

Effects of solution mining of salt on wetland hydrology as inferred from tree rings

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Abstract. Radial growth and concentrations of selected elements within rings were studied in white pine (*Pinus strobus*) trees from a wetland in central New York approximately 5 km north of a salt-solution mining field that operated from 1889 to 1988. Trees seemingly document three sequential episodes of mine-induced alterations of groundwater discharge irrigating the wetland during the 100-year period. The radial growth of trees established before the onset of mining declined abruptly in the early 1890s and remained suppressed until about 1960, as did growth of numerous other trees that became established after the onset of mining. Suppressed pre-1960 radial growth coincided with the interval that surface water was injected into the saltbeds, suggesting that losses of injected water to the bedrock and/or unconsolidated deposits increased groundwater flow into the wetland. An abrupt and sustained enhancement of radial growth beginning about 1960 indicates that the wetland became drier, and thus more conducive to tree growth, when injection practices were discontinued in the late 1950s despite the continued pumping of brine. Following the cessation of mining in the late 1980s, head pressures again increased in the upper valley, driving chloride-enriched flow northward along regional bedding-plane fractures and into the wetland. Large concentrations of chloride were detected within the most recently formed rings of some trees. As the result of chloride-enriched irrigation, the radial growth of some trees declined, and some trees died. Thus trees have preserved evidence of a century of hydrologic alterations, unobtainable by other means, where the effects of brine mining have not been documented previously.

Introduction

The rings formed each year by trees in temperate latitudes preserve evidence of local environmental conditions during or just prior to ring formation [Fritts, 1976; Stahle *et al.*, 1988; Cleaveland and Duick, 1992]. Because the year of ring formation can be determined precisely, environmental inferences from tree rings can be resolved at the scale of individual years. Thus “sensitive” trees, that is, trees in which the width, cell structure, and/or element composition of rings respond strongly to environmental variations, sometimes can be used to document past conditions if instrumented records are incomplete or lacking. This investigation of white pine (*Pinus strobus* L.) trees growing in a central New York wetland was conducted to determine the extent to which observed episodes of suppressed and enhanced radial growth have resulted from hydrologic alterations caused by solution mining of salt about 5 km to the south. In addition to measurements of ring widths, multielemental analysis of selected rings was performed to investigate historical changes in the quality of artesian flow irrigating the wetland. Thus the purpose of the study was only secondarily to assess the effects of solution mining upon tree growth; the primary purpose was to use tree rings to investigate 100 years of episodic hydrologic change, both in the amount

and quality of flow, at a location where hydrologic effects of salt mining have been unreported previously.

Hydrogeology of the Study Site and History of Solution-Brine Mining

The Tully Valley is approximately 30 km south of Syracuse, New York (Figure 1), in the Finger Lakes Region of the Allegheny Plateau. Bedrock beneath the valley floor is primarily shale with small amounts of limestone and sandstone and is overlain by about 130 m of unconsolidated glacial and post-glacial deposits. The elevation of the valley floor ranges from 250 m to the south to about 170 m near the wetland study area and from about 500 to 550 m along ridgetops to the east and west. Alluvial fans and floodplain deposits on the valley floor consist of silt, sand, and gravel and are underlain by interlayered glaciolacustrine clay, silt, and very fine sand. Two unconsolidated aquifers are within the glacial deposits: an upper freshwater unit composed of very fine sand to small gravel and underlain by a 3-m-thick layer of dense clay till; and a deeper brackish-water aquifer composed of mixed glacial deposits. Head pressures within both aquifers generate artesian flow 6–12 m above land surface.

Hydrology within parts of Tully Valley, including the study wetland, seemingly has been altered by solution brine-mining operations in the southern end of the valley. By the mid 1800s a considerable saltworks industry had developed in Syracuse

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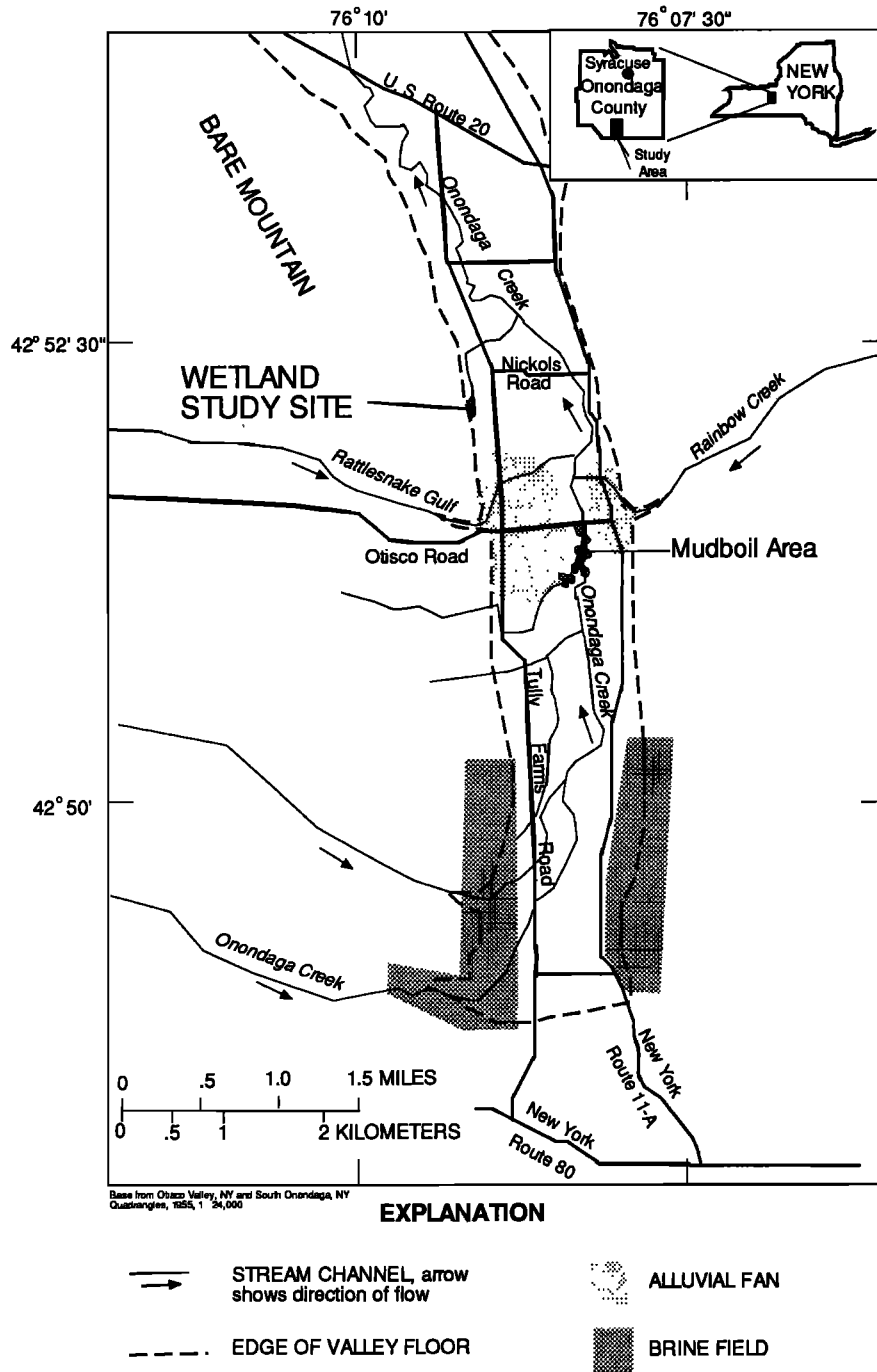


