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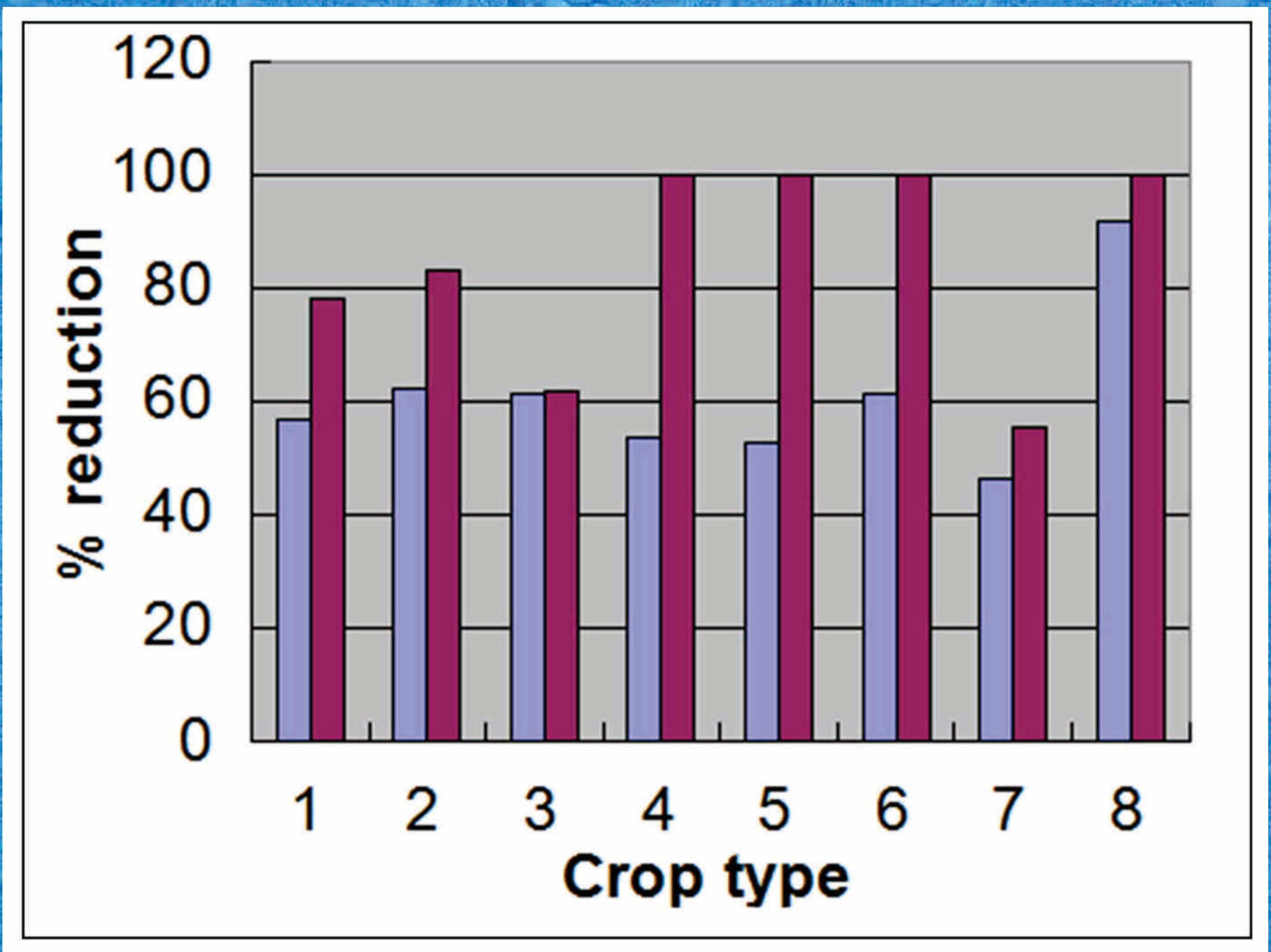

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Soil Nutrients, Landscape Age, and *Sphagno-Eriophoretum vaginati* Plant Communities in Arctic Moist-Acidic Tundra Landscapes

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Abstract

Most research exploring the relationship between soil chemistry and vegetation in Alaskan Arctic tundra landscapes has focused on describing differences in soil elemental concentrations (e.g. C, N and P) of areas with contrasting vegetation types or landscape age. In this work we assess the effect of landscape age on physico-chemical parameters in organic and mineral soils from two long-term research sites in northern Alaska, the Toolik Lake and Imnavait grids. These two sites have contrasting landscape age but similar vegetation composition. We also used correlation analysis to evaluate if differences in any of these parameters were linked with between-site variation in the abundance of growth forms. Our analysis was narrowed to soils in *Sphagno-Eriophoretum vaginati* plant communities. We found no significant differences between these sites for most parameters evaluated, except for total Ca which was significantly higher in organic soils from Imnavait vs. Toolik and total Na which was significantly higher in mineral horizons from Toolik compared to Imnavait. Moreover, the abundance of non-*Sphagnum* mosses was positively correlated with total Ca in organic soils, whereas the abundance of forbs, non-*Sphagnum* mosses and bryophytes was negatively correlated with total Na in mineral soils. We suggest that differences in the concentration of these two elements are most likely tied to landscape age differences between these sites. However, since observed dissimilarity in terms of total Ca in organic soils and total Na in mineral soils is concordant with correlation patterns observed between these elements and the aforementioned growth forms, it is likely that existing differences in vegetation composition between these sites are also influencing the concentration of these elements in soils, particularly that of Ca, since non-*Sphagnum* mosses are dominant above organic soils and are therefore expected to significantly influence biogeochemical processes at this horizon. Thus, we conclude that

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except for organic Ca and mineral Na, there is little difference between these sites in terms of their soil physico-chemical properties. We suggest that most of the influence of landscape age on evaluated parameters is masked by factors such as moderate cryoturbation and similarities in terms of vegetation properties and climate. These observations are relevant as they suggest a linkage between soil chemistry and vegetation composition in this tundra region.

Keywords

Arctic Alaska, Soil Nutrients, Moist-Acidic Tussock Tundra, Vegetation

1. Introduction

Studies have shown that landscape age (time since deglaciation) is an important factor influencing essential biogeochemical processes in Arctic tundra soils [1]-[6]. For instance, Hobbie and Gough [7] compared foliar and soil nutrients between landscapes that were deglaciated > 50,000 (moist-acidic tundra [MAT]) and less than 11,500 years ago (moist non-acidic tundra [MNT]) and found higher rates of net N mineralization, cation exchange capacity and exchangeable base cations in soils at the geologically older site. Contrasting landscape age has also been proposed as a potential factor explaining variation in litter decomposition rates [8] and the rate of processes like C and N cycling in tundra soils [9].

In the Alaskan Arctic, differences in landscape age are also intimately related to differences in soil acidity [2] [3]. A number of important biological attributes are influenced by gradients of soil pH in this region. For example, some studies have documented the relationship between contrasting vegetation types with a distinct pH boundary that separates MAT and MNT [7] [9]. Considerable variation in species and growth form dominance within some tussock tundra communities has been associated with variation in soil pH [10] [11]. Differences in soil pH can also affect specific plant community attributes like vascular-plant species richness [12]. More recently, Eskelinen *et al*. [13] proposed an indirect effect of soil pH on vegetation via the evolution of bacteria-based microbial communities in alkaline soils where the properties of forb-produced organic matter were possibly sustaining the prevalence of soil bacteria.

Vegetation can also influence important soil processes like nutrient cycling which regulate nutrient concentrations and the size of C and N pools in tundra soils [14]. Since vegetation effects on soils are thought to be primarily related to the accumulation of organic material and nutrients [15], variation in specific traits influenced by plant communities, such as litter chemistry, is believed to play an important role in some of these processes. For instance, altered litter quality resulting from changes in species composition is known to affect processes like soil N mineralization [16]. However, some evidence appears to indicate that other landscape-scale soil processes are less likely to be significantly affected by vegetation. For example, Hobbie and Gough [8] demonstrated that variation in plant species composition did not account for differences in litter decomposition between MAT and MNT.

The linkage between patterns in vegetation composition and soils in tundra landscapes has not been characterized thoroughly, although several studies have contributed significantly in this direction. Chu and Grogan [17] found that variation in total C and N, Dissolved Organic Carbon (DOC) and N (DON), mineral N and N mineralization potential in organic soils in Daring Lake, Canada has been directly related to differences in vegetation types. Likewise, Eskelinen *et al*. [13] observed that forb-rich non-acidic heaths were associated with low C:N and low soluble N:phenolics ratios in soils, whereas shrub-dominated acidic heaths were associated with high values of these ratios. Understanding the reciprocal relationship between vegetation and soil dynamics in Arctic tundra ecosystems is challenging mostly because vegetation is ultimately controlled by meso-topographic relationships (slope position and soil moisture), micro-scale disturbances and factors related to long-term landscape evolution [4] [18]. This suggests that plant communities exhibit considerable spatial variability along soil chemical gradients.

In this study we compare a number of soil physico-chemical parameters from organic and mineral horizons of two study sites in northern Alaska that differ in landscape age, *i.e.*, time since deglaciation 55 k and 125 k years, but have similar vegetation composition [18]. These are long- term vegetation monitoring areas which have been intensively used since the late 1980s to study the effects of climate change on tundra vegetation [19]-[21]. Our analysis is focused on soils derived from areas dominated by *Sphagno-Eriophoretum vaginati* plant communities' sensu Walker *et al*. [18], the most ubiquitous plant community within these sites. Little information on soil chemistry has been published from soils within these long-term monitoring sites. Only recently the works of Whittinghill and Hobbie [5] [6] and Keller *et al*. [23] have shown that the two landscape ages represented by these two study sites are similar in terms of several soil chemical parameters. The present work aims to advance the understanding of soil processes in this region by including analyses on physico-chemical properties of both mineral and organic horizons and other aspects of soil chemistry that are not necessarily evaluated in detail by those studies.

