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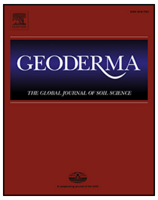

Temporal variation in the strength of podzolization as indicated by lysimeter data

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ABSTRACT

This study examines trends in podzolization – both temporally and with depth – as indicated by translocation of dissolved organic carbon (DOC), iron (Fe) and aluminum (Al) in soil water. Water as saturated flow was captured by zero-tension lysimeters installed below the O, E and B horizons of six Spodosol pedons in Michigan, USA. Over a 2-year timespan, we sampled soil water on 36 different dates, resulting in 505 samples. All samples were analyzed for DOC, whereas Fe and Al contents were determined for a subset of 227 samples.

Cumulative water fluxes are high during both spring snowmelt and the fall (autumn) season, when much water is moving as saturated flow. Water flux *rates* are much greater during snowmelt, and when averaged over all horizons, 1.15 times more water is translocated through the soil during snowmelt than in fall, even though the latter is routinely twice as long. Translocation of DOC out of the O horizon is a dominant process in these soils during snowmelt, peaking in mid-snowmelt. It peaks again – even higher – in fall, as rains strip C from fresh litter. Overall, little DOC leaves the soil system; B horizons are effective traps for C being transported in soil water. Surprisingly, E horizons retain DOC in almost all seasons, but particularly in fall and early snowmelt, as water percolates through C-rich, fresh litter. The thick, bright, C-poor E horizons in these soils suggest that, over long timescales, in situ mineralization of C exceeds the net retention of DOC from the O horizons above. Translocation of Fe and Al in soil water also has a distinct annual bimodality, largely following that of DOC. This component of podzolization peaks in mid-snowmelt and again late in fall. On an annual basis, considerably more Al moves in soil water than Fe; 1.9 times more Al than Fe is translocated out of E horizons, and 1.8 times more Al is lost from B horizons. Our study supports existing pedogenic theory for the snowy midlatitudes, in which snowmelt is seen as a key period for podzolization. Daily rates of translocation of metals and DOC moving in saturated flow during snowmelt are considerably higher than for any other time of year. Our study also sheds new light on the importance of fall rains to podzolization. Although the daily rates of translocation for fall are much less than during snowmelt, the greater length of the season, the relatively high frequency of rain events, and the abundance of fresh C combine to make fall an important period for translocation of metals and DOC. Thus, our study highlights that podzolization here has a short but intense "pulse" during snowmelt, and a second, less intense but longer period during fall. Little podzolization occurs during winter, and during summer, translocation occurs only during infrequent, large storms.

1. Introduction

During podzolization, soluble organic materials and Al^{3+} cations, often in association with Fe^{3+} cations, are translocated from the upper profile, forming a distinct eluvial zone, to a lower, illuvial horizon (Petersen, 1976; DeConinck, 1980; Buurman and van Reeuwijk, 1984; Courchesne and Hendershot, 1997; Lundström et al., 2000; Schaetzl and Harris, 2011). The process is best exemplified in coarse-textured soils that have formed under vegetation that produces acidic litter, capable of releasing large quantities of soluble organic materials during decomposition (Van Breeman and Buurman, 1998; Schaetzl, 2002). Coarse-textured soils, when they occur in areas of cool, humid climate, also facilitate deep wetting and percolation, which enable the translocation of these soluble compounds to the lower profile. Acidic litter, such as is commonly found under vegetation like heath and coniferous forest, not only decomposes to produce large amounts of soluble organic compounds, but many of these compounds are able to complex free Fe and Al released from primary minerals by weathering (van Hees et al., 2000). This chemical process of complexation, or chelation, renders these cations soluble and available for translocation. Percolating water can then translocate these compounds to the lower profile. Research has shown that up to 80–85% of the soluble Al in E horizons of Spodosols is bound in organic complexes of this type (Petersen, 1976; Lundström,

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1993). Under ideal conditions, an acidic E horizon is formed quickly; it is impoverished in Al, organic matter and usually Fe (Franzmeier and Whiteside, 1963; Barrett and Schaetzl, 1992; Sauer et al., 2008). Below, a reddish brown to black B horizon, enriched in metals and organic matter, develops. If it becomes sufficiently enriched in these types of "spodic materials" (Soil Survey Staff, 2010), it can meet the criteria for a spodic horizon and the soil classifies as a Spodosol (or Podzol).

Podzolization and podzolic soils continue to be the focus of much research (Lundström et al., 2000; van Hees et al., 2000; Sauer et al., 2007). Such studies have traditionally used any of three different methodological approaches:

(1) Examination of podzolic soil morphologies. Because there are usually few mechanisms by which Spodosol morphologies, once formed, can get degraded, e.g., pedoturbation or erosion, contemporary soil morphologies are good indicators of the long-term strength of podzolization, the length of time that podzolization has been operative, or both (Jauhiainen, 1973; Barrett and Schaetzl, 1992; Schaetzl, 2002). This relationship is so reliable that numerical indexes have even been developed that quantify Spodosol morphology; these can be correlated to podzolization strength and/or longevity (Duchaufour and Souchier, 1978; Schaetzl and Mokma, 1988).

(2) Examination of the liquid extracts derived from solid phase soil samples. These extracts are formulated to remove the grain coatings, which assumedly capture the long-term record of illuviation (in the B horizon), or the degree to which the E horizon has been leached of potentially translocatable materials. To do this, soil samples, usually from the E and B horizons, are exposed to a chemical extractant, and the extract is then analyzed for Fe, Al, and/or Si; such data are then used to determine the amount of soil development. Three different kinds of extractants have traditionally been used to extract metal and Si cations in spodic soils (Schnitzer et al., 1958; McKeague and Day, 1966; McKeague et al., 1971; Petersen, 1976; Olsson and Melkerud, 1989; Skjemstad et al., 1992): (i) amorphous, poorly crystalline, and crystalline (commonly referred to as free) forms of Fe and Al oxides, are extracted using a sodium citrate-dithionite solution (Mehra and Jackson, 1960; Holmgren, 1967), (ii) organically bound forms of Fe and Al, normally referred to as organometallic complexes, are extracted using sodium pyrophosphate (McKeague, 1967; Bascomb, 1968; Higashi et al., 1981), and (iii) in poorly crystalline minerals such as ferrihydrite, allophane, and imogolite (known as imogolite-type materials, or ITM) plus organically complexed Fe and Al are extracted using acidified ammonium oxalate (Schwertmann, 1973; Daly, 1982; Kodama and Wang, 1989; Wilson et al., 1996). Ratios and mathematical differences of these kinds of data are often used to interpret the strength of podzolization and to infer more about the process itself (Schaetzl and Thompson, 2015).

(3) Examination of soil solutions, as captured by zero-tension or suction lysimeters (Holzhey et al., 1975; Ugolini et al., 1977a, 1977b; Herbauts, 1980; Litaor, 1988; Shepard et al., 1990). This method is particularly useful for the study of podzolization, because (1) most of what is being translocated is moved in solution, and (2) the process is sufficiently rapid that individual percolation events can produce measureable data. Metals and organic materials from soil water captured in lysimeters provide an instantaneous picture of the podzolization process, albeit for a single pedon. And the data can be isolated on a per-horizon basis. Longer-term data from lysimeter water can, therefore, provide an excellent picture of the kinds and amounts of soluble materials moving in the soil during podzolization, at different times of the year, for individual horizons, and under different pedogenic circumstances (Ugolini et al., 1977a, 1977b; Ugolini and Dahlgren, 1987; Ugolini et al., 1988; Brahy et al., 2000; Mossin et al., 2001).