Figure 1. Map of Tully Valley showing location of solution-brine fields and study wetland.

adjacent to a series of salt springs along the western side of the city. Overexploitation of local salt springs spurred the discovery in the late 1880s of salt layers approximately 300–425 m below land surface at the southern end of the Tully Valley. Solution-mining operations were established in 1889 and continued until the late 1980s; a total of approximately 90 million metric tons of salt were removed [Walker and Mahoney, 1993]. Operators drilled along both valley walls (Figure 1) and injected surface water from lakes 150 m higher than wellheads to lift the saturated brine. Company records from near the turn of the century estimated that 40–60% of injected waters were “lost” [Larkin, 1950] to bedrock fractures and/or unconsoli-

dated glacial deposits. Mining operations along the eastern side of the valley ceased in 1957. Injections continued along the western side of the valley until about 1958 or 1959, after which infiltration of ground water into the salt caverns was sufficient to supply all the brine needed. Up to 3.8×10^9 L of brine per year were pumped after injection practices were abandoned. Mining activities were reduced greatly in 1986 and ended in 1988.

Mining operations caused land subsidence at the southern end of the valley, possibly as early as the 1920s. Large collapses occurred or were discovered during the 1940s, and subsidence since the 1950s has ranged from 1.5 to 7.5 m [Walker and Mahoney, 1993]. Several sinkholes also developed within both

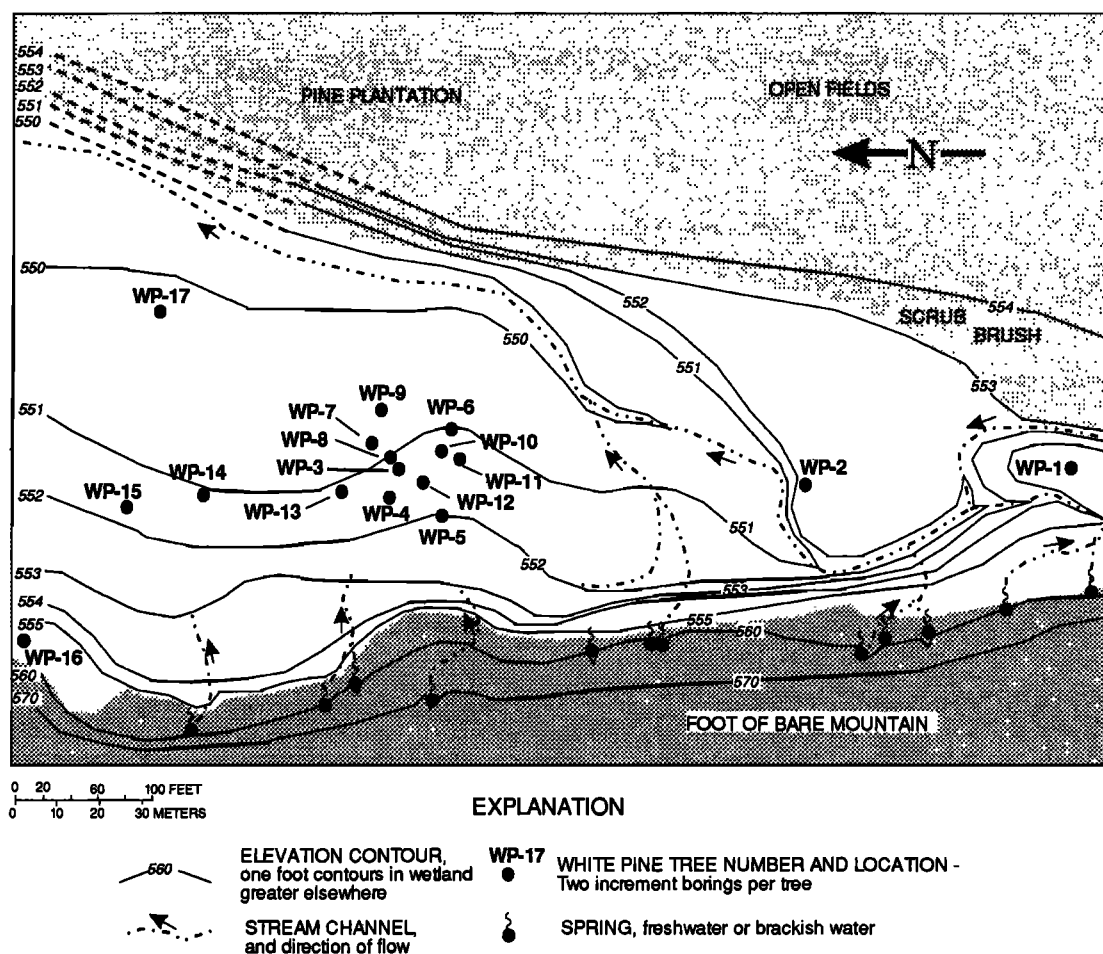


Figure 2. Map of study wetland showing location of 17 white pine trees and freshwater and brackish springs.

mining fields. The cracking and collapse of rock overlying the salt deposits probably allowed formerly discrete fracture systems within the bedrock and highly permeable glacial drift to become interconnected and contribute water to the salt caverns, sustained in part by enhanced recharge from surface streams.