We also assess between-site differences in the abundance of a number of growth forms and subsequently evaluate the relationship between those differences and the variation between sites in terms of particular physico-chemical parameters to make inferences regarding how vegetation composition may be affecting soil physico-chemical properties at these two sites, and vice versa. These observations will contribute to a better understanding on how vegetation composition, landscape age and soil chemistry are reciprocally linked in this region.

2. Materials and Methods

2.1. Study Area

This study was carried out in two 1 km^2 research grids, Toolik Lake and Imnavait Creek, in the vicinity of the Toolik Lake Field Station, Alaska, located north of the Brooks Range in the Southern Foothills Physiographic Province of the Alaskan North Slope [24] [25] (**Figure 1**). The region is underlain by continuous permafrost which is 250 - 300 m thick [26]. Both grids are dominated by MAT vegetation; however their landscapes are slightly different due primarily to differences in glacial age [18] [27] [28]. The Imnavait grid is in the headwaters of the Imnavait Creek, a small beaded tributary of the Kuparuk River basin [18]. This site lies on the Sagavanirktok (Middle Pleistocene) glacial drift which deglaciated about 125,000 years ago [27] [28]. Topography is

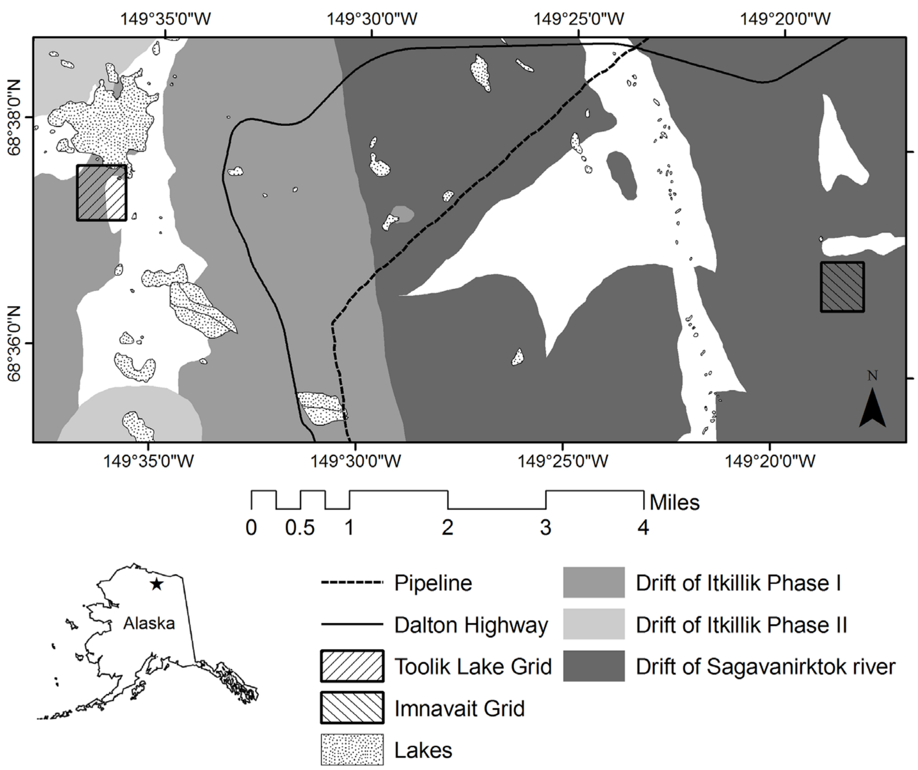


Figure 1. Landscape ages and the location of the Toolik Lake and Imnavait Creek 1 km^2 grids in the Upper Kuparuk River region in Northern Alaska.

dominated by gently rolling hills and elevation within the watershed varies from about 770 to 980 m [22]. Most of the Toolik Lake grid lies in a younger substrate (Itkillik I glacial drift) which deglaciated during the late Pleistocene (ca. 55,000 years), but includes areas of Itkillik II outwash towards the east [27] [28]. The landscape at this site is more heterogeneous than at Imnavait and is dominated by small glacial lakes, kames and moraines. Elevations range from 670 to 850 m [18].

Both grids share similar meteorological conditions due to their close proximity (<12 km). Mean annual surface atmospheric temperature (SAT) from 1989-2008 have been −8.5˚C; whereas average annual precipitation during the same period was 312 mm [29]. Linear trend analysis of mean annual SAT and mean annual precipitation revealed no trends in these parameters suggesting that they have remained stable over the last two decades [29].

2.2. Study Design

There are 157 permanent 1m^2 vegetation plots within these grids, 72 at Imnavait and 85 at Toolik. Plots are located equidistantly at 100 meters from each other within the grids [19]. These are non-manipulative plots that are currently being studied for analyzing long term changes in vegetation composition and structure in this region [30]. We limited our analysis to a subset of these plots that are established in areas with *Sphagno-Eriophoretum vaginati* plant communities. This plant community has a broad spatial extent which allows us to extrapolate results to a landscape-scale level. Likewise, confounding effects that may result from grid-scale variation in plant communities could be reduced by focusing on a single plant community. The *Sphagno-Eriophoretum vaginati* plant community is the most dominant plant community within the grids and is considered the zonal vegetation of mesic slopes throughout the Arctic Foothills [18]. It typically occurs on ice-rich sediments with shallow active layers and low soil pH [31]. The most conspicuous plant species is the tussock-forming sedge *Eriophorum vaginatum* which dominates particularly in stable hillslope shoulders and upper backslopes; whereas shrubs like *Betula nana* and *Salix pulchra* tend to become dominant on footslopes and associate with deep *Sphagnum* spp. mats, other mosses like *Aulacomnium turgidum*, *Hylocomnium splendens* and lichens like *Peltigera aphtosa* and *Cladonia* spp. [18] [22] [32]. *Sphagno-Eriophoretum vaginati* plant communities' sensu Walker *et al*. [18] are contained within the *Moist-tussock sedge*, *dwarf shrub*, *moss tundra* physiognomic unit [24] and mostly coincide with *Eriophorum vaginatum-Sphagnum* spp. plant communities' sensu Walker *et al*. [22].

Plant communities within the Toolik and Imnavait grids were identified using geographical layers prepared by Walker [33] and published maps of the region [24]. There are 33 vegetation types represented in the Upper Kuparuk river region [22] [31]. Walker *et al*. [18] classified vegetation of both Toolik and Imnavait grids into five associations and 15 community types. We performed an overlay analysis using a geographic information system (GIS) and selected 24 plots (12 at Toolik and 12 at Imnavait) representing *Sphagno-Eriophoretum vaginati* plant communities. We extracted growth form abundance data from selected plots from a long-term plant community dataset. This data corresponded to vegetation sampling realized in 2007 (Imnavait) and 2008 (Toolik) [34].

2.3. Sampling and Nutrient Analysis

Soil samples were collected 1 - 2 meters apart from selected plots in areas with visually similar vegetation composition. Samples of organic and mineral soils were collected near each plot following the procedures described below. Mineral soils near two of the 24 plots (both at Toolik) were frozen at the time of collection and not sampled. Soil sampling was realized during August, 2008.

A shovel was used to create a 25 × 25 cm pit to collect soil samples in each selected plot. Pits reached an approximate depth of 20 cm, or deeper until the upper 5 - 7 cm portion of the mineral horizon was exposed. Three samples of mineral soils (n = 3) were taken at each pit by pushing a stainless steel soil core with plastic core inserts (aprox. 98 cc.) horizontally into the soil profile. These samples were used individually to calculate soil moisture, bulk density and elemental concentrations in this horizon. Mineral soil moisture was calculated after oven drying samples at 105˚C for 48 hours in laboratory facilities at Toolik Lake Field Station. Depending on soil conditions, each organic soil sample (n = 1) was extracted horizontally at the soil profile or vertically using a small bread knife and were then placed into labeled cloth bags. When samples were collected vertically, we removed the upper layer of soil where live material was evident and the lower layer where the organic layer diffuses into the mineral soil layer. Each organic soil sample had approximately twice the volume of mineral soil samples. All samples (except those used for estimating mineral soil moisture) were sent to the International Institute of Tropical Forestry Soils Laboratory (USDA-USFS) in San Juan, Puerto Rico and were processed within 8 days. Mineral soil samples for elemental concentration and bulk density determinations were oven dried at 40˚C for two weeks, whereas those from organic soils were air dried over the same period. We used a Foss Tecator Cyclotec (model 1093) mill to ground the samples and then passed them through a 1 mm stainless steel sieve. Roots of considerable size and other live material were excluded from the samples.

Total Nitrogen (N) and Total Carbon (C) were analyzed using the dry combustion method by means of a LECO TruSpec CN Analyzer [35]. The procedure used is a modified version of the Organic Application Note titled "Carbon and Nitrogen in Soil and Sediment" obtained from LECO Corp. [36]. The dry combustion method was also used to determine Total Sulfur (S), utilizing the LECO TruSpec (Add-On Module) S Analyzer [37]. The procedure used is from LECO [38] and is titled "Sulfur in Cement, Fly Ash, Limestone, Soil, and Ore". In the dry combustion method a small weighted sample is combusted in a high temperature furnace (950˚C for the LECO TruSpec CN Analyzer and 1450˚C for the LECO TruSpec S Analyzer) and in a stream of purified oxygen. Total Carbon is measured as CO_2 by an infrared detector and Total Nitrogen is determined as N_2 by a thermal conductivity cell detector. Total Sulfur as SO_2 is also detected by an infrared.