In a companion paper, Schaetzl et al. (2015) reported on the timing and magnitude of percolation events in Spodosols at our study sites, using lysimeter data on water volumes to inform a hydrologic model. They observed that these soils are usually dry during the summer, when almost no deep percolation takes place, and slowly wet up in autumn. Although not empirically examined, they suggested that the autumn "wet-up" facilitates decomposition of fresh litter, liberating soluble organic materials for potential translocation. The soil-climate system here effectively stores winter precipitation in a thick snowpack, releasing this water rapidly during snowmelt (Schaetzl and Isard, 1991, 1996; Teoharov, 2002). Translocation of organic materials generated in autumn and winter in the O horizon is therefore most pronounced during snowmelt, during which they are driven by steady, cold, percolating water to the lower profile (Rothstein et al., under review).

The above research generated a number of additional questions about the seasonal dynamics of the podzolization process in the mid- and high latitudes. For example, we asked when the translocation of metal cations and soluble organic materials was most pronounced, what drives the process, and what may be the limiting thresholds and factors to podzolization during these periods of deep translocation? To answer these questions, we adopted all three approaches to podzolization discussed above. We examined static data on soil morphology for six Spodosol pedons to determine the amount and type of spodic development that is typical for the study area. Data from chemical extracts were used to add detail to the picture of soil development. Our main focus, however, was on the chemistry of soil water captured from these soils, as a way to assess the temporal (and seasonal) variations in the strength and character of podzolization. As such, this work — with its two full years of soil water data, often collected at short temporal intervals, and within strongly developed Spodosols, represents a comprehensive and direct study of podzolization.

2. Materials and methods

2.1. Study area and sites

Our six study sites are in Michigan's (USA) Upper Peninsula, about 37 km east of Newberry (Fig. 1). Here, Spodosols may be better developed than anywhere else in the Great Lakes region (Schaetzl et al., 2015). Presently, the region is forested, either in mixed hardwoods or red pine (*Pinus resinosa*) plantations. Reconstructed, presettlement vegetation records from the General Land Office (GLO) survey notes indicated that this area was forested with beech (*Fagus grandifolia*) – sugar maple (*Acer saccharum*) – hemlock (*Tsuga canadensis*) – yellow birch (*Betula allegheniensis*) forest (Comer et al., 1995) in the mid-19th century. Areas currently under pine plantation were replanted in the 1930s, following severe post-logging fires.

The climate here is cool and humid, with a frigid soil temperature regime and a udic-aquic soil moisture regime (Soil Survey Staff, 2010). The National Weather Service (NWS) station at Newberry reports an average of 812 mm of annual precipitation and a mean annual temperature of 4.7 °C. The area lies within a Lake Superior snowbelt, with Newberry receiving an annual average of 255 cm of snowfall (Schaetzl et al., 2015). Snowmelt generally begins in March or early April and continues until about the beginning of May. In some years, snowpacks can be quite thick and snowmelt can be rapid. Nonetheless, because the sandy soils remain largely unfrozen under the thick snowpacks, runoff is minimal.

Soils here are sandy Haplorthods and Durorthods with thick, bright E horizons and with varying amounts of ortstein in the spodic horizons below (Figs. 1, 2). Tongueing of the B horizon suggests that preferential flow is common. Water tables are deep, such that soil water can

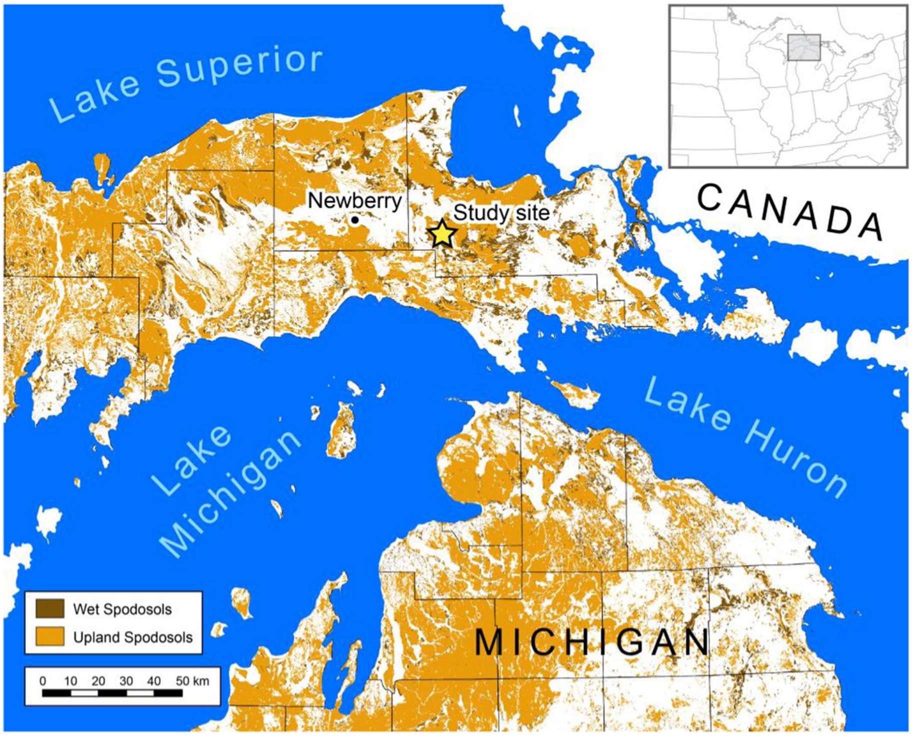

Fig. 1. Map of Spodosols in northern Michigan, showing the location of the study sites and the nearest National Weather Service station (Newberry).

percolate freely within the profile. Most soils have formed in well-sorted, sandy, quartz-rich, glacial outwash from the last glaciation, ca. 13,500–12,000 years ago (Blewett et al., 2014).

2.2. Field and laboratory methods

Our data come from a dry, sandy upland known locally as Hulbert Island (Schaetzl et al., 2013). Here, we excavated and thoroughly sampled six pedons, three each in the red pine plantations and in naturally regenerated northern hardwoods. All of the sites are within 3 km of each other. At each site we excavated a 5–6 m long and ≈1.8 m deep soil pit on level ground, avoiding areas of obvious tree uprooting disturbance (Šamonil et al., 2013, in press). Pit faces were cleaned and described according to guidelines in Schoeneberger et al. (2012), and sampled by horizon.

We installed zero-tension lysimeters below the O, E and B horizons, to capture soil water moving as saturated flow. Average depths for the O, E and B horizon lysimeters were 9, 35 and 59 cm, respectively. Each lysimeter was built using 16 cm dia. HDPE funnels filled with combusted (550 °C), acid-washed (10% HCl) quartz sand (MacDonald et al., 1993; Fig. 3A). This type of lysimeter is suitable for collecting soil solution in fast flowpaths (Weihermüller et al., 2007), as expected in sandy soils like these. Lysimeters were installed approximately 30 cm into the face of the trench, at staggered horizontal locations (Fig. 3C). PTFE tubing carried drainage water from the lysimeter, by gravity, to a 4-L glass collection bottle located at the bottom of the pit, with a separate PTFE tube running from the bottle to the surface. Plastic sheeting was carefully stretched across the pit face prior to backfilling, to isolate the lysimeters and the soil system from the disturbed soil within the in-filled pit. Every effort was made to minimize disturbance, trampling, etc. of the surface in the area immediately above the lysimeters (Fig. 3E).

Although the plots were instrumented in May 2012, leachate collected prior to October 1, 2012 was discarded, so as to provide for an equilibration period following the disturbance associated with instrumentation. Subsequently, leachate was collected shortly after rain or snowmelt events of ≈2 cm or more water equivalency, as guided by precipitation models from the NWS's Advance Hydrologic Prediction Service (http://water.weather.gov/precip/) and snowmelt models from the NWS's National Operational Hydrologic Remote Sensing Center (http://www.nohrsc.noaa.gov/nsa/). In total, we sampled on 36 different dates from October 1, 2012 through September 30, 2014. Lysimeter samples recovered in the field were stored in HDPE bottles and kept on ice for transport back to the lab, where they were filtered (0.45 μm) and immediately frozen (−20 °C). Soil water flux data (water volumes in the lysimeters) were also recorded at the time of sampling. Flux volumes were highly variable, however, even at sites within close proximity, probably due to preferential flow (Kung, 1990; Boll et al., 1996; Bogner et al., 2012).

