begin{aligned} M(1998)_{Highest} &= 0.54 \times 0.21\,\mathrm{g\,l^{-1}} \times 140\,\mathrm{l\,m^{-2}\,a^{-1}} \\ &= 15.8\,\mathrm{g\,Ca\,m^{-2}\,a^{-1}}. \end{aligned}$$

[37] Converting these estimates into carbon we obtain: 1.6 and 4.7 g C m^{-2} a^{-1} respectively.

[38] The resulting range of the net sequestration of atmospheric carbon in Kamennaya Steppe during 1970–1998 due to accumulation of dissolved carbonates in groundwater (1.6–4.7 g C m^{-2} a^{-1}) plus that due to transport from the watershed by rivers (0.4–2.0 g C m^{-2} a^{-1}) was estimated to range from 2.0 to 6.7 g C m^{-2} a^{-1}. Increasing these numbers on 10% due to additional carbon sequestration through leaching of magnesium (see above), we obtain 2.1–7.4 g C m^{-2} a^{-1}.

[39] This estimate of increased C sequestration ($\sim$2.1–7.4 g m^{-2} a^{-1}) is up to several times higher than the value of 1.2 g C m^{-2} a^{-1} reported for the Mississippi River Basin for 1954 to 2000 by *Raymond and Cole* [2003], who based their estimate solely on river export. If we apply our estimate to the entire area of Russian and Ukrainian Chernozems (129 million ha), where precipitation, soil moisture, groundwater tables, and runoff have been increasing, we estimate the net sink of atmospheric carbon due to increased leaching of pedogenic carbonates as $\sim$3 to 12 Tg a^{-1} C.

5.7. The Seasonal Pattern of CO_2 Consumption and Release

[40] According to our estimates, net carbon sequestration accounts only to 1–3% of the total loss of inorganic carbon from the first 1 m of the soil profile during 1970–1998 (240 ± 62 g C m^{-2} a^{-1}). The bulk of dissolved inorganic carbon was apparently redeposited deeper in the soil or subsoil, and perhaps to some degree, upon discharge to surface water as equilibrium with atmospheric CO_2 was re established. The precipitation of pedogenic carbonates usually occurs in late summer, which suggests a strong seasonal pattern of CO_2 consumption and release. Averaged for the period of 1970–1998, the soil of the Kamennaya Steppe consumed carbon dioxide each spring through carbonate dissolution at a rate of approximately 240 g m^{-2} but, later in the summer, released $\sim$232–237 g C m^{-2} back into the air as carbonates reprecipitated. Applying this number to the entire area of Russian and Ukranian Chernozems, we find that in the spring months the steppe absorbs about 310 Tg C, and during summer-fall releases back to the atmosphere $\sim$300–307 Tg C. Thus the seasonal amplitude of this flux is $\sim$610 Tg. It is unlikely, that these large seasonal fluxes existed before 1960–1970 when little or no leaching of pedogenic carbonates occurred because annual precipitation was less than potential evapotranspiration. Therefore these fluxes of atmospheric carbon are a relatively recent development.

[41] Monitoring of the atmospheric concentration of CO_2 at Mauna Loa, Hawaii demonstrates an increase in the average seasonal amplitude of this gas during 1970–1998 of $\sim$0.7 ppm or $\sim$1600 Tg C [*Keeling and Whorf*, 2005]. The seasonal amplitude of atmospheric carbon dioxide is an important tool that has been used to estimate changes in the productivity of the biosphere [*Keeling et al.*, 1996; *Nemani et al.*, 2003]. According to these studies, the net primary productivity of the biosphere did increase during 1982–1999 on 6% [*Nemani et al.*, 2003]. The seasonal changes in the atmospheric concentration of carbon dioxide in Northern Hemisphere reach its maximum in May–June, and the minimum in December–January [*Keeling and Whorf*, 2005]. The seasonal intake of carbon dioxide to the steppe soil, however, reaches its maximum in spring, while the release of soil CO_2 occurs in late summer–early fall. Therefore the increase in the seasonal amplitude of atmospheric CO_2, thus estimates of biota productivity, could be

30–40% larger due to opposite seasonal changes in the atmospheric carbon flux in steppe soil.

6. Conclusions

[42] The study of archived soils from Kamennaya Steppe preserve collected through most of 20th century enabled us to detect pronounced changes in the status of pedogenic carbonates. Detailed chemical analysis indicated significant loss of total calcium in the top meter of the soil profile during 1970–1998. The most likely explanation for this large loss of pedogenic carbonates is an increase in the downward flux of soil water caused by changes in steppe climate. Our calculations of carbon sequestration suggests that the climate related sink of carbon due to export of carbonate alkalinity by steppe rivers, and due to accumulation of dissolved carbonates in groundwater exceed that of the carbon sink in soils of Mississippi River watershed of North American prairies estimated by *Raymond and Cole* [2003], who based their estimate solely on river export. The total net sink of atmospheric carbon due to leaching of pedogenic carbonates in Russian and Ukrainian Chernozems is ~3–12 Tg C a^{-1}. This is significant in relation to the carbon sequestered in the live biomass of the entire Russian forest (~72 ± 50 Tg a^{-1} C) [*Lapenis et al.*, 2005; *Shvidenko and Nilsson*, 2003] and therefore of consequence to Northern hemisphere carbon budgets. We also found that increase in leaching of pedogenic carbonates could moderate recent increase in seasonal amplitude of atmospheric CO_2 concentration.

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B. F. Aparin, Central Dokuchaev’s Soil Museum, 6 Birzhevoi Pr., St. Petersburg, Russia 199034.

S. W. Bailey, USDA Forest Service, Hubbard Brook Experimental Forest, RR1, Box 779, Campton, NH 03223, USA.

M. Calef and A. G. Lapenis, University at Albany, Department of Geography and Planning, 1400 Western Avenue, Albany, NY 12222, USA. (andreil@albany.edu)

G. B. Lawrence, USGS, 425 Jordan Road, Troy, NY 12180, USA.

A. I. Shiklomanov, University of New Hampshire, Complex Systems Research Center, 39 College Road, Durham, NH 03824-3525, USA.

N. A. Speranskaya, State Hydrologic Institute, 23 Second Line, St. Petersburg, Russia 199053.

M. S. Torn, Lawrence Berkeley National Laboratory, 1 Cyclotron Rd, Berkeley, CA 94720, USA.