Ground material was analyzed for elemental concentrations of Phosphorus (P), Aluminum (Al), Potassium (K), Calcium (Ca), Magnesium (Mg), Manganese (Mn), Sodium (Na) and Iron (Fe). Soil samples were digested with concentrated HNO_3, 30% H_2O_2 and concentrated HCl using a modified version of the method recommended by Luh Huang and Schulte [39] and analyzed by means of a Spectro Plasma Emissions Spectrometer (Spectro Ciros ICP).

Subsamples were oven dried at 105˚C for 24 hrs. A moisture factor was calculated and applied to each analysis [40]. These same subsamples were later ignited at 490˚C in a muffle furnace (for at least 8 hrs.) to determine Loss-on-Ignition (LOI). Soil pH was measured in a 1:1 (soil:water) solution using an Orion Ionanalyzer Model 901 with a combination pH electrode [41].

Soil moisture of mineral and organic soil samples was determined by calculating the percentage weight loss after drying. Organic horizon thickness was averaged for each plot and was calculated using three different measurements of the organic horizon width at randomly selected areas of each pit.

2.4. Statistical Analysis

We analyzed and treated as independent variables each physico-chemical parameter and the abundance of particular growth forms. We used Exploratory Data Analysis (EDA) to corroborate if these variables conformed to parametric testing assumptions. We assessed normality using the Shapiro-Wilk test along with Normal Q-Q plots. Except for "% Moisture" which was analyzed using non-parametric Mann-Whitney *U*-test, results from EDA supported the use of Independent Samples T-Test for most variables. Variables that initially failed EDA tests were mostly affected by few extreme outliers and behave normally after their exclusion.

We used Pearson's correlation coefficient (r) to evaluate how physico-chemical parameters that were significantly different between sites relate to growth forms that were also found to have significantly different abundances at each site. We combined data from both sites that corresponded to these two variables. This resulted in 22 data points for correlation analysis. Correlation tests were performed after absolute abundances values in the dataset were converted to percent cover of growth forms at each plot.

3. Results

We found no significant differences between Imnavait and Toolik in terms of the thickness of the organic horizon and the bulk density of the mineral horizon (**Table 1**). Soils at both sites were similarly acidic whereas comparable LOI values are indicative of similar organic matter content. Only percent moisture was significantly higher in mineral soils from Imnavait vs. Toolik. Nonetheless, higher moisture recorded at Imnavait is possibly linked to higher precipitation activity that was observed at this site during sampling.

There were no differences in the concentration of C, N and S between both sites for both organic and mineral horizons (**Figure 2(a)**, **Figure 2(b)** and **Table 1**). There were also no significant differences between sites for the concentration of other elements, except for Ca which was significantly higher in organic horizons of the older Imnavait site (M = 5.56, SD = 4.21) compared to the younger Toolik site (M = 2.74, SD = 1.97), $t(21) = 2.09$, $p < 0.05$ (**Figure 3(a)**) and Na which was significantly higher in mineral soils of Toolik (M = 0.27, SD = 0.07)

Table 1. Physical and chemical properties of mineral and organic soils from the *Sphagno-Eriophoretum vaginati* plant communities in Toolik Lake and Imnavait Creek grids. Between-site comparisons were assessed with Independent Samples T-Test unless otherwise noted. Sample size within parentheses unless otherwise indicated with superscripts. SD = Standard deviation. Statistical significance achieved at $p < 0.05$.

Variables	Mineral					Organic				
	Imnavait (n = 12)		Toolik (n = 10)		p-values	Imnavait (n = 12)		Toolik (n = 12)		p-values
	Mean	SD	Mean	SD		Mean	SD	Mean	SD	
Total elements										
C (%)	3.41[a]	2.13	4.01[c]	1.84	ns	34.85	7.36	29.15	10.74	ns
N (%)	0.14[a]	0.12	0.15[c]	0.10	ns	1.55	0.34	1.24	0.47	ns
S (%)	0.02[a]	0.01	0.02[c]	0.01	ns	0.19	0.05	0.17	0.08	ns
Al (mg/g)	12.18[a]	3.55	11.88	2.75	ns	8.57	4.78	8.70	3.09	ns
P (mg/g)	0.45	0.19	0.45[c]	0.18	ns	1.51	0.44	1.37	0.67	ns
Na (mg/g)	0.17[b]	0.10	0.27	0.07	p < 0.05	1.49	0.87	1.26	0.55	ns
Mn (mg/g)	0.30[a]	0.20	0.26	0.20	ns	6.70	7.80	4.81[a]	7.48	ns
Ca (mg/g)	0.79[a]	0.30	0.86	0.37	ns	5.56[a]	4.21	2.74	1.97	p < 0.05
Fe (mg/g)	27.20	7.82	27.51	8.26	ns	25.36[a]	12.64	22.32	12.27	ns
Mg (mg/g)	2.48[a]	0.84	2.14	0.28	ns	1.38[a]	0.33	1.14	0.53	ns
K (mg/g)	0.73[a]	0.27	0.79	0.20	ns	0.84[a]	0.22	0.78	0.26	ns
Organic horizon thickness (cm; n = 3)	-	-	-	-	-	13.04	1.22	10.63[c]	1.88	ns
Bulk density (g/cc)	1.25	0.14	1.46	0.12	ns	-	-	-	-	-
% Moisture	30.34	19.02	12.65	15.84	p < 0.05*	-	-	-	-	-
LOI (%)	10.52	6.18	9.88[c]	3.48	ns	68.64	12.95	58.23	19.74	ns
pH (H_2O)	4.53	0.12	4.41	0.19	ns	4.80	0.72	4.34	0.53	ns

[a]n = 11; [b]n = 10; [c]n = 9; *Mann-Whitney *U*-test.

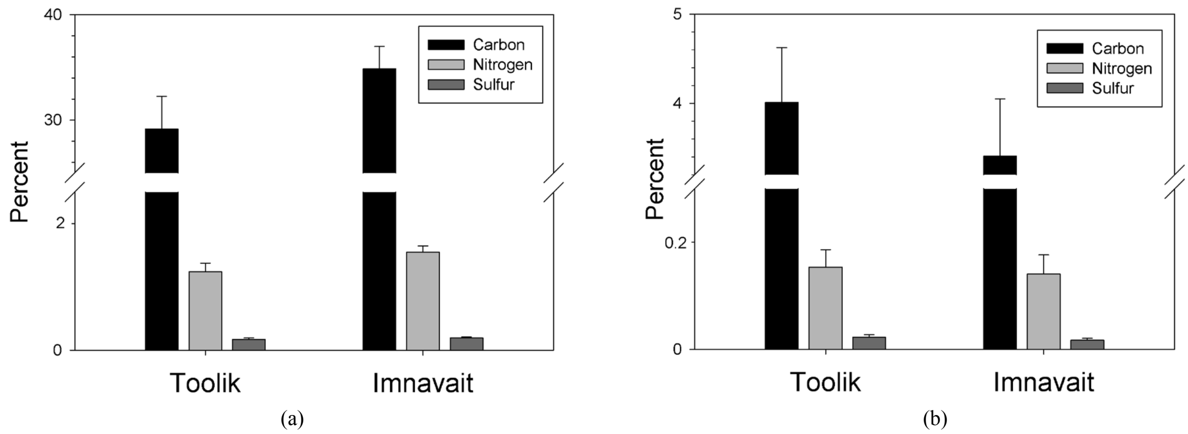
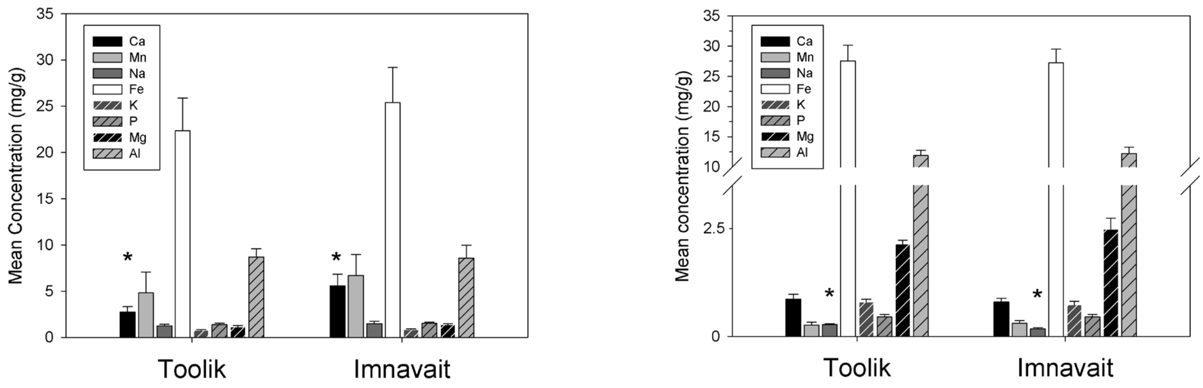


Figure 2. Differences between Toolik Lake and Imnavait Creek grids in terms of mean total concentration (%) of C, N and S in (a) organic horizons and (b) mineral horizons.

compared to Imnavait (M = 0.17, SD = 0.10), $t\,(20) = 2.75$, $p < 0.05$ (**Figure 3(b)** and **Table 1**).