Of the potentially 648 soil water samples, we collected only 505 samples, because lysimeters were sometimes empty, especially in summer. All 505 samples were analyzed for dissolved organic C (DOC) by oxidative combustion-infrared analysis on a total organic carbon analyzer (TOC-V_{CPN}; Shimadzu Corp., Kyoto, Japan). This instrument has a detection limit of 4 μg C L^{-1} and we maintained a coefficient of variation of 5% or less among analytical replicates. Mass fluxes of DOC were then calculated for each sample by multiplying the water volume by the DOC concentration of the sample. Flux data were calculated per volume of soil water and as mass flux per cm^2 of soil surface, by dividing flux volumes by the area of the lysimeter funnels. Generally, because of the inter-site variability, we report on mean soil water and DOC fluxes in most cases, grouped in various ways, e.g., by horizon type, by climate period.

Because podzolization involves translocation of metal cations, we also analyzed a subset of the water samples for Fe and Al by inductively-coupled plasma, atomic emission spectrometry (ICP-AES; limits of detection for Fe and Al were 0.008 mg L^{-1} and 0.001 mg L^{-1}, respectively). However, limited resources for the project prevented us from analyzing all 505 lysimeter samples. Instead, we analyzed only a subset of 227 samples, selecting primarily those from (1) snowmelt, summer and autumn periods, (2) the different stand types, and (3) consecutive "runs" of samples, i.e., periods during which lysimeters were not dry

Fig. 2. Typical profiles for the soils of the study area. The soils (Typic Haplorthods and Durorthods) are shown in trenches, prior to sampling and installation of the field equipment. Note the prominent tongueing that is typical for these soils, especially in the B horizon. Tape scale in cm. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

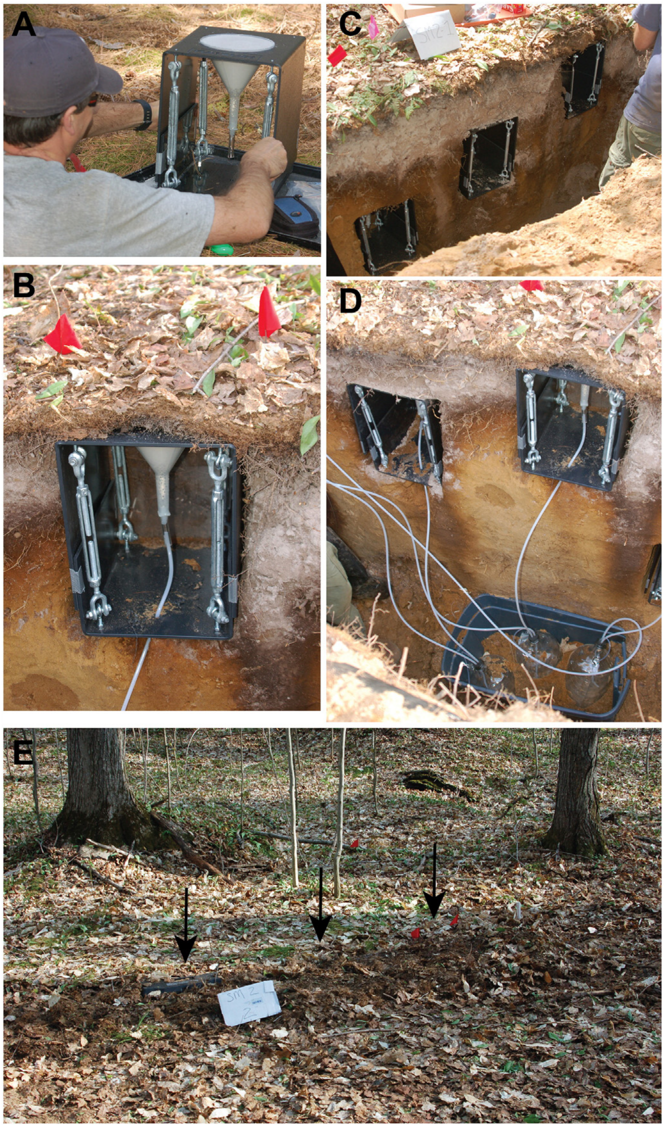

Fig. 3. Photos showing the lysimeter structure and field installation setup. A. Closeup of a zero-tension lysimeter, prior to installation. The funnel is filled with acid-washed, quartz sand. B. A lysimeter installed below the O horizon. The plastic tube will eventually carry leachate to a glass bottle stored below. C. A suite of three lysimeters, installed below the O, E, and B horizons. D. A nearly completed lysimeter array. Each lysimeter drains to a glass bottle, partially buried in a plastic box at the base of the pit. Leachate is stored in the bottle. A separate tube leads from each of the bottles to the soil surface, to facilitate removal of the leachate. E. A site shortly after lysimeter installation and backfilling. Arrows indicate the three locations on the soil surface that directly overlie the buried lysimeters. Red flags mark the location of the shallowest lysimeter (see part B), to help avoid stepping on the surface and disturbing the O horizon or the lysimeter below. (For interpretation of the references to in this figure legend, the reader is referred to the web version of this article.)

for at least four consecutive sampling events. Mass fluxes of metal cations in the subset of lysimeter samples were determined as for DOC; sample volumes were multiplied by mass concentrations to arrive at total flux for each sample.

Solid-phase samples from one of the six pedons, judged to be most typical of the six studied, were analyzed using standard methods. Amorphous and crystalline (for Fe, these compounds are commonly referred to as “free”) forms of Fe and Al were extracted using a Na-citrate-dithionite solution (Mehra and Jackson, 1960). A Na-pyrophosphate solution was used to extract organically bound forms of Fe and Al; these data are reasonable indicators of organo-metallic complexes residing as grain coatings (McKeague, 1967). Finally, acid ammonium oxalate was used to obtain the amounts of Al and Fe from organic complexes, as well as from poorly crystalline minerals such as ferrihydrite, allophane, and imogolite (Daly, 1982). Liquid extracts were then run in an inductively coupled plasma mass spectrometer.

3. Results and discussion

3.1. Study area climate

During the two-year period of study, the winters at the study sites were colder and snowier than normal. Our sites received abundant snowfall in both years, with Dec.-Jan.-Feb. precipitation totaling 202 mm in 2012–2013 and 166 mm in 2013–2014 (Fig. 4B), as compared to a 30-yr normal of 142 mm. The winter of 2013–2014 was particularly cold, with a mean Dec.-Jan.-Feb. temp of −12.0 °C, as compared to the 30-yr normal of −8.1 °C. The summer of 2013 was also particularly wet, with several large storms; July and August precipitation totaled 311 mm, as compared to the 30-yr normal of 169 mm.