Mudboils (miniature volcano-like cones discharging turbid groundwater and fine sediment) were first reported in 1899 on the valley floor near Onondaga Creek (Figure 1), about 2.5 km north of the brine fields. Mudboils are not known to have been caused by salt mining. Increased mudboil activity and resulting land subsidence in the late 1970s may have resulted from a breach in the confining clay-till layer between the underlying freshwater and brackish-water aquifers. Mudboil activity caused the collapse in 1991 of a bridge over Onondaga Creek and necessitated the rerouting of a petroleum pipeline and buried telephone cables [Kappel, 1995].

The study site is a small (1 ha) wetland at the base of Bare Mountain, in the northwestern part of Tully Valley about 5 km from the brine fields (Figure 1). The wetland is bounded to the east by open fields and a small pine plantation (Figure 2). Wetland soils are poorly drained Fonda mucky silty clay loams derived from silty clay and generally limit tree roots to the upper 30 cm of soil [U.S. Department of Agriculture (USDA), 1977]. Sources of water to the wetland consist of freshwater and brackish (sulfurous) springs at the foot of the hillside. Freshwater springs are recharged rapidly by precipitation in-

filtrating the shallow colluvium and highly weathered till and upper bedrock on the slopes of Bare Mountain. Discharge typically is least in summer, increases in fall, remains fairly stable throughout winter, and increases again during the spring in response to rain and snowmelt. The brackish springs are fed from longer, deeper flow systems through the shale bedrock. Brackish discharge is more uniform than freshwater discharge, although brackish flow typically is greatest during the spring. Brackish water contains high concentrations of sulfate, sodium, and chloride (Table 1). Thus freshwater and brackish water discharge into the wetland during the spring, but brackish discharge predominates during summer. Several small drainageways traverse the wetland and join to form a small stream that carries outflow to the northeast. Field reconnaissance in 1994 determined that the flow of this stream is derived entirely from the freshwater and brackish-water springs at the base of Bare Mountain.

Anecdotal information from local residents suggests that flow of the small stream draining the wetlands may have increased and become more brackish since the mid to late 1980s. The presence within the wetland of a scattered forest of white pines, some with dying foliage and thinning crowns, suggested that the vigor of trees had declined since the mid to late 1980s, perhaps in response to alterations in the amount and/or quality of flow irrigating the wetlands. Chloride-enriched water originating from the upper valley may have flowed along a bedding-

Table 1. Selected Element Concentrations and Chemical Properties for Water Samples From Springs at and Near Study Wetland

Analysis	Fresh-water ^a	Fresh-water ^a	Brackish ^b	Brackish ^c
Calcium	65	66	680	250
Iron	0.09	2	<0.05	0.08
Magnesium	14	13	260	90
Manganese	<0.05	<0.05	0.24	<0.05
Potassium	<5.0	<5.0	15	<5.0
Sodium	4	17	2,800	780
Chloride	2	22	5,300	1,700
Sulfate	72	92	890	390
Specific conductance ^d	440	520	16,000	5,900
Total alkalinity	180	170	105	130
Total solids	340	370	10,000	3,700
pH ^e	7.5	7.7	6.6	7.7

Concentrations are dissolved, in milligrams per liter.

^aSprings at base of Bare Mountain, just south of study wetland, May 1994.

^bSpring discharging into study wetland, November 1994.

^cSame spring but with freshwater dilution, May 1994.

^dIn microsiemens per centimeter.

^eIn standard units.

plane fracture and into the wetland as the result of an increase in hydraulic heads following the cessation of mining in the late 1980s. Because increment corings showed that some trees germinated before or just after the start of mining within the valley, it seemed reasonable that these trees might preserve evidence of any additional hydrologic alterations of the wetland that occurred before the mid to late 1980s.

Tree Ring Analyses

White pine generally is clustered near the center of the wetland on moss-covered hummocks at elevations 0.3–0.6 m above the small drainageways that traverse the wetland. Only a few pines grow in northern and southern parts of the wetland (Figure 2). Pines range in age, diameter, and height from approximately 20 to 130 years, 17 to 47 cm, and 5 to 10 m, respectively. Numerous trees were observed in poor health in late 1994, particularly within the central part of the wetland, and at least four died during the ensuing year. Hemlock (*Tsuga canadensis* (L.) Carr.) is prevalent along the wetland edge at the foot of Bare Mountain, although a few grow within the northern and southern parts of the wetland. Other wetland vegetation consists of alder (*Alnus rugosa* (Du Roi) Spreng.), cattails (*Typha*), and various graminoids and mosses.

Two corings from opposite sides of 17 white pines were collected at breast height after the 1994 growing season with a steel increment borer. Cores were placed to dry in paper drinking straws and subsequently sanded to a fine surface with 320 grit sandpaper. After measuring each ring to the nearest 0.01 mm, the rings of each paired cores were crossdated with each other (the process whereby each ring is assigned an exact year of formation) and averaged together to form one composite ring width series for each tree. Because the rings of most mature trees typically are widest near the center and become progressively narrower near the bark, many dendrochronologists prefer to convert individual ring widths to ring areas when evaluating growth during the life of a tree or among groups of trees [Phipps, 1984; Hornbeck and Smith, 1985]. The area of each ring depends on its width and its distance from the in-

nermost ring, that is, on its relative position along the entire core radius. Thus the overall trend is for ring areas to increase linearly as a tree grows older and larger, although surprisingly little is known about tree-growth dynamics in natural settings. If desired, ring-area data can be smoothed by fitting a negative exponential function or spline [Cook and Peters, 1981] to the raw data. The transformed series has a slope proportional to the rate of tree growth, but the smoothing process also removes yearly fluctuations caused by rapid or slow growth in response to environmental variables [Phipps and Whiton, 1988]. For this reason, radial-growth analyses in this study were based on raw-ring areas.

The smoothing function also is used in the standardization process to remove growth trends and construct estimates of the environmental "signal" within rings [Fritts, 1976]. In this procedure, raw width or area values are divided by their corresponding smoothed values, resulting in the construction of a dimensionless index for each ring. A single chronology is produced by averaging corresponding indices from each individual tree in the collection. Chronology indices are calibrated with existing instrumented records to produce a regression used to estimate ("reconstruct") a desired environmental variable from rings that formed before the calibration period [Fritts, 1976; Stahle et al., 1988; Cleaveland and Duvick, 1992]. Reconstructions require trees with a common pattern of ring width indices indicative of a common response to environmental factors, generally regional climate. A chronology was not constructed from the study trees, nor could a useful chronology have been possible owing to standardization difficulties caused by the highly suppressed rings of some trees. Instead, each tree was considered individually because growth most probably is controlled primarily by highly localized hydrologic conditions within the wetland rather than by regional climate.