We found significant between-site differences in the abundances of several growth forms (**Table 2** and **Figure 4**). The abundance of shrubs was significantly higher at Toolik (M = 32.25, SD = 5.36) vs. Imnavait (M = 26.51, SD = 7.04); $t\,(22) = -2.25$, $p < 0.05$. In contrast, forbs were significantly more abundant at Imnavait (M = 5.99, SD = 5.52) vs. Toolik (M = 1.60, SD = 1.69); $t\,(22) = 2.64$, $p < 0.05$. Similarly, non-*Sphagnum* mosses at Imnavait (M = 27.42, SD = 4.92) were more abundant than at Toolik (M = 10.60, SD = 5.31); $t\,(22) = 8.05$, $p < 0.00$,



(a) (b)

Figure 3. Differences between Toolik Lake and Imnavait Creek grids in terms of mean total concentration (mg/g) of Ca, Mn, Na, Fe, K, P, Mg and Al in (a) organic horizons and (b) mineral horizons. Asterisks indicate significant differences ($p < 0.05$).

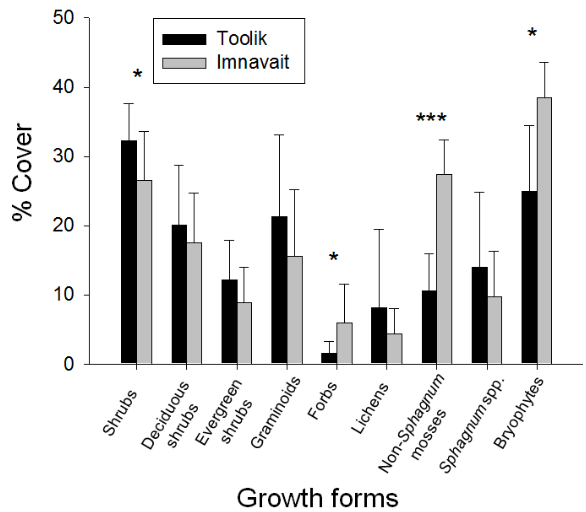


Figure 4. Differences between Toolik Lake and Imnavait Creek grids in terms of mean abundance of growth forms (% Cover). Abundance data correspond to years 2007-2008. Asterisks indicate significant differences ($p < 0.05$).

Table 2. Abundances (% Cover) of main growth forms in 24 one meter squared plots with vegetation classified as *Sphagno-Eriophore- tum vaginati* plant community. Abundance data correspond to years 2007-2008. Between-site comparisons were assessed with Independent Samples T-Test. Sample size within parentheses unless otherwise indicated with superscripts. SD = Standard deviation. Statistical significance achieved at $p < 0.05$.

Type	Growth form	Toolik		Imnavait		p-values
		Mean (n = 12)	SD	Mean (n = 12)	SD	
Vascular	Shrubs	32.25	5.36	26.51	7.04	<0.05
	Deciduous shrubs	20.12	8.61	17.56	7.21	ns
	Evergreen shrubs	12.13	5.77	8.94	5.06	ns
	Graminoids	21.31	11.77	15.63	9.52	ns
	Forbs	1.60	1.69	5.99	5.52	<0.05
Non-vascular	Lichens	8.14	11.39	4.44	3.59	ns
	Non-*Sphagnum* mosses	10.60	5.31	27.42	4.92	<0.001
	Sphagnum spp.	13.96	10.93	9.68	6.65	ns
	Bryophytes	24.99	9.45	38.50	5.07	<0.05

and bryophytes more abundant at Imnavait (M = 38.50, SD = 5.07) than at Toolik (M = 24.99, SD = 9.45); t (22) = 4.36, $p < 0.05$.

Because Ca in organic soils and Na in mineral soils were the only elements exhibiting a statistically significant difference between sites, correlation analysis was focused on evaluating the relationship of these two elements with the abundance those growth forms found to have contrasting abundances between sites. In this sense, we found the abundance of non-*Sphagnum* mosses to be positively correlated with the total concentration of Ca in organic soils ($r = 0.48$, $n = 24$, $p < 0.05$). We also found that the total concentration of Na in mineral soils was negatively correlated with the abundances of forbs ($r = -0.486$, $n = 22$, $p < 0.05$), non-*Sphagnum* mosses ($r = -0.470$, $n = 22$, $p < 0.05$) and bryophytes ($r = -578$, $n = 22$, $p < 0.01$).

4. Discussion

Determinations of several physico-chemical parameters, including total C, N and S and other elemental concentrations of soils occurring in *Sphagno-Eriophoretum vaginati* plant communities at Toolik Lake and Imnavait Creek grids, indicate that for most elements evaluated, and in spite of a 70 k year difference in landscape age, there are no significant differences between sites. In general, main patterns observed for many of the variables measured are not distant to what has been reported previously for this area [3] [5]-[7] [9] [23] [42]-[45]. Our observations confirm that both sites have similar soil acidity [3] [5] [43] and mineral soils bulk density values comparable to those reported in other studies [7] [42]. As expected, and in accordance with most of these studies, total C for both Toolik and Imnavait was 7 to 10 times larger in organic soils vs. mineral soils. Total N exhibited a similar pattern. There were no significant differences between Toolik and Imnavait in terms of the total concentration of both C and N in organic and mineral soils, hence confirming observations made by Whittinghill and Hobbie [5]. No between-site differences were found in terms of the amount of S in both organic and mineral soils, still, the concentration of this element in these soils is almost negligible.

Although some of our findings serve mostly as a confirmation of previously reported similarities in elemental concentrations between these two areas [5] [6] [24], others represent intriguing aspects of the soil chemistry of this region that are worth highlighting. For instance, similar to findings of Keller *et al*. [23], Fe had the largest concentration in both mineral and organic soils at both sites. Studies have demonstrated that Fe (as well as Al, the second highest) tends to accumulate in soils from tundra and other ecosystems [46]-[49]. Moreover, Fe is more soluble in acidic soils; therefore its availability tends to increase under these conditions [46] [50]. High concentrations of Al and Fe have been linked to substantial increases in the sorption capacity of organic soils. This situation may lead to reductions in P availability, causing plants to become P limited [47] [51] [52]. These observations suggest that due to its effect on P availability, changes in the concentration of Fe or Al in these soils could affect significantly the vegetation in this region. This is particularly relevant for wet sedge and some MAT areas where P availability is known to limit primary productivity [53] [54].

We consider atypical the higher concentration of Ca in organic soils from Imnavait. Organic soils from both sites have similar pH. Because soil pH is known to affect the availability of Ca [12] [46], contrasting Ca concentrations are expected to be more commonly be found between soils with significantly different acidity, as is the case for MAT vs. MNT tundra [3] [7], and less frequently between areas with the same type of vegetation (MAT), such as Toolik and Imnavait. Accordingly, Whittinghill and Hobbie [5] found that exchangeable Ca concentrations were not significantly different between soils derived from the landscape ages represented by these sites. It is likely that higher total Ca in organic soils from Imnavait is linked to differences in landscape age between these sites. This observation would agree with findings from Keller *et al*. [23] which found that organic and mineral horizons from Sagavanirktok glacial surfaces had higher Ca concentration than soils from Itkillik I surfaces (not statistically corroborated). Perhaps other processes that were not evaluated in this study, such as those related to biological and/or chemical immobilization, are variable in soils from these two landscape ages, and may account for some of these differences. However, as evidenced in this study, it is likely that the total Ca in organic soils is being influenced by between-site differences in vegetation composition, specifically, the abundance of non-*Sphagnum* mosses. In general, bryophytes tend to be in direct contact with underlying organic soils in these ecosystems and usually exert an influence on a number of soil processes [55]. Compared to Toolik, Imnavait had a significantly higher abundance of non-*Sphagnum* mosses and significantly higher concentration of Ca in organic soils, which agrees with the positive correlation found between these two parameters. Considering that both sites are influenced by similar climate and that plots are located in terrain of similar relief, dominated by MAT tundra; it seems plausible that besides landscape age, subtle variation in the abundance of non-*Sphagnum* mosses is contributing towards the differentiation of *Sphagno-Eriophoretum vaginati* plant community areas in terms of total Ca in organic soils. The work of van der Welle [56] partly support this hypothesis and revealed a significant positive correlation between non-*Sphagnum* moss cover and soil Ca content in several tussock tundra sites. Nevertheless, it remains to be tested if the effect of contrasting abundances on organic soil Ca concentration occurs via specific plant traits, like between-species variation in tissue concentration of this element, or via other plant community factors, like differences in species richness of non-*Sphagnum* mosses.

In terms of its ecosystemic effects, a higher total Ca in Imnavait soils imply that there may be less available substrate for microbial activity at that site. This is expected to diminish microbial respiration due to stabilization of organic matter by cation bridging with Ca ions [6]. However, rates of microbial activity are higher on older, more acidic landscapes [5] [8] [9] which may partly compensate for the effects of higher Ca on microbial respiration in these soils.

A significantly higher concentration of Na in minerals soils of Toolik was an unexpected finding considering that total Na have been found to be higher in mineral soils from Sagavarnirktok vs. Itkillik I glacial surfaces [23] (not statistically corroborated). However, because the dynamics of Na in mineral soils has not been characterized thoroughly in this region, we believe that between-site differences in the chemical composition of the parent material, perhaps the presence of Na-rich bedrock in sampled plots at Toolik, would be the most logical explanation for these observations. Although less likely, part of this dissimilarity might also be tied to differences in vegetation composition. Contrary to patterns observed between the abundance of non-*Sphagnum* mosses and total Ca in organic soils, significantly lower abundances of forbs, non-*Sphagnum* mosses and bryophytes in Toolik are responsible for the observed negative correlation between these growth forms and total Na in mineral soils. Assuming that forbs and bryophytes have low Na tissue concentration compared to other growth forms, it could be argued that in areas where they flourish (like Toolik), soils could reflect low Na concentration. However, in first instance, this assumption is undermined by the general scarcity of information regarding the concentration of Na in tissues of tundra plant species. Additionally, the effect of these growth forms on deeper mineral soil biogeochemical processes is expected to be negligible considering that their vertical distribution is limited to upper soil layers. Lastly, higher Na in mineral soils at Toolik might also be linked to other factors not evaluated in this study, for example, between-site variation in rates of chemical weathering of parent materials.