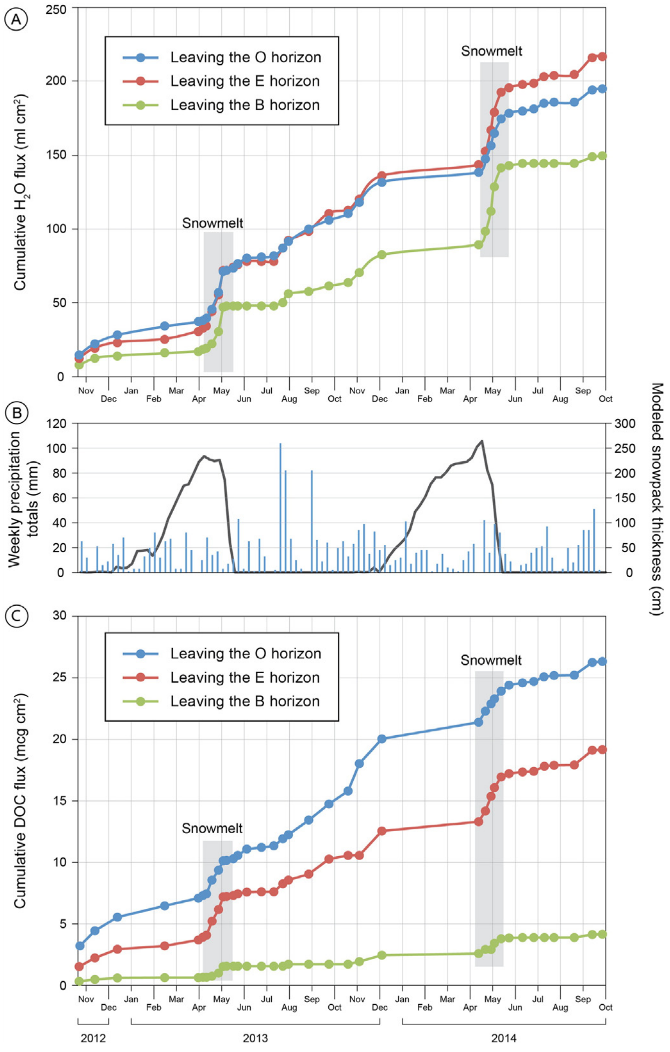

Fig. 4. Soil water flux (A), precipitation (blue) events and snowpack (black) thicknesses (B), and DOC flux data (C) for the two-year study period. Soil water and DOC fluxes are broken down by horizon. Each data point represents the mean for all six study sites, for that particular sampling date. The data are then summed over the two-year timespan of the study (October 1, 2012 through September 30, 2014). (For interpretation of the references to in this figure legend, the reader is referred to the web version of this article.)

The upshot of these data is that the two years of study represent an exceptionally snowy period, and thus, if winter is important to podzolization (as the literature has shown), our data may overshoot the "norms" for podzolization here (see below).

3.2. Soil characterization and development

All six soils classify as Spodosols, and are sandy and well-drained. All have well-developed E and B horizons, usually with pronounced tongueing (Fig. 2). A few soils have thin clay lamellae in the lower profile. O horizon character varies markedly, with red pine plantations having much thicker O horizons. Regardless, all six soils have continuous O horizons of 2–11 cm in thickness.

We first report on morphological and solid phase soils data for two of the six sampled pedons in Table 1. The pedons are characteristic of the varying degrees of development at the study site. The Wallace pedon (Table 1, pedon 1), currently under mixed hardwood forest, was the best developed of the six soils, with deep E and B horizon tongues and continuous ortstein in the B horizon (Fig. 2D). Ortstein was discontinuous, but common, in the lower B horizon (Table 1). All horizons except the Bhs were sand textured, with medium and fine sands dominating (Table 1). Clay contents were <2.5% for all horizons, confirming the sandy, well sorted nature of the outwash parent material. One of the other two soils in the hardwood stands was quite similar to this pedon.

The Rubicon pedon (Fig. 2A; Table 1, pedon 2) was typical of all three soils under red pine, and one of the soils beneath sugar maple. The E horizon here was slightly thinner and had a lower color value than did the Wallace pedon. The Rubicon B horizons were also lighter and had less ortstein.

Data from the chemical extracts from the Wallace pedon confirm that many of the soils in this study have typical to exceptional spodic development (Franzmeier and Whiteside, 1963; Messenger et al., 1972; Barrett and Schaetzl, 1992; Fig. 5). Due to space restrictions we only report data for the one pedon, which we view as representative of the six, although it may be slightly better developed than some of the pedons at the red pine sites. The upper B horizon of this pedon has very high amounts of extractable Fe, Al, and Si, regardless of the "form" (extractact). Similarly, the E horizon has very low amounts of these same elements. B horizon peaks for all three kinds of extraction data, coupled with very low minima for these same data in the E horizon, illustrate that metal cations are being actively translocated to the B horizon, probably as chelate-complexes (but also possibly as inorganic sols, see Fig. 5D) (Wang et al., 1986; Sauer et al., 2007).

One metric commonly used to indicate degree of spodic development is the Optical Density of the Oxlate Extract (ODOE), measured at 430 nm on a UV-spectrophotometer (Van Reeuwijk, 2002). According to the Soil Survey Staff (2010), spodic materials normally have an

Table 1
Physical and morphological characterization data for two representative pedons.

Horizon	Depth (cm)	Color moist	Structure	Texture class	Bulk density (g/cm^3)	Boundary (distinctness, topography)	Comments
Pedon 1: Wallace (sandy, mixed, frigid, shallow, ortstein Typic Durorthods; Fig. 2D)							
Oe	0–7	n/a	n/a	n/a	Not determined	Clear, smooth	Some Oi and Oe material also present
E	7–23	7.5 yr 6/3	w, f-m, sbk	Sand	1.18	Clear, irregular	
Bhs	23–34	2.5 yr 2.5/2	w, f-m, sbk	Loamy sand	1.08	Clear, broken	≈100% ortstein
Bsm	34–47	2.5 yr 2.5/3	Cemented	Sand	1.36	Gradual, broken	≈20% ortstein
Bs1	47–62	7.5 yr 4/6	w, m-c, sbk	Sand	1.37	Diffuse, broken	
Bs2	62–82	10 yr 5/6	Loose	Sand	1.56	Diffuse, irregular	
BC	82–130+	10 yr 5/4	Loose	Sand	1.60	–	Few, thin (1 mm) lamellae; 2% coarse fragments
Pedon 2: Rubicon (sandy, mixed, frigid Entic Haplorthods; Fig. 2A)							
Oe	0–15	n/a	n/a	n/a	Not determined	Clear, wavy	Patches, 2–4 cm thick, of Oa material also present on face
E	15–28	7.5 yr 5/3	w, f-vf, sbk	Sand	1.10	Abrupt, irregular	2% coarse frags.
Bs1	28–35	7.5 yr 4/3	w, m-f, sbk	Sand	1.09	Gradual, broken	≈10% ortstein; 2% coarse frags.
Bs2	35–46	7.5 yr 5/6	w, f-vf sbk	Sand	1.14	Gradual, broken	≈25% ortstein; 2% coarse frags.
Bs3	46–62	10 yr 6/6	Loose	Sand	1.50	Gradual, broken	≈25% ortstein; 2% coarse frags.
Bs4	62–108	10 yr 6/4	Loose	Sand	1.57	Gradual, wavy	Lamellae <2 mm thick; 2% coarse frags.
E&Bt	108–150+	10 yr 6/3	Loose	Sand	1.61	–	