A subset of five white pine trees (Table 2) was selected for multielement analysis by proton-induced X ray emission (PIXE). Cores were mounted in a specially constructed lucite holder and scraped to a flat surface with a high-quality stainless-steel scalpel. A proton beam with a fixed length of 2.0 mm was used to perform 6–12 analyses per core. The same suites of rings could not be analyzed in all five trees because of differences in age and ring widths. Thus in some instances an irradiation encompassed only one ring; in other cases, 2–10 small rings were analyzed simultaneously by a single irradiation. All together, 40 irradiations encompassing at least 125 rings or parts of rings were performed.

Calcium and potassium generally are the most highly concentrated (>1000 µg/g) elements detected by PIXE within tree rings, and smaller concentrations (in some cases <1.0 µg/g) are detected of approximately another dozen essential nutrients and trace elements [McClenahan et al., 1989; Yanosky and Vroblecky, 1995]. Variable concentrations of nonessential elements are sometimes detected, including those of lead, cadmium, nickel, chloride, sodium, and bromide. Chloride and sulfur were of particular interest because each is highly concentrated within brackish springs that discharge to the wetland (Table 1); accordingly, the respective concentrations within rings might reflect their historical availability for uptake by trees.

Radial Growth of Study Trees

Radial Growth During the Period of Injection Mining

White pine most typically grows on well-drained loam and sandy soils but occasionally becomes established on poorly

drained sites if hardwoods are absent [USDA, 1965]. White pine is classified as a facultative upland species [Reed, 1988] that "occasionally" is found in northeastern wetlands (estimated probability 1–33%). Radial growth of white pine at poorly drained sites, such as the study wetland, would be expected to be less than that of upland grown trees. However, the extremely suppressed pre-1960 growth noted in many study trees coincides with the interval during which surface-injection mining practices have been documented. If tree growth was suppressed by mine-induced overwatering of the wetland, it seems likely that trees established before the onset of mining would have formed wider rings than those postdating the onset of mining and that the duration of suppressed growth would approximate that of injection-mining practices. Furthermore, increased discharge of groundwater into the wetland would be expected to diminish the rapid juvenile growth (the initial 20 or so years) of trees that became established in the wetland after the onset of mining.

Unfortunately, only one tree (WP-4) had been growing for more than about 25 years before the onset of mining. The first measured ring at breast height formed in 1866, although the innermost (pith) ring probably formed 2–3 years earlier. Visual inspection of both cores collected from tree WP-4 shows that rings formed from the early 1890s to the late 1950s were much narrower than those formed before the early 1890s (Figure 3). Total radius length from the pith to the 1890 ring was about 50 mm, compared to only 20 mm from 1891 to 1957. This decline was far greater than that expected during the transition from juvenile to mature growth typically observed even in vigorous trees. The growth decline in tree WP-4 also was evident when ring widths were converted to ring areas (Figures 3 and 4) because, unlike the negative curvilinear trend of ring widths, the area-growth trend is expected to increase linearly even as rings gradually become narrower along the radius of growth [Phipps and Whiton, 1988]. Growth declines sometimes can be quantified by comparing actual growth to that predicted from previous growth [Phipps and Whiton, 1988]. For example, a positive linear growth rate constructed from areas of rings that formed from 1866 to 1889 in tree WP-4 (Figure 3) explained 65% of the variance between time and area ($F = 40.98$, $P < 0.01$). The model was used to predict growth of tree WP-4 at 5-year intervals from 1890 to 1955, during which surface-water injection mining may have altered wetland hydrology. The area of the 1890 ring (2.4 cm²) was well within the 95% confidence range of the predicted value (1.7 to 3.9 cm²); however, the area of the 1895 ring (1.0 cm²) was less than the lower 95% confidence limit of predicted growth (2.2 cm²), as were the areas of all other half decades from 1900 to 1955 (shown in Figure 3 only from 1890 to 1930). Disease, damage, or climatic factors could have caused a short-term growth decline of the magnitude observed in the early 1890s but would not be expected to suppress growth for nearly 70 years. Rather, the onset and duration of suppressed growth of tree WP-4 support the hypothesis that flows irrigating the wetland increased abruptly in the early 1890s and remained high until at least the late 1950s.

Tree WP-11 germinated in 1881 and grows approximately 20 m southeast from tree WP-4. Although tree WP-11 is the only other study tree predating the onset of mining, the small number of premining rings coupled with a slight decline in ring areas during the late 1880s (observed also in tree WP-4 and presumably caused by climate) resulted in an insignificant correlation between area and time ($F = 0.13$, $P = 0.73$). However, visual inspection of cores collected from tree WP-11

Table 2. White Pine Trees Selected for Growth-Trend Analysis

Tree	Diameter at Breast Height, cm	Year of Formation of Innermost Measured Ring ^a
<i>Southern Area</i>		
WP-1	35.8	1964
WP-2 ^b	35.6	1935
<i>Central Area</i>		
WP-3	29.0	1915
WP-4 ^b	34.0	1868
WP-5	27.2	1938
WP-6	24.4	1904
WP-7 ^b	26.2	1903
WP-8	17.3	1894
WP-9	18.0	1890
WP-10	26.4	1906
WP-11 ^b	22.1	1881
WP-12	22.4	1946
WP-13	18.0	1961
<i>Northern Area</i>		
WP-14	16.5	1900
WP-15 ^b	20.3	1889
WP-16	46.5	1952
WP-17	29.2	1975

^aJudging from the curvature of innermost rings, the center (pith) ring of most trees was within 2–4 rings of the innermost measured ring. The actual age of trees is greater (probably about 4–6 years) because cores were collected at breast height rather than near the base of the trunk.

^bTree also selected for element analysis.

showed that, as in tree WP-4, ring widths declined abruptly in the early 1890s (Figure 3) and continued to be narrow thereafter. Rings from 1881 to 1891 formed by tree WP-11 ranged from 0.4 to 2.3 mm but were less than 0.2 mm from 1892 to 1897; thereafter, radial growth was suppressed during the entire interval of surface-water injection mining (Figure 4). Thus the synchronized onset and duration of suppressed growth in trees WP-4 and 11 strengthen the assumption that wetland hydrology changed shortly after the onset of mining, although the lack of additional old pine trees makes this conclusion tentative.