Soil Na has not been properly characterized in studies of soil chemistry in tundra ecosystems, except for few notable studies [3] [7] [23]. As an element, Na is present in small quantities in soils and is not an essential element for plant growth. Nevertheless, Na concentration in soils or water has been shown to promote maximal biomass yield and perform other important functional roles in plants [57]. High levels of Na could be detrimental to soil structure, soil permeability and plant growth, and in spite of its overall low levels, projected climate warming in tundra ecosystems may result in reduced soil moisture conditions [58] which may in turn affect Na dynamics in soils. Under this scenario, it becomes important to increase efforts towards a better understanding of Na dynamics in tundra soils as they are likely to change under a warming climate.

Based on our results and those of others [5] [6] [23] [42]-[44], it is evident that landscape age differences between our sites do not result in a robust chemical imprint that might help discriminate these sites in terms of their soil physico-chemical properties. While we were able to detect significant differences in two (Ca in organic soils and Na in mineral soils) of the 11 chemical parameters evaluated, these differences are subtle compared to the conspicuous differences in concentration of other elements, like Ca, between MAT and MNT [5] [7]. It has been recognized that variation in elemental concentrations in tundra soils of the Toolik-Imnavait region are tied to larger landscape-scale factors like changes in vegetation physiognomy and pH which show considerable variation at different spatial and temporal scales in this region [1] [3] [5] [7] [9] [18] [23]. Additionally, other processes like cryoturbation and frost boil formation could cause the continuous movement and mixing of soil material [3] [15] [59], thus preventing long term soil stability and causing continuous homogenization of nutrients throughout soil horizons [42] [60]. Freeze-thaw processes like cryoturbation are more frequent on MNT [3] [61], though discontinuous surface organic horizons resulting from cryoturbation are common throughout the southern foothills [62]. Therefore, we suggest that while possibly occurring in a lower frequency and magnitude, these processes are at least partly responsible for the little differentiation that organic and mineral soils of these two sites reflect in terms of most of the elemental concentrations and other physico-chemical properties evaluated in this study.

Most importantly, after detecting the differences between Toolik and Imnavait in terms of the concentration of Ca in organic soils and Na in mineral soils, we were able to discern that abundance patterns of several growth forms at these sites were concordant with correlations found between these growth forms and the concentration of these elements in organic and mineral soils respectively. These observations are relevant as they demonstrate that minimal differences in soil chemistry, possibly linked to contrasting landscape ages between these two sites, are influencing aboveground patterns in vegetation composition. In turn, by directly influencing the biophysical environment through variation in moisture or temperature regimes, through differences in root mycorrhizal processes [33], or by indirectly influencing the rates of litter input and decomposability [8], this variation in vegetation composition could be reciprocally influencing soil chemistry, therefore perpetuating the differentiation between these two sites in terms of these two elements.

5. Conclusion

Investigations analyzing the relationship between soil chemistry and vegetation in tundra ecosystems in this region have shown that conspicuous soil chemical differences (e.g. pH and Ca concentration) between some different aged landscapes (e.g. Itkillik II vs. Itkillik I) are accompanied by notable differences in vegetation types (MAT vs. MNT) [3] [7] [9]. In this respect, our study indicates that soil evolution may be governed by vegetation cover as much as by time. Landscapes of different age (Itkillik I vs. Sagavariktok) and very similar vegetation type (*i.e.*, MAT) are not distinguishable in terms of most of their soil physical and chemical properties. However, total concentration of elements like Ca and Na may vary between them. This variation, although likely linked to differences in the chemical composition of the geologic substrates underlying these soils, appears to reflect some level of agreement with abundance patterns of specific growth forms. These observations are relevant as they testify in favor of the reciprocal relationship between soil chemistry and vegetation composition in moist acidic tundra landscapes in Arctic Alaska.

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Fluoride Uptake and Net Primary Productivity of Selected Crops

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Abstract

Crop field soil collected from Sambalpur University campus of Odisha and treated with various fluoride concentrations was used to raise selected local crops. Background concentration of total and leachable fluoride content in soil was 95.19 and 8.89 ppm respectively. At the time of harvest of the crops, the total fluoride content was found to decrease and leachable fluoride content was found to increase both in control and experimental sets. This might be due to the addition of fluoride to soil in the experimental set up as well as availability of background fluoride content in soil and the irrigated water (*i.e.* 0.5 ppm). The fluoride accumulation in plant tissue increased with increase in the fluoride content in soil. Net Primary Productivity (NPP) of fluoride treated plants decreased in Brinjal by 6.64% - 56.72%, Tomato by 14.46% - 62.24% and Mung by 10.27% - 53.61%, all in 20 - 100 ppm fluoride range. However, NPP of Mustard, Ladies finger and Chili decreased by 15.58% - 61.21%, 12.28% - 52.78% and 40.8% - 90.65% in 10 - 50 ppm fluoride treated sets respectively in 10 - 50 ppm fluoride range. Maize NPP decreased by 12.17% - 61.20% in 20 - 100 ppm fluoride range as Rice NPP decreased by 6.64% - 56.72% in 20 - 100 ppm fluoride range. Pod formation was inhibited at 100 ppm fluoride amended soil in case of Mung, and 50 ppm in Ladies finger, 40 - 100 ppm in Maize and 30 - 50 ppm fluoride amended soil in case of Chilli. Thus, Maize and Chilli are more sensitive to fluoride contamination than other crops. In all the crops NPP decreased with increase in fluoride content in soil with significant decrease in highest concentration of fluoride.

Keywords

Fluoride, Uptake, Crops, Net Primary Productivity

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1. Introduction

Fluorine (F) is an element of the halogen family and Fluoride (F^-) is the anion the reduced form of fluorine. Both organic and inorganic fluorine compounds are sometimes called fluorides. Fluoride, like other halides, is a monovalent ion (−1 charge). Its compounds often have properties that are distinctly relative to other halides. Structurally, and to some extent chemically, the fluoride ion resembles the hydroxides ion. Fluoride-containing compounds range from potent toxins such as Sarin to life-saving pharmaceuticals such as Efavirenz and from refractory materials such as calcium fluoride to the highly reactive sulfur tetrafluoride. The range of fluorine-containing compounds is considerable as fluorine is capable of forming compounds with all the elements except for helium and neon [1]. Fluorine in the environment is therefore found as fluorides which together represent about 0.06 - 0.09 percent of the earth's crust. The average crustal abundance is 300 $mg \cdot kg^{-1}$ [2]. Fluorides are found at significant levels in a wide variety of minerals, including fluorspar, rock phosphate, cryolite, apatite, mica, hornblende and others [3]. Fluorite (CaF_2) is a common fluoride mineral of low solubility occurring in both igneous and sedimentary rocks. Fluoride is commonly associated with volcanic activity and fumarolic gases. Thermal waters, especially those of high pH, are also rich in fluoride [4]. Minerals of commercial importance include cryolite and rock phosphates. The fluoride salt cryolite is used for the production of aluminium [3] and as a pesticide [5]. Rock phosphates are converted into phosphate fertilizers by the removal up to 4.2 percent fluoride. The purified fluoride (as fluorosilicates) is added to drinking-water in some countries in order to protect against dental caries [6] and [7]. It forms inorganic and organic compounds called fluorides. Living organisms are mainly exposed to inorganic fluorides through food and water. Based on quantities released and concentrations presented naturally in the environment as well as the effects on living organisms, the important inorganic fluorides are hydrogen fluoride (HF), calcium fluoride (CaF_2), sodium fluoride (NaF), Sulphur hexafluoride (SF_6) and Silico fluorides. Fluoride in the form of HF or SiF_4 is one of the most important and damaging air pollutants affecting forests, crops and natural vegetation [8]. Fluoride occurs naturally in plants, but its presence has attracted attention primarily in certain areas where concentrations are elevated above normal by accumulation from the atmosphere.

Human activities releasing fluorides into the environment are mainly the mining and processing of phosphate rock and its use as agricultural fertilizer, as well as the manufacture of aluminums. Other fluoride sources include the combustion of coal (containing fluoride impurities) and other manufacturing processes (steel, copper, nickel, glass, brick, ceramic, glues and adhesives). In addition, the use of fluoride-containing pesticides in agriculture and fluoride in drinking water supplies also contribute to the release of fluorides into the environment. However, the greatest concentrations are found near anthropogenic point sources. In air, because of its extensive industrial use, hydrogen fluoride is probably the greatest single atmospheric fluoride contaminant [9]. Fluorides can be present as gases or particulates. They can be transported by wind over large distances before depositing on the earth's surface or dissolving in water. In general, fluoride compounds do not remain in the troposphere for long periods, nor do they move up to the stratosphere. In areas where fluoride-containing coal is burned or phosphate fertilizers are produced or used, the fluoride concentration in air is elevated leading to increased exposure by inhalation and absorption routes. High levels of atmospheric fluoride occur in areas of Morocco and China [10] and [11]. In some provinces of China, fluoride concentrations in indoor air ranging from 16 to 46 $\mu g/m^3$ owing to indoor combustion of high-fluoride coal for cooking, or drying and curing food [12]. Indeed, more than 10 million people in China are reported to suffer from fluorosis, related in part to the burning of high fluoride coal [13].