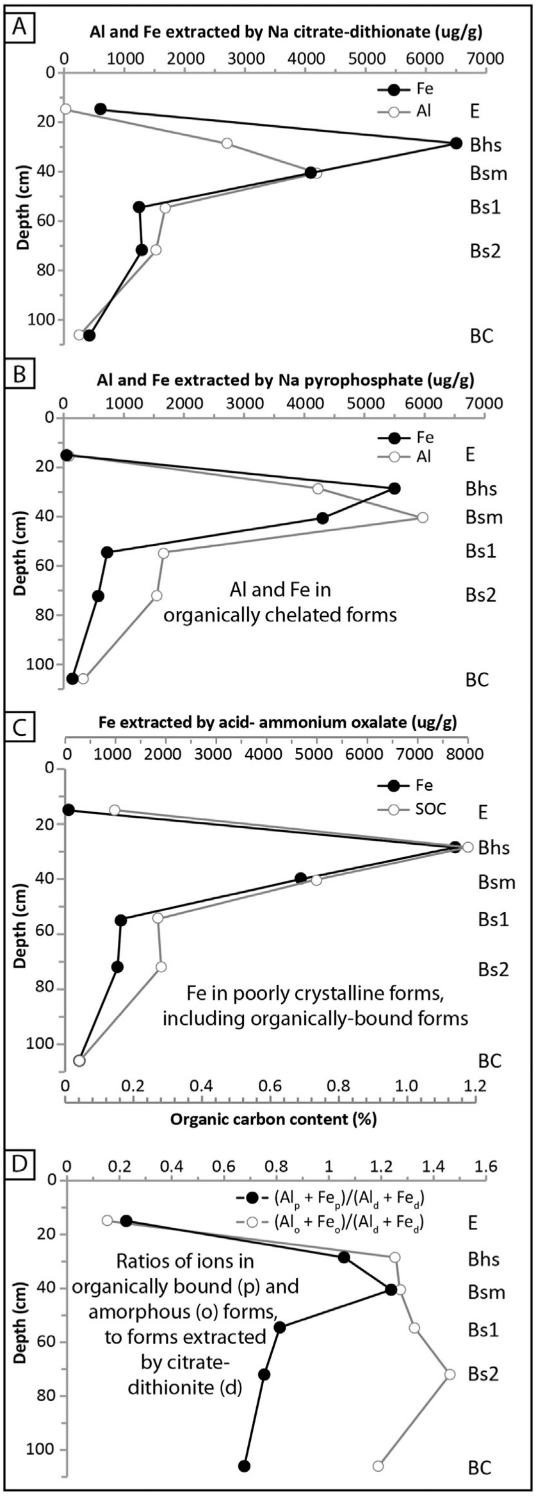

Fig. 5. Depth plots for various chemical extractants related to podzolization, for the Wallace pedon. Also included are data on soil organic carbon (SOC) content (solid phase). Data are reported on a horizon-basis.

ODOE value ≥0.25, and that value is normally ≥2 times that of the ODOE of the E horizon extract. In the Wallace pedon, the ODOE value of the Bhs horizon is 1.16, which is 145 times the ODOE of the E horizon (0.008). The Wallace pedon's POD Index of 31 is also unusually high; most well-developed, upland Spodosols have POD Indices between 6 and 15 (Schaetzl and Mokma, 1988), and most Spodosols across the Lake States region have POD Indices <6 (Schaetzl et al., 2015). Clearly, this soil, like others in this study, exhibits exceptional development.

3.3. Temporal translocation patterns for water and DOC

In a previous paper, Schaetzl et al. (2015) used modeled hydrologic data to estimate fluxes of water for Spodosols near Newberry. In the present paper, we use water data collected from lysimeters in soils here to examine trends in podzolization throughout the year. First, we focus on fluxes of *water*, which ultimately drive translocation processes. Then, we examine fluxes of the dissolved components in that water: DOC, Fe, and Al. For all our data, we provide both mean daily fluxes, which can be equated to *rates* of transport, as well as cumulative, seasonal fluxes, which equate to temporally-cumulative *quantities* of translocation.

Modeled water flux data have the potential advantage of providing excellent temporal detail, but like any modeled data, they may lack accuracy. Alternatively, lysimeter data usually do a good job of capturing information on water flux (and contents of dissolved substances therein) for a given site. However, because of preferential flow, data from any one lysimeter may be so site-specific as to limit extrapolation. For these reasons, we used six suites of lysimeters, so as to negate some of the inter-lysimeter and inter-site variability, and we report mean or cumulative data, by horizon.

Likewise, temporal detail from lysimeter data is constrained by the frequency of sampling. Instead, such data are often reported as "data packages" that span the time periods between sampling events. Water collected over such periods provides only cumulative information for the sampling period. Nonetheless, although the data we present here lack the temporal resolution that hydrologic models can sometimes provide, the soil water data we present do provide detailed empirical information about podzolization in situ.

Fig. 4A and C show cumulative water and DOC fluxes by horizon, for the two years of study. The figure can also be used to infer flux *rates*; steeper slopes indicate greater rates of flux, whereas lower slopes indicate periods with diminished flux rates. At the Newberry study site, snowpacks steadily thicken during the winter, with few to no significant mid-winter melt events (Fig. 4B). Hence, there is often little to no wintertime water flux through the soils (Fig. 4A; Schaetzl et al., 2015). At the time of peak snowpack accumulation, ca. early March, snowpacks are routinely 50–70 cm thick within the forest, and store an average of ≈140 mm of liquid water equivalent (Schaetzl et al., 2015). By late March, snowpacks begin to melt, often rapidly (Fig. 4B). The 4–5 week long "pulse" of meltwater, as Schaetzl et al. (2015) referred to it, is thought to be especially effective at translocating soluble materials – organic or otherwise – because (1) evapotranspiration rates are low and soils are normally unfrozen and permeable under the thick snowpack, such that almost all of the meltwater can enter the soil and percolate freely, and (2) biological demand is low because of the cold soil temperatures, minimizing decomposition of organo-metallic complexes being translocated in soil water (Schaetzl and Isard, 1991, 1996; Schaetzl, 2002; Schaetzl et al., 2015). Explanations of the strong spatial correlation among thick snowpacks and strong podzolization rest mainly on these process links.

Our data confirm that fluxes of water moving as saturated flow through the soils of the study area are temporally focused during snowmelt, but also are high in autumn (hereafter, "fall") (Fig. 4A). Percolation/flux *rates* in the fall are lower than during snowmelt, but water flux *totals* for fall are nonetheless impressive, because of their longer duration (Fig. 4A). Averaged across all lysimeters and all sites, water fluxes for the spring snowmelt period were 1.7 times that for the fall period, even though the fall period over which the data are tallied is normally twice as long. The equivalent water flux ratio for snowmelt/summer is 3.61, illustrating the relative "dryness" of the summer season here, as is common at other midlatitude sites (Teoharov, 2002). The fall flux coincides with rains that normally occur after leaf-fall. Fall percolation events may be larger than for comparable summertime precipitation events, because during fall there is negligible evapotranspiration and considerably less canopy interception. Few deep fluxes of water or

DOC occur in summer, except for the occasional heavy rain event associated with a thunderstorm (Rothstein et al., under review). Indeed, our data in Fig. 4A (and other figures) may overestimate deep summertime water fluxes, because of the several anomalously large storms in summer 2013.

Water flux volumes at most times of the year are roughly equivalent for the O and E horizons (Fig. 4A). Fluxes attenuate with depth in the mineral soil, as expected, such that total flux through the B horizons is only about 73% of that for the O and E horizons. This depth trend is especially noteworthy in the context of pedogenesis; most of the larger fluxes of water into (and through) the B horizon occur during snowmelt and fall, not in summer (Schaetzl et al., 2015). As a result, snowmelt and fall represent the primary periods of water flux, and likely, groundwater and deep subsoil recharge as well.

When examined temporally, fluxes of DOC have a similar signature to that for water, varying in amplitude more-or-less similarly among the horizons (Fig. 4C). Once again, snowmelt and fall rains are the main drivers of DOC into the mineral soil. DOC fluxes from O and E horizons follow predictable patterns, i.e., O horizons contribute large amounts of DOC to the mineral soil below, most of which (73%) then exits the E horizon. Likewise, B horizons see strong net influxes of DOC from the E horizon, most of which (78%) is retained. Annually, then, B horizons realize significant annual additions of DOC from percolating soil water (see below).

These temporal patterns support a model of podzolization in which snowmelt is a strong component. This model was first outlined by Schaetzl and Isard (1991, 1996) and later reinforced by modeled data (Schaetzl et al., 2015). They point to a system whereby DOC is released from decaying organic materials in the O horizon and, at preferred times of the year, translocated, often under saturated flow conditions, into and through the mineral soil. Here, the C compounds can complex with metal cations, facilitating their solubility and forming the podzolic profiles that are so strongly expressed in this region (Fig. 2). Many of these compounds end up accumulating in B (spodic) horizons.

3.4. Details of the temporal translocation of DOC

Our lysimeter data add considerable temporal detail to the podzolization model mentioned above. Various temporal data on the podzolization process are presented in Figs. 4, 6, 7, and 8; in some of these figures the year is partitioned into discrete parts. Winter is not included because little or no translocation occurs then.