Eight white pines in addition to trees WP-4 and 11 became established in central and northern parts of the wetland within about 25 years after the onset of mining. The amount and persistent trend of pre-1960 ring-area growth in seven of these trees (WP-3, 6, 7, 8, 9, 14, and 15) were comparable to the suppressed growth (<4.0 cm²) of trees WP-4 and 11 after the onset of mining (Figure 4); in the remaining tree (WP-10), radial growth increased between 1906 and the late 1930s (maximum ring area, 7.9 cm²) but declined abruptly thereafter (minimum ring area, 0.5 cm²) until 1960. Of these eight trees with suppressed pre-1960 growth, six are in the central part of the wetland, and two (trees WP-14 and 15) are in the northern part. Two additional trees (WP-5 and 12) became established within the central part of the wetland in about 1938 and 1946, respectively. Pre-1960 growth was suppressed in both trees relative to that of an adjacent tree (WP-13) that germinated just after 1960.

One study tree (WP-2) established about 1935 produced moderately suppressed rings until the mid-1940s, after which radial growth exceeded that of all other wetland trees established before the mid-1940s. Area growth of rings that formed from 1948 to 1960 ranged from 7.1 to 14.5 cm². This tree,

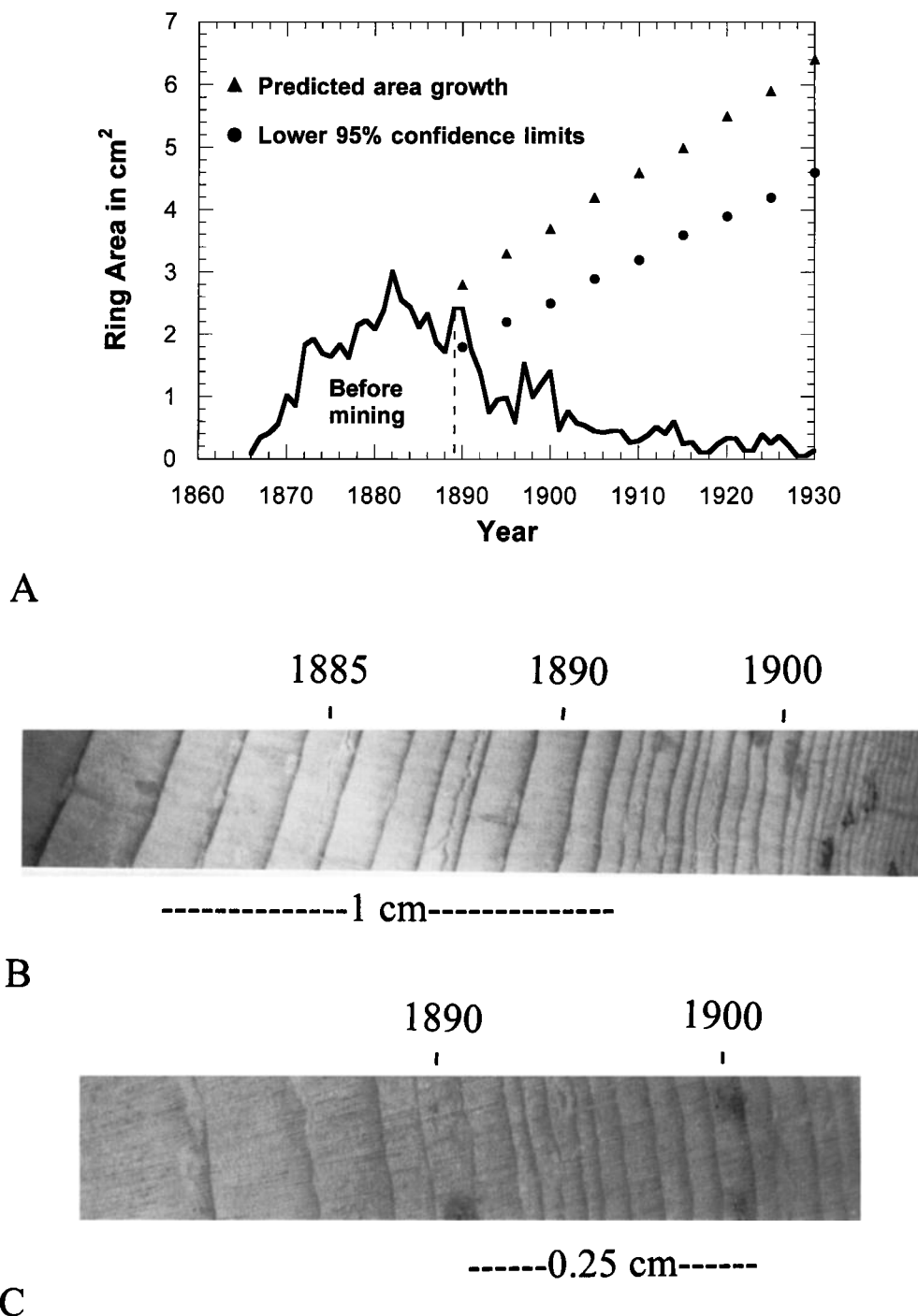


Figure 3. (a) Areas of the rings of tree WP-4 that formed from 1866 to 1930 and areas from 1890 and thereafter at 5-year intervals as predicted from actual growth from 1866 to 1889. (b) Photograph of part of a core from tree WP-4 showing a growth decline in the early 1890s, just after the onset of mining. Note crack in 1888 ring. (c) Photograph of part of a core from tree WP-11 showing a growth decline in the early 1890s.

however, grows about 80 m south of the closest central tree and does not receive flow from the same group of springs that irrigate the central area. Additionally, tree WP-2 is near a small channel (Figure 2) expected to divert at least some flow from the foot of Bare Mountain.