Fluoride is a component of most types of soil, with total concentrations ranging from 20 to 1000 μg/g in areas without natural phosphate or fluoride deposits and up to several thousand mg/g in mineral soils with deposits of fluoride [14]. Airborne gaseous and particulate fluorides tend to accumulate within the surface layer of soils, but they may be displaced throughout the root zone, even in calcareous soils [15]. Calcium fluoride is the most common in alkaline soils, and fluoroaluminate complexes are the most common in acidic soils. Thus, exposure to hydrofluoric acid will occur at a hazardous waste site only if someone comes in to contact with material leaking from a storage container or contaminated air before it is dispersed. Once in a stable form, fluoride persists in the environment for a relatively long time unless transforming to another compound or decomposed by radiation. The clay and organic carbon content as well as the pH of soil is primarily responsible for the origin and/or retention of fluoride in soils. It has also been reported that in saline soils the bioavailability of fluoride to plants is related to the water-soluble component of the fluoride present [14]. In living organisms, the quantity of fluoride accumulation depends on the route of exposure, on how well the particular fluorides are absorbed by the body and on how quickly they are taken up and excreted. Soluble fluorides are bioaccumulated by some aquatic and terrestrial biota. However, information concerning the biomagnification of fluoride in aquatic or terrestrial food-chains is scanty [16] and [17]. Inorganic fluorides tend to accumulate preferentially in the skeletal and dental hard tissues of vertebrates, exoskeletons of invertebrates and cell walls of plants [14] [16] [18]-[20]. Bio-concentration factors greater than 10 (expressed on a wet weight basis) were reported in both aquatic plants and animals following exposure to solutions up to 50 mg/l of fluoride [21]. Moeri [22] has reported effect of fluoride emission on enzyme activity in metabolism of plants.

The undivided Sambalpur District of Odisha is an industrial belt where two aluminium industries—Vedanta Aluminum Company at Jharsuguda and Hindalco Industries Limited at Hirakud Town have been established. The former started operating from 1965 while Vedanta, a major industry, is operating since last 8 years. Both the industries have their coal-based captive thermal power plants. The local people in Hirakud complain every year of crop damage during growing season due to emissions from aluminium and power industries in Hirakud. There are research reports on fluoride accumulation in soil, plants and animals to the extent of 40 - 80 ppm in Hirakud, which may be because of emissions from industrial activities [23] [24]. Effects of such accumulations on various environmental segments in Hirakud have also been studied [25] [26]. A survey of field soil around Vedanta Aluminium Limited shows a total and leachable fluoride content ranging from 94.01 - 467.7 mg/kg and 10.60 - 104.86 mg/kg respectively [27]. Therefore, the present study was undertaken to assess the fluoride uptake by selected crops and its effect on NPP.

2. Materials and Methods

Sodium fluoride (NaF) was used to prepare fluoride (F) solutions in various concentrations, *i.e*. 20, 40, 60, 80, and 100 ppm with distilled water for treatment. Tap water was used as control. Culture experiments were set up to monitor the growth of the plants in various concentrations of F^- amended soil. Plant seeds were collected from a Government authorized seed store located at Goshala, Sambalpur and the seedlings were collected from OUAT Chipilima, Sambalpur for pot culture. For pot culture experiment, 21 days old healthy seedlings were collected from OUAT, Chiplima and transplanted in to the pots containing F^- treated crop field soil. After harvest total yield (NPP) was calculated. Following local crops were assessed:

Winter crops—Brinjal (*Solanum melongena* L.), Tomato (*Lycopersicon esculentum*), Mustard (*Brassica compestris*) and Mung (*Vigna radiata*);

Summer crops—Ladies finger (*Abelmoschus esculentus*) and Maize (*Zea mays* L.);

Rainy crops—Paddy (*Oryza sativa*) and Chilli (*Capsicum annuum*).

NPP is usually estimated by harvest technique, in which above ground plant biomass (AGP) is harvested from all the pots and below ground Plant Biomass (BGP) were washed from soil cores. The short term harvest method [28] was employed for biomass estimation at 15 days intervals. The plant parts were oven dried at 80˚C for 24 hours. After harvest total yield was calculated. The F^- content in soil and plants was estimated by Ion Selective Analyzer.

3. Results

3.1. Brinjal

The total and leachable F^- content in soil at the beginning of the experiment was found to be 95.19 and 8.89 ppm respectively. The F^- content in plant sample after harvest was found to be 1.45, 1.89, 2.12, 2.85, 3.24 and 3.83 mg/kg in 0, 20, 40, 60, 80 and 100 ppm of F treated soils (**Table 1**). NPP on the day of harvest (*i.e.* 75th day) was 117.4, 109.6, 89.6, 69.1, 60.3 and 50.8 g dry wt/plant in 0, 20, 40, 60, 80 and 100 ppm F^- amended soils respectively (**Table 2**). Compared to control, NPP was decreased by 6.64% and 56.72% in 20 and 100 ppm of F^- concentrations respectively. The yield (pod weight) decreased by 78% at 100 ppm F^- application compared to control.

3.2. Tomato

The total and leachable $\mathbf{F}^-$ content in soil at the beginning was 95.19 and 8.89 ppm respectively. At the time of harvest *i.e.* on 75th day, the total F^- content showed decreasing trend whereas leachable F^- showed an increasing trend in both control and treated soil (**Table 3**). The F^- content in plant sample after harvest was found to be

Table 1. Fluoride content in soil and Brinjal plant.

Conc.	At Start in Soil (mg/Kg)		At Harvest (mg/Kg)		
	Total Fluoride	Leachable Fluoride	Total Fluoride in Soil	Leachable Fluoride in Soil	Total F^- in Plant Sample
Control	95.19	8.89	86.40	18.56	1.45
20 ppm	95.19 + 20	8.89	92.40	21.58	1.89
40 ppm	95.19 + 40	8.89	110.20	25.63	2.12
60 ppm	95.19 + 60	8.89	124.60	29.76	2.85
80 ppm	95.19 + 80	8.89	138.50	35.80	3.24
100 ppm	95.19 + 100	8.89	158.40	38.14	3.83

Table 2. NPP (g dry wt/plant) in Brinjal in fluoride treated soil.

Days	Concentration	BGP Root	AGP			NPP (BGP + AGP)	% Decrease in NPP over control
			Leaf	Stem	Pod		
	60 Days Control	7.1	16.6	32.2	61.5	117.4	00
	20 ppm	6.8	15.8	29.7	57.3	109.6	6.64
	40 ppm	6.2	15.1	27.2	41.1	89.6	23.67
	60 ppm	5.9	13.7	24.2	25.3	69.1	41.14
	80 ppm	5.1	12.1	23.5	19.6	60.3	48.63
	100 ppm	4.2	11.5	21.6	13.5	50.8	56.72

Table 3. Fluoride content in soils of Tomato crop.

Soil →	At the Start (mg/Kg)		During Harvest (mg/Kg)		
Conc.	Total Fluoride	Leachable Fluoride	Total Fluoride in Soil	Leachable Fluoride in Soil	Total F^- in Plant Sample
Control	95.19	8.89	86.40	22.87	1.05
20 ppm	95.19 + 20	8.89	92.40	23.70	1.66
40 ppm	95.19 + 40	8.89	110.20	27.52	2.08
60 ppm	95.19 + 60	8.89	124.60	31.47	2.68
80 ppm	95.19 + 80	8.89	138.50	33.30	3.17
100 ppm	95.19 + 100	8.89	158.40	37.28	3.49

1.05, 1.66, 2.08, 2.68, 3.17 and 3.49 mg/kg in 0, 20, 40, 60, 80 and 100 ppm of F^- amended soils respectively.

NPP on the day of harvest (*i.e.* 60th day) was 116.0, 99.2, 69.3, 65.2, 54.4 and 43.8 g dry wt/plant in 0, 20, 40, 60, 80 and 100 ppm F^- amended soils respectively (**Table 4**). NPP decreased by 14.48% - 62.24% in 20 - 100 ppm F^- amended soils compared to control set. The pod weight decreased by 83% in 1000 ppm F^- treated soils over control.

3.3. Mustard

The total and leachable F^- content in soil in the beginning was 95.19 and 8.89 ppm respectively. At the time of harvest *i.e.* on 60th day, the total F^- content decreased whereas leachable F^- increased both in control and treated soils (**Table 5**). The F^- content in plant sample on harvest was found to be 1.13, 1.46, 1.76, 1.95, 2.18 and 2.37 mg/kg in control, 10, 20, 30, 40 and 50 ppm of F^- treated soils respectively.

On 60th day, the highest NPP (0.263 g dry wt/plant) was recorded in case of control set and least (0.102 g dry wt/plant) in 50 ppm F^- treated soil. The percentage decrease in NPP on 60th day was found to be 15.58, 27.37, 49.04, 58.93 and 61.21% in 10, 20, 30, 40 and 50 ppm F^- treated soils respectively (**Table 6**) whereas Mustard yield got reduced by 62% in 50 ppm F^- treated soil.

Table 4. NPP (g dry wt/plant) of Tomato in fluoride treated soils.