Daily flux *rates* of DOC start out strong in the snowmelt period, peak during mid snowmelt, and then decline (Fig. 6). The decline is driven by rapidly declining concentrations of DOC in solution from the beginning to the end of the snowmelt period (Fig. 8), rather than by slower overall water flux rates. Declining concentrations of DOC in soil water likely occur as readily-soluble C is removed from the litter by the percolating snowmelt and only slowly replenished via decomposition under the snowpack. Cumulative DOC transport shows similar trends during the snowmelt period, peaking in mid snowmelt for water leaving both the O and E horizons (Fig. 7A). DOC transport from the O and E horizons then stays comparatively low throughout spring (including late snowmelt) and summer. By late summer and fall, litter decomposition and leaf fall replenish the O horizon with fresh C stocks, and precipitation totals increase. As a result, DOC fluxes from the O and E horizons increase steadily throughout the fall, in association with a warm (warmer than during snowmelt), decomposing litter layer, rich in soluble C. On a seasonal basis, cumulative DOC fluxes from the O horizon actually peak in late fall (Fig. 7A), although rates of DOC transport at that time are much lower than during snowmelt (Fig. 6). For the O horizon, DOC fluxes in fall comprise half of the cumulative annual flux, and late fall constitutes over 58% of the flux for the season. DOC fluxes from the E horizon follow similar temporal trends as from the O horizon, but with decreased amplitudes (Figs. 6, 7A). B horizon leachate maintains comparatively low DOC concentrations in all seasons (Figs. 6, 7A), as consistently shown in the field, by the "clearer" water that is routinely collected from the B horizon lysimeters (Fig. 9) and explaining why B horizons here are dark and rich in C, Fe and Al (Figs. 2, 5). Mean daily *rates* of DOC flux from the B horizon are lowest in fall, probably because many of the precipitation events are small, such that many wetting fronts may not reach the lower profile (Figs. 4A, 6). Indeed, water fluxes through the B horizons in fall average only 62% of that for spring, when deeper and more rapid percolation events are occurring. Thus, because more wetting fronts are likely to pause or stop in the lower profile in fall than during snowmelt, the likelihood of B horizons retaining more DOC in fall is increased.

The concept of E horizon genesis is one of overall, long-term loss of soluble constituents, i.e., eluviation (Schaetzl and Thompson, 2015), and our data add interesting insight into eluviation in this environment, where it is so well expressed. We begin this discussion by examining gains (retention) and losses of DOC. Influxes of DOC to E horizons are especially large in early and mid snowmelt, and in fall (Fig. 7A). As expected, rates of DOC input to the E horizons decline through the later snowmelt period (Fig. 6), probably because the litter layer supplying DOC to the O horizons gets increasingly stripped of soluble C compounds (Fig. 8). E horizon DOC losses to B horizons, however, exceed gains only in the mid snowmelt period. Thus, somewhat surprisingly, summary lysimeter data show that E horizons maintain net retention of DOC in almost all seasons (Fig. 7C). Net retention of C in E horizons is especially large in the early snowmelt and then, after a brief interval of net loss, increases again throughout the summer and fall (Fig. 7C). The low C contents and bright white colors of E horizons in this region (Fig. 2, Table 1) must therefore occur because long-term mineralization rates of C compounds translocated into the E horizons are as fast or faster than the rate at which they gain DOC from percolating soil water. Soils are warmest in summer and early fall, facilitating in situ decomposition of C in E horizons, accentuating their whitening. We also caution that our lysimeter data were derived from two winters with above average snowfall. Thus, the data more likely represent an extreme condition, rather than the norm, of podzolization. It seems likely that in years with more "normal" weather, E horizons may realize net losses of

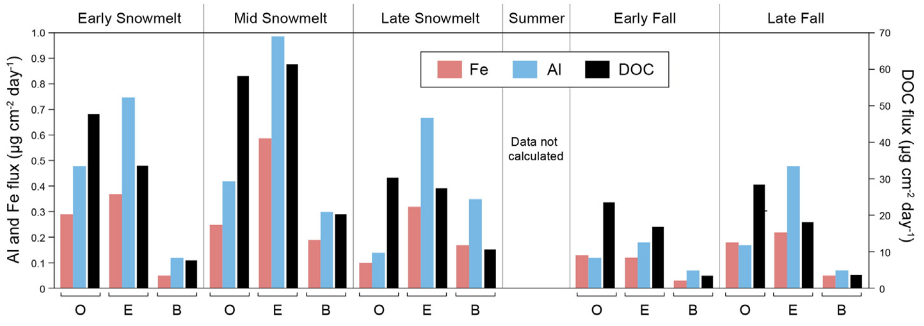

Fig. 6. Mean daily fluxes of Fe, Al and DOC, for different pedo-hydrologic periods. These data can be considered flux *rates*. Because of the wide daily variability in summertime precipitation and translocation events, data for this period were not calculated. Note the different units used for DOC vs Fe and Al.

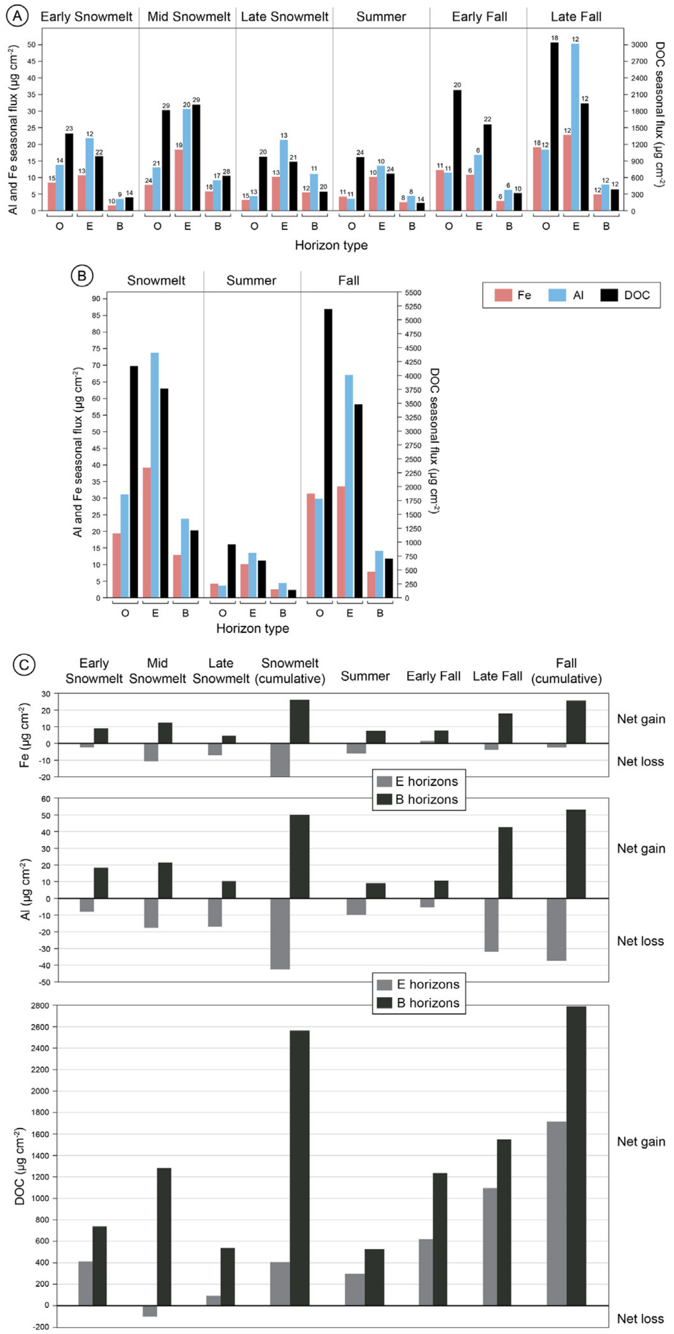

Fig. 7. Mean, cumulative, seasonal flux data for metals and DOC passing through the O, E, and B horizons, during different pedo-hydrologic periods. In part C, the data are variously summed by season. DOC data are from water collected from lysimeters on 505 sampling dates, i.e., for all dates in which water was present in the collection bottles. Fe and Al data are from water collected on representative dates only (see text for criteria). In part A, the number of samples (n) that were used to compile the means for is shown above each bar.