Radial Growth After the Period of Injection Mining

The abrupt and sustained increase in radial growth that occurred about 1960 or shortly thereafter in many study trees

(Figure 4) indicates that conditions for tree growth improved strikingly and quickly. According to *Lorimer* [1985], a growth enhancement consisting of 15 or more consecutive rings can be considered unrelated to climate. The growth release in wetland pines coincides with the closure of the eastern brine field in 1957 and the discontinuance 1–2 years later of surface-water injections into the salt beds. Pumping from the salt beds continued as before, however, and drawdowns of nearby domestic water wells were as much as 20 m, compared to the more

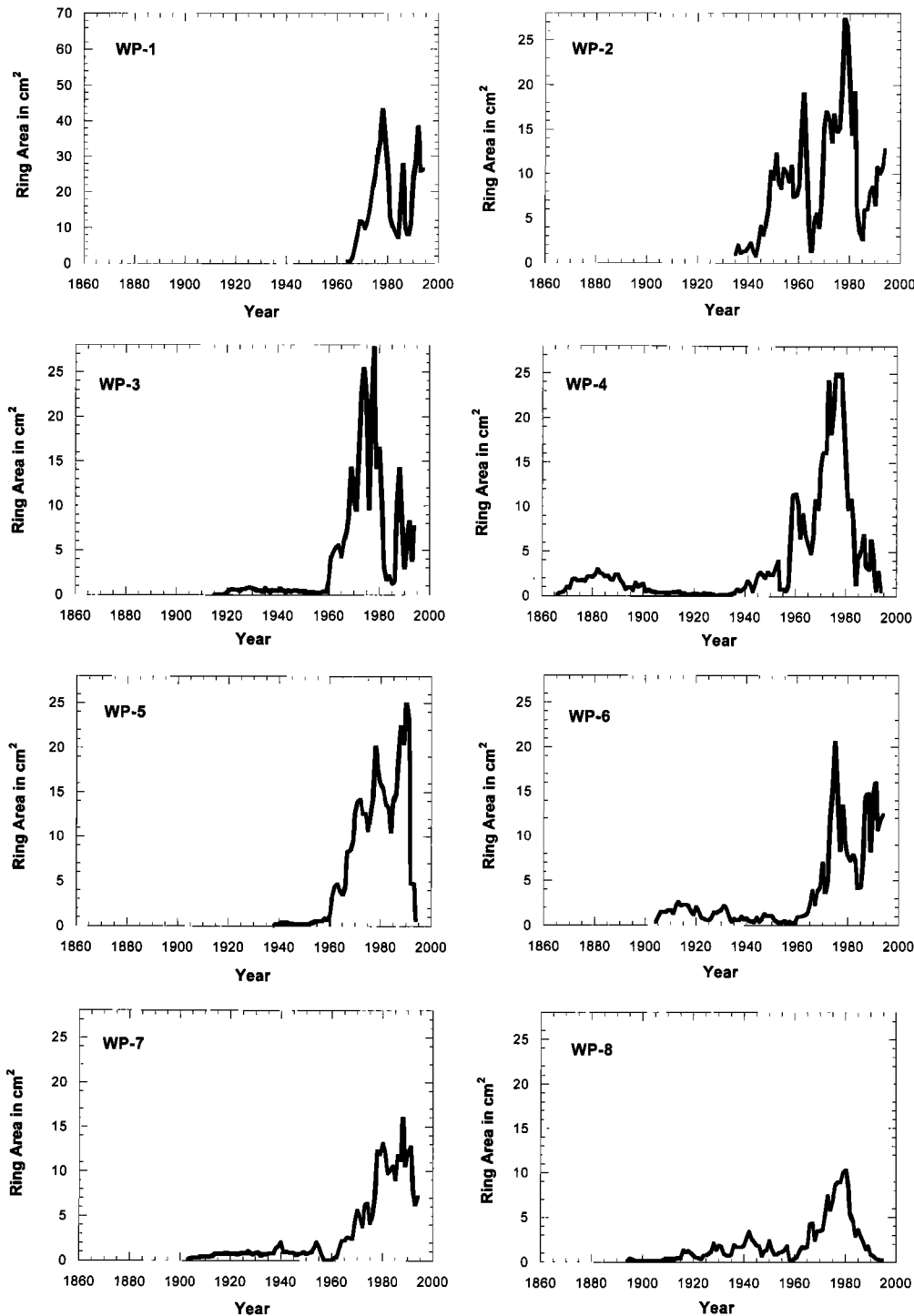


Figure 4. Ring-area measurements (growth trends) of 17 white pines, shown consecutively. Trees WP-1 and 2 are from the southern part of the wetland, trees WP-3 through 13 are from the central part, and trees WP-14 through 17 are from the northern part. Note that y axis scale of trees WP-1, 16, and 17 differs from that of the other trees.

typical range of 3–5 m. The decreased head in the bedrock near the south end of Tully Valley probably diminished the hydraulic gradient driving deep-circulation springs as far north as the wetland. Thus the discharge of brackish flow into the wetland would be expected to decrease, unlike that of freshwater springs. In addition to stimulating the growth of established trees, drier conditions within the wetland also would be

expected to favor vigorous juvenile growth in trees established after 1960.

Abrupt and sustained growth enhancements began about 1960 in 8 of the 10 central-area pines established no later than the mid-1940s. Enhanced growth in the remaining two trees (WP-10 and WP-11) began about 1970. The magnitude of the growth release in central-area trees was greatest (some post-