Days	Concentration	BGP Root	AGP			NPP (BGP + AGP)	% Decrease in NPP over Control
			Leaf	Stem	Pod		
60 Days	Control	6.3	20.0	31.3	58.4	116.0	00
	20 ppm	5.0	18.6	28.0	47.6	99.2	14.48
	40 ppm	4.8	16.4	26.2	39.9	69.3	40.25
	60 ppm	4.3	14.3	24.1	22.5	65.2	43.79
	80 ppm	3.1	13.7	22.8	14.8	54.4	53.10
	100 ppm	2.2	11.5	20.4	9.7	43.8	62.24

Table 5. Fluoride content in soils and Mustard plant.

Soil →	At the Start (mg/Kg)		During Harvest (mg/Kg)		
Conc.	Total Fluoride	Leachable Fluoride	Total Fluoride in Soil	Leachable Fluoride in Soil	Total F^- in Plant Sample
Control	95.19	8.89	81.38	16.37	1.13
10 ppm	95.19 + 10	8.89	87.70	18.95	1.46
20 ppm	95.19 + 20	8.89	93.37	22.61	1.76
30 ppm	95.19 + 30	8.89	99.61	26.57	1.95
40 ppm	95.19 + 40	8.89	106.72	30.59	2.18
50 ppm	95.19 + 50	8.89	112.58	32.18	2.37

Table 6. NPP (g dry wt/plant) of Mustard in fluoride treated soils.

Days	Concentration	BGP Root	AGP			NPP (BGP + AGP)	% Decrease in NPP over Control
			Leaf	Stem	Pod		
60 Days	Control	0.034	0.046	0.091	0.092	0.263	0
	10 ppm	0.033	0.043	0.07	0.076	0.222	15.58
	20 ppm	0.03	0.035	0.063	0.063	0.191	27.37
	30 ppm	0.024	0.031	0.054	0.025	0.134	49.04
	40 ppm	0.022	0.026	0.043	0.017	0.108	58.93
	50 ppm	0.021	0.021	0.036	0.014	0.102	61.21

3.4. Mung

The total and leachable F^- content in soil in the beginning was 95.19 and 8.89 ppm respectively. At the time of harvest *i.e.* on 60th day, the total F^- content decreased whereas leachable F^- increased both in control and treated soils (**Table 7**). The F^- content in plant sample after harvest was found to be 1.23, 1.72, 2.18, 2.76, 3.35 and 3.63 mg/kg in control, 10, 20, 30, 40 and 50 ppm of F^- treated soils respectively.

NPP on the harvest day was 36, 32.3, 28.8, 26.9, 25.0 & 16.7 g of dry wt/plant in control, 20, 40, 60, 80 and 100 ppm F^- treated soils respectively (**Table 8**). In comparison with control, NPP decreased by 10.27%, 20%, 25.27%, 30.55% and 53.61% in 20, 40, 60, 80 and 100 ppm F^- amended sets respectively. Mung yield decreased by 14% at 80 ppm F^- treatment and no pod formation took place at 100 ppm F^- concentration.

3.5. Ladies Finger

On harvest day *i.e.* 60th day, the total F^- content decreased and leachable F^- increased both in control and treated soils (**Table 9**). The total and leachable F^- content in soil in the beginning of the experiment was 95.19 and 8.89 ppm respectively. The F^- content in ladies finger plants during harvest was found to be 1.44, 1.55, 1.86, 2.03, 2.35 and 2.72 mg/kg in control, 10, 20, 30, 40 and 50 ppm of F^- treated soils respectively.

On the day of harvest (*i.e.* 60th day), NPP was found to be 87.9, 77.1, 69.9, 64.6, 60.8 and 41.5 g of dry

Table 7. Fluoride content in soils and Mung plants.

Soil → Conc.	At the Start (mg/Kg)		During Harvest (mg/Kg)		
	Total Fluoride	Leachable Fluoride	Total Fluoride in Soil	Leachable Fluoride in Soil	Total F^- in Plant Sample
Control	95.19	8.89	86.40	22.93	1.23
20 ppm	95.19 + 20	8.89	92.40	24.52	1.72
40 ppm	95.19 + 40	8.89	110.20	29.25	2.18
60 ppm	95.19 + 60	8.89	124.60	33.07	2.76
80 ppm	95.19 + 80	8.89	138.50	36.76	3.35
100 ppm	95.19 + 100	8.89	158.40	42.04	3.63

Table 8. NPP (g dry wt/plant) of Mung in fluoride treated soils.

Days	Concentration	BGP Root	AGP			NPP (BGP + AGP)	% Decrease in NPP over control
			Leaf	Stem	Pod		
60 Days	Control	2.5	8.6	14.7	10.2	36.0	00
	20 ppm	2.2	7.4	13.6	10.2	32.3	10.27
	40 ppm	1.9	7.0	10.0	9.9	28.8	20
	60 ppm	1.6	6.4	10.0	8.9	26.9	25.27
	80 ppm	1.1	6.0	10.1	8.8	25.0	30.55
	100 ppm	1.0	5.8	9.9	---	16.7	53.61

Table 9. Fluoride content in soils and ladies finger plants.

Soil → Conc.	At the Start (mg/Kg)		During Harvest (mg/Kg)		
	Total Fluoride	Leachable Fluoride	Total Fluoride in Soil	Leachable Fluoride in Soil	Total F^- in Plant Sample
Control	95.19	8.89	81.38	17.89	1.44
10 ppm	95.19 + 10	8.89	87.70	19.24	1.55
20 ppm	95.19 + 20	8.89	93.37	23.56	1.86
30 ppm	95.19 + 30	8.89	99.61	28.67	2.03
40 ppm	95.19 + 40	8.89	106.72	32.46	2.35
50 ppm	95.19 + 50	8.89	112.58	35.04	2.72

wt/plant in control, 10, 20, 30, 40 and 50 ppm F^- treated soils respectively (**Table 10**). NPP decreased by 12.28% - 52.78% in 10 - 50 ppm F^- treated soils. There was no pod found at 50 ppm F^- treatment.

3.6. Maize

On the harvest day (75th day), the total F^- content decreased and leachable F^- increased both in control and treated soils (**Table 11**). The total and leachable F^- content in soils in the beginning of the experiment was 95.19 and 8.89 ppm respectively. In maize samples F^- was found to be 1.98, 2.46, 2.65, 3.22, 3.54 and 4.02 mg/kg in control, 20, 40, 60, 80 and 100 ppm of F^- treated soils respectively on the harvest day.

NPP on 75th day was 11.42 g of dry wt/plant in control and 4.43 g in 100 ppm F^- amended soils. The decrease in NPP was found to be 12.17%, 36.66%, 40.45%, 52.62% and 61.20% in 20, 40, 60, 80 and 100 ppm F^- treated sets respectively (**Table 12**). No pod formation was found in sets beyond 20 ppm treatment.

3.7. Paddy

On the harvest day, the total and leachable F^- content in soil at the start of the experiment was 95.19 and 8.89 ppm respectively. The F^- content in plant sample on harvest was found to be 2.16, 2.63, 2.95, 3.62, 3.84 and 4.37 mg/kg in control, 20, 40, 60, 80 and 100 ppm of F^- treated soils respectively (**Table 13**).

Table 10. NPP (g dry wt/plant) of Ladies finger in fluoride treated soils.

Days	Concentration	BGP Root	AGP			NPP (BGP + AGP)	% Decrease in NPP over Control
			Leaf	Stem	Pod		
60 Days	Control	7.8	10.0	39.3	30.1	87.9	00
	10 ppm	7.7	9.6	23.0	29.8	77.1	12.28
	20 ppm	6.3	9.4	25.1	29.1	69.9	20.47
	30 ppm	5.9	9.2	20.8	28.7	64.6	26.50
	40 ppm	4.3	8.7	20.8	27.0	60.8	30.83
	50 ppm	4.1	8.5	28.9	---	41.5	52.78

Table 11. Fluoride content in soils and Maize plants.

Soil →	At the Start (mg/Kg)		During Harvest (mg/Kg)		
Conc.	Total Fluoride	Leachable Fluoride	Total Fluoride in Soil	Leachable Fluoride in Soil	Total F^- in Plant Sample
Control	95.19	8.89	86.40	20.90	1.98
20 ppm	95.19 + 20	8.89	92.40	22.52	2.46
40 ppm	95.19 + 40	8.89	110.20	26.85	2.65
60 ppm	95.19 + 60	8.89	124.60	29.82	3.22
80 ppm	95.19 + 80	8.89	138.50	35.57	3.54
100 ppm	95.19 + 100	8.89	158.40	41.02	4.02

Table 12. NPP (g dry wt/plant) of Maize in F^- treated soils.

Days	Concentration	BGP Root	AGP			NPP (BGP + AGP)	% Decrease in NPP over Control
			Leaf	Stem	Pod		
75 days	Control	2.63	0.78	5.73	2.28	11.42	0
	20 ppm	2.46	0.74	5.33	1.5	10.03	12.17
	40 ppm	1.95	0.663	4.62	xxx	7.233	36.66
	60 ppm	1.89	0.62	4.29	xxx	6.8	40.45
	80 ppm	1.81	0.6	3.0	xxx	5.41	52.62
	100 ppm	1.4	0.55	2.48	xxx	4.43	61.20

Table 13. Fluoride content in soils and Paddy samples.