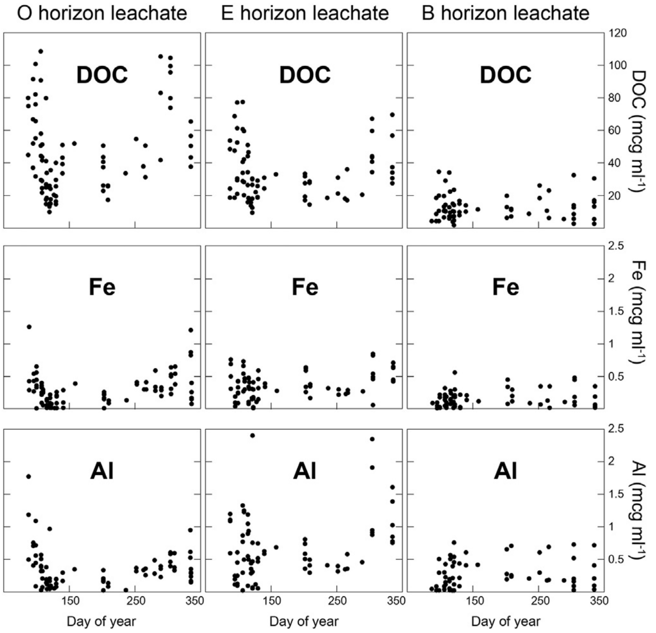

Fig. 8. Data, arranged temporally for the period of study, showing concentrations of DOC, Fe, and Al in lysimeter water. Each dot represents one sample.

DOC in late snowmelt as well, and which may even persist into summer, resulting in a much smaller net *annual* gain in DOC from O horizons above. In sum, our data do not describe a model of podzolization in which E horizons are continually being depleted of DOC by percolating water; rather, we observed retention of DOC in E horizons throughout the year, mainly during early snowmelt and the fall season, but which we hypothesize are balanced or exceeded by losses due to mineralization.

In comparison, B horizon melanization/darkening (as indicated by DOC additions) is strongest in mid snowmelt and fall. B horizons realize large total gains in DOC in all seasons, even in summer (Fig. 7C), not only because of influxes of C from the E horizons above, but also due to their ability to retain and immobilize DOC, slowing its mineralization. Because of the lack of deep percolation events in summer, losses of DOC from the profile, i.e., through B horizons, are almost nil during the warm season (Fig. 7B).

3.5. Details of the temporal translocation of DOC

DOC is, in theory, the agent by which most metal cations get translocated during podzolization (Buurman and van Reeuwijk, 1984, Sauer et al., 2007). Thus, translocation (fluxes) of metal cations should generally follow the same temporal trends as DOC fluxes, and our data show that they generally do, although with subtle but important differences (Fig. 6). Key to this discussion may be an examination of *mass ratios* of DOC to metals in the soil water (Fig. 10), as podzolization theory states that chelated metal-cation complexes become insoluble if saturated with metals (Buurman and van Reeuwijk, 1984). O horizon leachate is high in DOC and comparatively low in Fe and Al, leading to high DOC/metal ratios and presumably unsaturated chelate complexes, i.e., metal cations are free to translocate in soil water (Fig. 10). These C compounds, migrating in soil water, are then able to complex free Fe and Al cations as the soil water passes through the upper profile. As a result, a marked lowering of the DOC/metal ratio is realized after soil water passes through E horizons (Fig. 10). Lower DOC/metal ratios for water exiting the E horizon show that DOC has complexed additional, free, metal cations, resulting in net losses of metal cations from the E horizon (Fig. 7C); this is the essence of podzolization, and it occurs in almost all seasons. In support of this point, net flux of DOC from E horizons peaks in mid snowmelt, paralleling the period of greatest net flux of *metals* (Fig. 7A). Similar associations occur in fall, when DOC transport peaks at the same time as transport of metals. Summer is a time of low DOC and metal transport from E horizons.

When compared to E horizon leachate, DOC/metal ratios *increase* for water leaving the B horizon, likely because saturated metal-chelate complexes precipitate in the B horizon, leaving unsaturated complexes and DOC unassociated with metals to pass through. However, such data for water leaving the B horizon is less meaningful than is the fact that far less water, DOC, Al, or Fe leave this horizon, in all seasons, than for the O and E horizons (Figs. 4A, 6). As a result, B horizons gain DOC, Fe and Al

Fig. 9. Photos showing soil water sampled during spring snowmelt, 2014. A. Water being pumped from the buried bottle, into a glass collection bottle. B. Determining the content of the leachate in the bottle. C. Comparison of soil water recovered from lysimeters beneath the (left to right) B, E and O horizons of a soil. Note the yellow-brown colors of the leachate, rich in DOC, in all the photos. Water leaving the B horizons in summer and early fall typically shows no yellow color at all. (For interpretation of the references to in this figure legend, the reader is referred to the web version of this article.)

over time, in all seasons (Fig. 7C). Gains in metals for B horizons are especially pronounced in early and mid snowmelt, declining into summer and then reaching their annual seasonal peak in late fall (Fig. 7C).

Fig. 7A confirms that O horizon leachate is a non-trivial source of Fe and Al cations in all seasons, implying that considerable amounts of Fe and Al are biocycled in this ecosystem (Fuss et al., 2011). As litter decomposes, metals are translocated into the mineral soil in percolating water. As with DOC, by late fall O horizon leachate shows large increases in metals, due to stripping of metals from fresh litter. More metals are released from O horizons in fall than in spring (Fig. 7B), although, as with other processes, at far slower rates (Fig. 6).

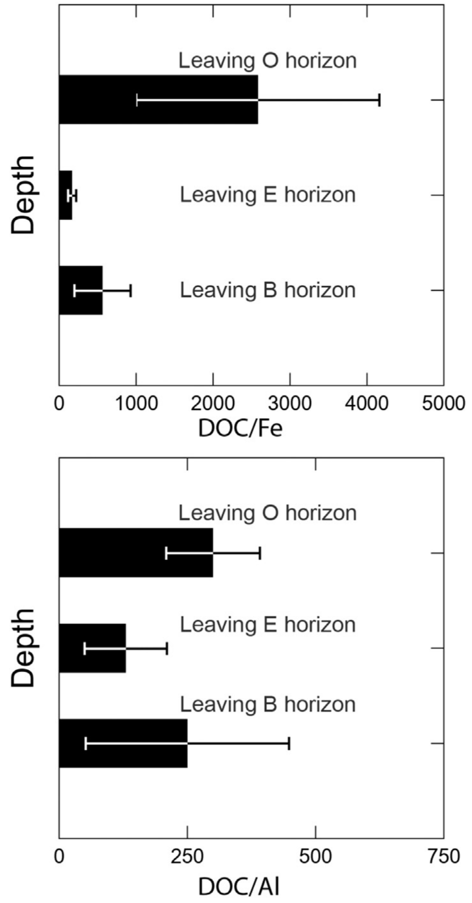

Fig. 10. Mass ratios (mean data) of DOC to metal cations in soil water, for the three depths of sampling, averaged over the two year period of study.