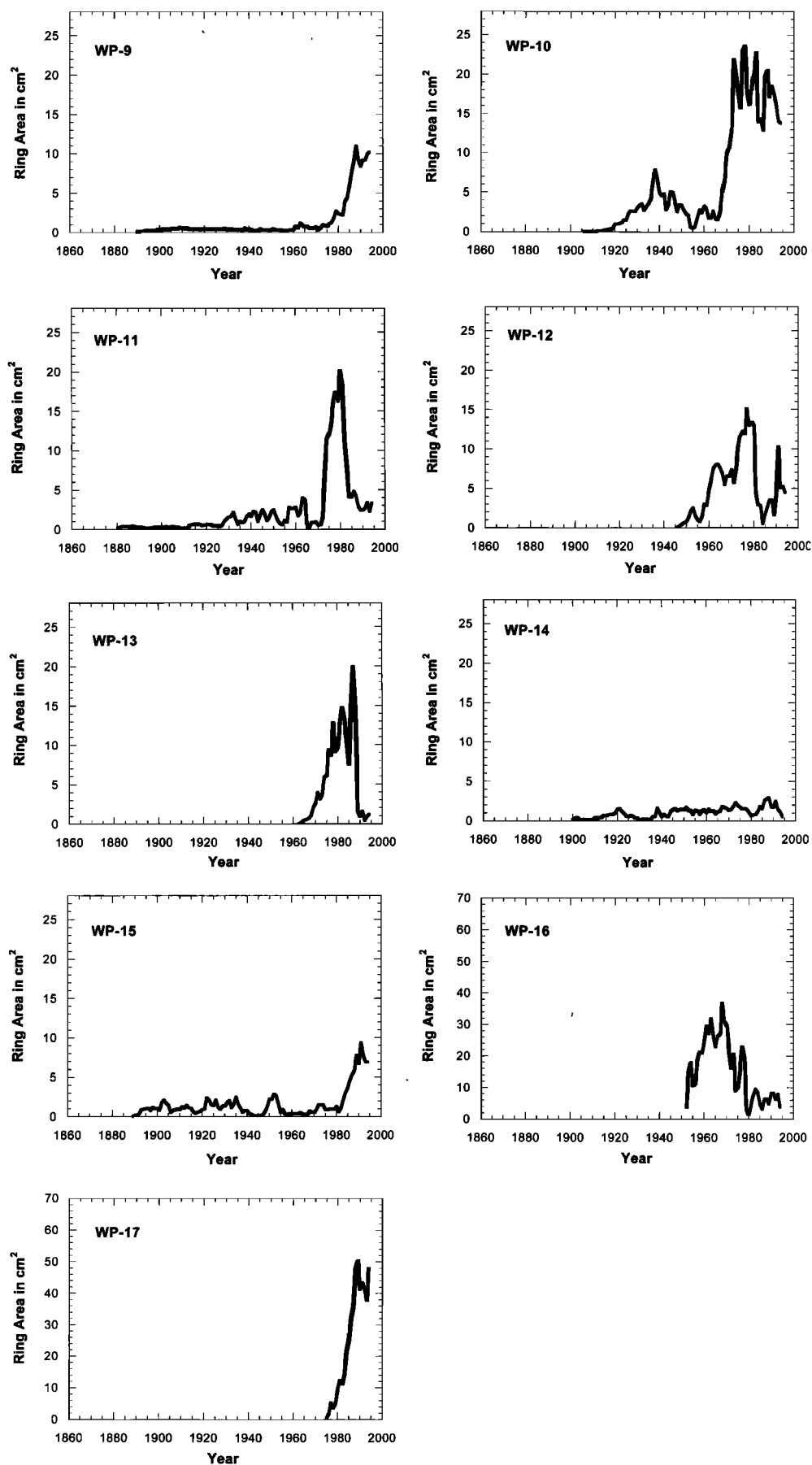


Figure 4. (continued)

1960 ring areas exceeding 20 cm²) in trees WP-3, 4, 5, 6, and 10, although some ring areas exceeded 15 cm² in trees WP-7, 10, and 12. As would be expected if conditions became more mesic within the wetland, a tree (WP-13) that became established within the central area in about 1960 produced juvenile growth that greatly exceeded that of adjacent trees established between the 1880s and 1940s. The area of the 1978 ring of tree WP-13 was 12.8 cm², and that of the 1987 ring was 19.9 cm².

Within the northern part of the wetland, suppressed growth continued from 1960 through 1994 in tree WP-14, as well as in tree WP-15 until the early 1980s, after which an abrupt growth release occurred (maximum ring areas approximately 8 cm²). By contrast, the two other trees (WP-16 and WP-17) within the northern part of the wetland began growth in the early 1950s and mid-1970s, respectively, and exhibited the most rapid juvenile growth of any tree sampled within northern and central parts of the wetland. Tree WP-16 grew along the wetland margin at an elevation approximately 1.2 m higher than surfaces supporting trees WP-14 and 15 and the central-area trees, possibly explaining why pre-1960 growth was not suppressed.

Tree WP-2, within the southern part of the wetland, did not exhibit severely suppressed growth before or after 1960. Moderately suppressed growth from 1963 to 1968, observed in tree WP-2 but not in other trees, may be attributed to regional drought during that time [Ku *et al.*, 1975]. Tree WP-1 became established in the mid-1960s at the southernmost end of the wetland and formed wide juvenile rings comparable to those of trees WP-5 and 17. Tree WP-1 grows on a surface that is 0.6–1.0 m higher than those of all trees within the central area and of trees WP-14 and 15 within the northern area.

Tree Growth Since the Cessation of Mining

The cessation of mining in 1988 probably increased groundwater flow into the wetland as the result of increased heads in the upper valley. Trees in the wettest areas would be expected to grow slower after 1988 than during the period of enhanced growth that followed the cessation of injection practices in the late 1950s. Growth of most southern- and central-area trees declined during the first half of the 1980s (Figure 4), presumably in response to a series of regional droughts [U.S. Department of Commerce, 1980, 1981, 1995] but generally recovered immediately thereafter. However, a decline in growth of some central-area trees since 1988 apparently was not caused by drought because growth reductions were unsynchronized and varied considerably among trees, suggesting that growth was limited more by local than regional environmental factors.

Tree growth since the cessation of mining in 1988 was evaluated from absolute and relative areas of the 1989–1994 rings. Generally, growth during 1989–1994 was considered suppressed if the cumulative area was less than 24.0 cm² (6 years × 4.0 cm²), and to have declined if the cumulative area of the 1992–1994 rings was less than half that of the 1989–1991 rings. Additionally, the average area of the 1989–1994 rings was considered to have declined if it was less than half that of the widest rings that formed during growth enhancements of the 1960s and 1970s. The combination of suppressed and declining growth was considered the most likely indication of a negative impact of recent environmental factors upon trees. Additionally, monitoring was conducted periodically during 1994 and 1995 to record yellowing and death of the most recent needle crops.

Within the southern part of the wetland, cumulative growth of the outermost six rings of trees WP-1 and WP-2 was 154.1

and 59.8 cm², respectively (Figure 4). Growth decreased in both trees during the early to mid-1980s, presumably from the effects of regional drought, but increased thereafter. Similarly, growth was neither suppressed nor in decline in three trees (WP-15, 16, and 17) within the northern part of the wetland, although an abrupt and persistent change in the growth rate of tree WP-16 during the late 1970s probably resulted from its damaged crown. Tree WP-14 was the only tree within the southern and northern parts of the wetland in which recent growth was suppressed and also in decline. However, the amount of suppressed growth of individual rings (0.7–3.7 cm²) is comparable to, and in some cases greater than, that of most pre-1989 rings. Thus it is difficult to determine if conditions affecting the recent growth rate of tree WP-14 have changed since the cessation of mining, even though tree WP-14 is closer to the central part of the wetland than any other northern or southern pine. With the exception of the old wound to the crown of tree WP-16, no external symptoms of decreased vigor were noted among southern- and northern-area trees during 1994. However, some browning of needle tips of tree WP-14 were observed in late 1995.