Soil →	At the Start (mg/Kg)		During Harvest (mg/Kg)		
Conc.	Total Fluoride	Leachable Fluoride	Total Fluoride in Soil	Leachable Fluoride in Soil	Total F^- in Plant Sample
Control	95.19	8.89	86.40	21.87	2.16
20 ppm	95.19 + 20	8.89	92.40	23.45	2.63
40 ppm	95.19 + 40	8.89	110.20	29.40	2.95
60 ppm	95.19 + 60	8.89	124.60	32.52	3.62
80 ppm	95.19 + 80	8.89	138.50	35.73	3.84
100 ppm	95.19 + 100	8.89	158.40	41.13	4.37

On the day of harvest (*i.e.* 75th day), the NPP of Paddy was 105.9, 97.2, 84.9, 72.1, 65.8 and 56.6 g dry wt/plant in 0, 20, 40, 60, 80 and 100 ppm F^- treated soil (**Table 14**). Compared with control, the NPP decreased by 8.2% - 46.5% and yield by 9.5 - 55.5 in 20 - 100 ppm F^- treated soils respectively.

3.8. Chilli

The total and leachable F⁻ content in soils in the beginning was 95.19 and 8.89 ppm respectively. On the harvest day *i.e.* on 75th day, the total F⁻ content decreased and leachable F⁻ increased both in control and experimental soils (**Table 15**).

F⁻ content in plant samples on harvest was found to be 1.56, 1.76, 1.98, 2.35, 2.58 and 2.94 mg/kg in control, 10, 20, 30, 40 and 50 ppm of fluoride treated soils respectively. NPP on the day of harvest (*i.e.* 75th day) was 7.56, 4.47, 2.77, 1.74, 1.06 and 0.71 g of dry wt/plant in 0, 10, 20, 30, 40 and 50 ppm F⁻ treated soils (**Table 16**). Thus NPP decreased by 40.8% - 90.65% in 20 - 100 ppm in F⁻ treated sets. No pod formation was seen beyond 20 ppm treatment.

Table 17 presents a comparative figure on plant uptake of fluoride and respective NPP and yield in the crops tested. Mung, Ladies finger, Maize and Chilli had no pod yield at the highest concentration of F⁻, indicating that they are very sensitive plants compared to other four crops. **Figure 1** shows a comparative picture of percent reduction of NPP and yield.

Figure 1 presents a comparative figure on the rate of NPP and yield reduction at the highest concentration of F tested. All such crops are sensitive to F with Mung, Ladies finger, Maize and Chilli being far more sensitive than other four.

Table 14. NPP (g dry wt/plant) of Paddy in F⁻ treated soils.

Days	Concentration	BGP Root	AGP			NPP (BGP + AGP)	% Decrease in NPP over Control
			Leaf	Stem	Pod		
	60 Days Control	7.9	21.0	25.3	51.7	105.9	00
	20 ppm	6.8	20.6	23.0	46.8	97.2	6.64
	40 ppm	6.1	18.4	21.1	39.3	84.9	23.67
	60 ppm	5.7	16.1	18.7	31.6	72.1	41.14
	80 ppm	5.1	14.2	16.8	29.7	65.8	48.63
	100 ppm	4.7	13.5	14.9	23.5	56.6	56.72

Table 15. Fluoride content in soils and Chilli plants.

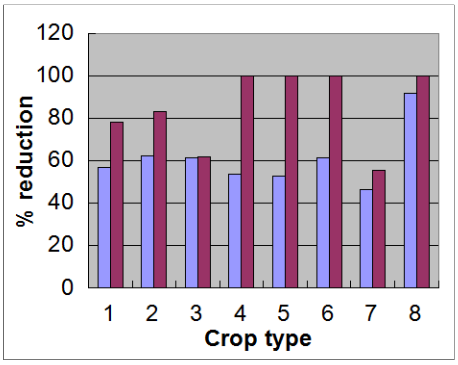
Soil →	At the Start (mg/Kg)		During Harvest (mg/Kg)		
Conc.	Total Fluoride	Leachable Fluoride	Total Fluoride in Soil	Leachable Fluoride in Soil	Total F⁻ in Plant Sample
Control	95.19	8.89	81.38	12.50	1.56
10 ppm	95.19 + 10	8.89	87.70	16.72	1.76
20 ppm	95.19 + 20	8.89	93.37	21.47	1.98
30 ppm	95.19 + 30	8.89	99.61	25.45	2.35
40 ppm	95.19 + 40	8.89	106.72	28.56	2.58
50 ppm	95.19 + 50	8.89	112.58	33.70	2.94

Table 16. NPP (g dry wt/plant) of Chilli in F⁻ treated soils.

Days	Concentration	BGP Root	AGP			NPP (BGP + AGP)	% Decrease in NPP over Control
			Leaf	Stem	Pod		
75 days	Control	1.22	0.89	2.95	2.5	7.56	0
	10 ppm	1.03	0.8	2.06	0.56	4.47	40.8
	20 ppm	0.87	0.8	1.68	0.42	2.773	63.32
	30 ppm	0.42	0.38	0.93	xxx	1.74	76.9
	40 ppm	0.30	0.37	0.39	xxx	1.06	85.9
	50 ppm	0.26	0.24	0.21	xxx	0.71	90.65

Table 17. Leachable Fluoride (ppm) content, NPP and yield (g dry wt/plant) of Crops in highest concentration of F^-.

Crop	F Conc.	Soil F	Plant F	NPP	Yield
Brinjal	100	38.14	3.83	50.8	13.5
Tomato	100	37.28	3.49	43.8	9.7
Mustard	50	32.18	2.37	0.102	0.014
Mung	100	42.04	3.63	16.7	Nil
Ladies Finger	50	35.04	2.72	41.5	Nil
Maize	100	41.02	4.02	4.43	Nil
Paddy	100	41.13	4.37	56.6	23.5
Chilli	50	33.7	2.94	0.71	Nil



(1: Brinjal; 2: Tomato; 3: Mustard; 4: Mung; 5: Ladies finger; 6: Maize; 7: Paddy; 8: Chilli.)

Figure 1. Percent reduction in NPP and yield in crops.

4. Discussion

Terrestrial plants may accumulate inorganic fluorides following airborne deposition and uptake from the soil [14]. Sloof *et al*. [21] reported that the main route of uptake of fluoride by plants was from aerial deposition on the plant surface. Plant uptake from soil is generally low (except for accumulators) unless the fluoride has been added suddenly, such as following amendment with sludge or phosphate fertilizer. The availability of plants tends to decrease with time following application of fluoride. The degree of accumulation depends on several factors, including soil type and most prominently pH. At acidic pH (below pH 5.5), fluoride becomes more phyto-available through complexation with soluble aluminium fluoride species, which are themselves taken up by plants or increase the potential for the fluoride ion to be taken up by the plant [29] (Stevens *et al*. (1997)). Plant uptake of fluoride from solution culture is dependent on plant species and positively related to the ionic strength of the growth solution. Once a threshold fluoride ion activity in nutrient solutions is reached, fluoride concentrations in plants increase rapidly [30]. Ample evidences are also available relating to fluoride accumulation in different parts of the plants [31]. When fluoride contaminated plant tissue is ingested by the animals including human beings, fluoride associated problems are encountered. In the present study the same thing is also observed. Maximum fluoride accumulation in plant tissue was found in higher concentration of fluoride treated soils. Among all soils, it is the soluble fluoride content that is biologically important to plants and animals. It has also been reported that in saline soils, the bioavailability of fluoride of plants is related to the water-soluble component of the fluoride present [14]. Hocking *et al*. [32] indicated that although there was some accumulation of inorganic fluoride in marine vegetation, the rate of accumulation was far lower than that of airborne inorganic fluoride by terrestrial plants. Fluoride (F^-) contamination of soil, water and vegetation has been a continuing problem in the world. Various sources of F^- and their impact on the biology of plants and animals have been well documented. The detrimental effects of F^- on plants and animals have been known for more than hundred years [8]. Agricultural soils high in fluoride are common due to long term accumulation of fluoride from multisources. It may be extensive application of phosphate fertilizers, leaching from fluoride deposited rocks or industrial activities. Overall, the present study shows varied tolerance towards fluoride in the plant species tested and provides information about how fluoride can affect their germination, biochemistry and growth. Such knowledge is potentially useful for farmers to help them avoid excessive application of F^- containing fertilizers and selection of crops. As the fluoride endemicity is a great problem in recent days, much more studies on fluoride toxicity are needed not only to explore some viable remedial measures but also to save the present and future generations form fluoride related hazards. The study reveals that among the vegetable crops tested Chilli is more sensitive to fluoride contamination whereas Brinjal shows less sensitivity. Similarly, in case of grain crops (*i.e.* Maize and Rice) Maize shows more sensitivity to fluoride contamination as compared with Paddy.

The present work also indicates that the biomass of plants (both Mustard and Maize) grown in fluoride amended soil is less as compared with the control soil. This may be due to changes in above biochemical parameters which in consequence retard the growth and biomass of plants. Fluoride concentration more than 28 ppm significantly decreases dry weight of shoots [30], thus significantly reducing leaf surface area and weight in mature and immature leaves resulting in the inhibition of growth. This may be the reason for decrease in RGI with increase in fluoride concentration. Black [33] has reported that Fluoride in mesophyll cells disturbs mineral metabolism, reduces chlorophyll pigments and alters other morphological and physiological parameters such as height, number of leaves, biomass productivity, fruiting and yield of the plant, while higher fluoride accumulation causes leaf damage [31] and thus may retard growth.

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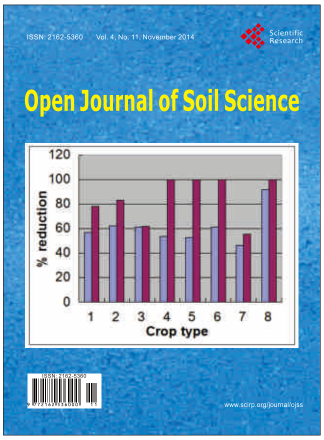

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