Translocation of Fe and Al cations through the mineral soil shows important and interesting temporal and depth trends. On an annual basis, contents of Fe and Al in soil water leaving E horizons are 1.80 and 2.69 times larger, respectively, than in water entering from overlying O horizons. Thus, E horizons generally accrue large net losses of Fe and Al, annually — the essence of podzolization (Fig. 7C). Net seasonal losses of metals from E horizons are exceptional during snowmelt (Fig. 7C). With regard to metal transport from E horizons, declining rates (Fig. 6) and totals (Fig. 7A) during snowmelt are likely due to (1) depletion of the soluble reserves of free cations in the eluvial zone above, and (2) declining DOC concentrations over time, for water entering the mineral soil from above (Fig. 8). Thus, despite their inert, quartz-rich appearance, E horizons here remain a source of Fe and Al to soil water, and thus they can supply metal cations to soil water whenever DOC also inputs exist to complex them. E horizons in these soils are particularly bright and poor in weatherable minerals (Fig. 2), suggesting that few cations would normally be released from primary minerals each year. As a result, any such cations could quickly be complexed and translocated out of the E horizon, provided that DOC is present in freely percolating water. As with DOC, the amounts of metals translocated out of E horizons and into B horizons peak again in late fall (Fig. 7C), although this peak is much more pronounced for Al than for Fe (Fig. 7C).

qqLosses of metal cations from the B horizon, i.e., from the soil system, are comparatively low throughout the year, averaging only 23.3 μg Fe $\mathrm{cm^{-2}}$ and 42.3 μg Al $\mathrm{cm^{-2}}$ annually (Figs. 7A, B). As a result, B horizons realize net gains of metals in all seasons, but especially during mid snowmelt and in late fall (Fig. 7C). Net losses of metal cations from the E horizon – a hallmark of podzolization –– vary between the two cations (Fig. 9). The largest losses of Fe occur during snowmelt, whereas for Al, the largest losses occur in both snowmelt and late fall (Fig. 7C). High inputs of metals to E horizons in fall may be due to stripping of metals from fresh litter, which as noted above does contain non-trivial amounts of Fe and Al. Thus, E horizons may actually realize net retention of metals (especially Fe) in early fall, but by late fall most of these metals are nonetheless effectively flushed to the B horizon by steady rains.

On an annual basis, considerably more Al moves in soil water than Fe; 1.9 times more Al than Fe is translocated out of E horizons, and 1.8 times more Al is lost from B horizons.

3.6. Contributions to pedogenic theory

Our data confirm, and add considerable detail to the previously unsubstantiated hypothesis of Schaetzl and Isard (1991, 1996) that thick snowpacks and the large, almost continuous pulse of cold, snowmelt water they produce play a key role in podzolization (Schaetzl and Harris, 2011). And subsequent work, using modeled hydrologic data, has added support to this theory (Schaetzl et al., 2015). We caution that our findings may not be universal, and are most applicable to areas in the snowy, cool, mid- and high latitudes.

Our work builds on this body of work by using empirical data from soil water – the type of data that reflect the actual, ongoing process (Ugolini et al., 1977a, 1977b, 1988, Ugolini and Dahlgren, 1987) – to confirm some parts of, and modify other parts of this theory. Specifically, the data confirm the importance of DOC to the podzolization process and transport of metal cations in these soils; podzolization peaks at times when fresh litter and potentially soluble C contents on the soil surface are maximal, releasing large amounts of DOC (and metals) to the soil system. Our data also confirm that podzolization *rates* are particularly large during snowmelt, especially during early and mid snowmelt, when ample amounts of labile C are able to be translocated from the O horizon in freely percolating snowmelt water (Fig. 6).

In this snowy climate, net fluxes of water during the short snowmelt season are considerably (1.15 times) larger than for all of the fall season. Overall, the net gains of spodic compounds by B horizons are high in mid snowmelt, low in summer, and peak in fall, especially late fall (Fig. 7C). Thus, our data add a new dimension to podzolization theory, i.e., podzolization in snowbelt and thick snowy areas may have a distinctly bimodal temporal distribution. Indeed, the late fall period appears to be most important for B horizon genesis and development in our study area. In addition, it is clear that the B horizons are efficient "traps" for DOC, despite their sandy textures and rapid permeabilities, i.e., little DOC leaves the soil (Figs. 6, 7).

An unexpected finding of this study centers on the net retention of DOC by E horizons, which occurs throughout most of the year, as DOC-rich water is transported in from the thick O horizons above. The bright, well-developed E horizons at the study site (Fig. 2) must, therefore, realize long-term losses of C to mineralization that at least balance out any gains via percolating water. The balance of processes we discuss here allows E horizons to thicken and brighten over time, while B horizons below darken and become redder due to almost continuous gains of DOC and metals.

Earlier theory, mentioned above, had assumed that summer was a time of minimal pedogenesis in soils undergoing podzolization, due to the often dry conditions, and our data support this assertion (Figs. 4A, 6, 9). Nonetheless, during heavy summer rain events, as occurred at our sites in 2013, translocation of significant amounts of DOC and metals can and does occur (Rothstein et al., under review; Fig. 9). It is the general paucity of such events in most years that makes summer a period of weak podzolization.

New to this study are data that show the importance of the fall period to podzolization. Indeed, late fall may summarily be the most important period for podzolization in this area; net gains of metals and DOC in B horizons are all large in fall, especially late fall, as are net losses of Al from E horizons (Fig. 7C). However, examination of data in Fig. 6 paint an important distinction — during snowmelt, *rates* of translocation are highest. Daily flux data show that the early and mid snowmelt periods are a time of intense podzolization; *cumulative* podzolization may be greater in fall, but this is due mainly to its comparatively greater (almost twice as long) duration (Fig. 10).

Spring snowmelt and fall represent times when soil water is often moving under saturated conditions. Partly for that reason, our study design may disproportionately represent these periods and may underrepresent summertime pedogenesis, when more water is moving as unsaturated flow. Our study did not capture the latter kinds of data, leaving the door open to future research, perhaps using tension lysimeters. Nonetheless, because of the single-grain structure and lack of silt and clay in these soils, unsaturated flow should not dominate water fluxes here.

4. Summary and conclusions

We used data on soil water moving as saturated flow and captured in zero-tension lysimeters installed in six Spodosol pedons, to examine the temporal variation in fluxes of water, DOC, Fe and Al. These data help enrich our understanding of podzolization, illustrating when various processes are operative, and how they vary in strength throughout the year.

In the study area, snowpacks are often thick and podzolization is intense. Spodosols here are strongly developed. Our study period spanned two full years, during which time we acquired 505 water samples on 36 sampling dates. In both winters, snowpacks accumulated to normal or greater-than-normal depths. One summer was wetter and stormier than normal, while the other was near normal with respect to precipitation.

Fluxes of saturated flow are, as expected, largest and most rapid during snowmelt. Although fall rains also add considerable water to the soils, this flux is spread over a longer period of time, and thus, is not the short, intense "pulse" that epitomizes snowmelt. Although the snowmelt period has been thought to be key to podzolization in snowy areas, it also appears that soils here also undergo a slower, more prolonged – but equally important – period of podzolization in the fall. B horizons realize maximal gains in DOC and metals during the long, sometimes persistently wet, fall season, enhanced by a thick mat of fresh litter that is easily stripped of C and biocycled metal cations. Nonetheless, snowmelt here remains a time of intense translocation and pedogenesis; rates of translocation of soluble compounds are all maximal during the early snowmelt period, decreasing later. Fluxes of DOC are particularly pronounced during the early and mid snowmelt periods, and in late fall. Fluxes of metal cations peak later during snowmelt, suggesting that early DOC additions to the mineral soils are unable to complex and translocate all available "free" metal cations. Fluxes of water, and hence, podzolization, are episodic in summer, occurring mainly when large thunderstorms produce deep percolation events.

Together, our data represent important additions to pedogenic theory for soils like these. The moist, permeable and unfrozen soils lie under a thick snowpack throughout the winter, primed for the brief but intense snowmelt flux/pulse of saturated flow, with its large load of DOC. This 28–40-day pulse of snowmelt water results in an intense but comparatively short burst of pedogenesis. During summer the soils are often dry, but weathering of primary minerals and mineralization of surface litter and C compounds within the mineral soil are ongoing. Translocation is almost entirely limited to infrequent, large storm events. Most soil water in summer is in unsaturated conditions; DOC and metal concentrations might be very high in soil solutions at this time, due to the lack of dilution. Summertime translocation, however, is minimal. After litterfall, intermittent fall rains drive DOC into the mineral soil. Thus, fall represents a slower, more protracted, period of pedogenesis, but one that is overall equivalent to snowmelt in many ways. Together, these two periods of deep percolation drive DOC rapidly and deeply into the mineral soil, leading to thick, white E horizons, and concomitantly forming B horizons enriched in C, Fe and Al.

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