Within the central part of the wetland, however, four trees (WP-4, 5, 8, and 13) with thinning branches and some loss of the most recent needle crop during 1994 were, by all appearances, dead in 1995. Trees ranged in age from about 35 to 130 years. Death of all trees except WP-5 followed suppressed growth during 1989–1994; in tree WP-5, individual areas of the 1989–1991 rings ranged from 20.5 to 25.0 cm², but areas decreased abruptly thereafter (4.8, 4.7, and 0.7 cm² in 1992, 1993, and 1994, respectively). The decline preceding death was most striking in tree WP-5, but declines (as defined previously) also were detected in the remaining three trees, in which areas of the respective 1994 rings were 0.6 cm² (tree WP-4), 0.3 cm² (tree WP-8), and 1.2 cm² (tree WP-13).

Of the remaining seven central-area trees, growth of tree WP-11 was suppressed but did not decline further during 1989–1994; growth of the remaining six trees also did not decline, although growth of tree WP-7 from 1992 to 1994 was only 60% that from 1989 to 1991. The growth of these seven trees was reduced somewhat during droughts of the early 1980s, as was that of nearly all other study trees. However, the areas of rings that formed from 1989 to 1994 declined by at least 50% relative to maximum growth from 1960 to 1980 in trees WP-3, 11, and 12 but remained approximately the same in trees WP-6, 7, 9, and 10 (Figure 4). That is, the three former trees, but not the latter four, grew more slowly, on average, since 1989 than during the 1960s and 1970s, even though the rate of recent growth of each of the seven trees has remained fairly constant. Brown needle tips were noted in some central-area trees, and foliage in general seemed less lustrous than in trees to the north and south.

When the dead pines were grouped with the seven living central-area trees, a relation was noted between recent tree growth and distance from brackish springs irrigating the wetland. The three trees closest to springs (WP-4, 5, and 13) were living in 1994 but appeared to have died during 1995; the four farthest trees (WP-6, 7, 9, and 10) have the highest rates of recent growth and show little if any foliar symptoms of decreased vigor. However, of four trees occupying a more intermediate position, one (tree WP-8) died, and growth of the others (WP-3, 11, and 12) declined relative to maximum previous growth, and foliar symptoms indicative of declining vigor became progressively evident during 1995; death of trees WP-3

and 12 seems imminent based on a site visit in February 1996. Thus it seems likely that the pattern of tree growth and mortality within the central area was not caused exclusively by overwatering. Rather, tree growth might be affected by the eastward migration of chloride-enriched groundwater through the Fonda mucky silty clay loam soil, as will be discussed in the following section.

Element Analysis of Tree Rings

Episodes of suppressed and enhanced tree growth may have resulted from changes in the quantity of springflows irrigating the wetland, but the historical quality of flows cannot be estimated from ring areas alone. However, trees might preserve evidence of changes in flow quality if element concentrations within rings are proportional at least in part to those of flows irrigating the roots when the rings formed. This assumption is central to the dozens of studies using ring-element data to infer undocumented environmental histories. Some elements in the transpirational stream are complexed to the walls of water-conducting cells, whereas others are incorporated into newly synthesized ring-structural materials or stored within a system of living cells (rays) oriented perpendicular to the axis of transpirational flow [Cutter and Guyette, 1993].

In theory, an alteration in flow quality confined to a single year could be detected if the element composition of the corresponding ring reflected only element availabilities in the year of hydrologic change, that is, if element composition subsequently was not modified by movement of elements into or out of the ring following its formation. This lateral movement, or translocation, has been documented for some elements, although the extent of movement seems species specific and, perhaps, even site specific [Yanosky and Vroblecky, 1995]. Additionally, unlike some hardwoods, conifers seemingly transport water through more than one ring simultaneously [Bondi-etti and Momoshima, 1990; Kozlowski et al., 1991], although this process and its significance to element sequestration within rings remain poorly understood. Thus conclusions based on ring-element data require more circumspection than those based on ring width. Further assumptions, limitations, and applications of tree ring element studies are summarized by Cutter and Guyette [1993], Hagemeyer [1993], and Yanosky and Vroblecky [1995]. Ring-element studies have been applied with some success to several hydrologic problems, including contaminated groundwater [Vroblecky and Yanosky, 1990; Yanosky and Vroblecky, 1992; Yanosky and Carmichael, 1993], saltwater intrusion [Yanosky et al., 1995], and contaminated river sediments [Sheppard and Funk, 1975; Hupp et al., 1993].

Element analysis was performed on selected rings of three trees (WP-4, 7, and 11) from the central area, where suppressed and enhanced growth in turn were followed by the death of some trees, and on rings of one tree each from the southern (tree WP-2) and northern (tree WP-15) parts of the wetland. Selected rings that formed during the long episodes of suppressed and enhanced growth were analyzed in order to determine whether element concentrations preserved a generalized signal suggestive of flow-quality differences despite possible modifications by translocation or multiring transpirational flow. The constant 2.0-mm beam width resulted in the simultaneous analysis of as many as 10 extremely narrow rings but prevented the analysis of a suite of rings common to all trees. Analysis also was performed simultaneously of 2–4 rings just inside the bark, where conductance presumably is greatest

and ring-element compositions are most likely to reflect recent water quality [Yanosky et al., 1995].

At present, chloride and sulfur are highly concentrated in brackish waters irrigating the wetland (Table 1), and brackish flow within the stream draining the wetland has increased according to local residents. Sulfur is ubiquitous within the bedrock shales beneath the valley and along its walls; salt deposits are primarily within the deepest shales underlying the valley floor. Chloride and sulfur potentially could be subject to translocation on the basis of solubility and the ratio of ionic charge to ionic radius [Cutter and Guyette, 1993]. However, Vroblecky and Yanosky [1990] concluded that chloride was not translocated across ring boundaries in tuliptree (*Liriodendron tulipifera* L.), although chloride seemingly was mobile within rings of sassafras (*Sassafras albidum* (Nutt.) Nees) and southern red oak (*Quercus falcata* Michx.) [Yanosky and Vroblecky, 1995]. No evidence of chloride mobility was detected in baldcypress (*Taxodium distichum* (L.) Rich.) growing along a freshwater river, but those flooded periodically by saline water translocated chloride from outer to inner rings [Yanosky et al., 1995]. McClenahan et al. [1989] found no evidence of translocation of chloride or sulfur in tuliptree. Wardell and Hart [1973] found no evidence to suggest the enrichment of sulfur or chloride at the heartwood/sapwood boundary of white oak (*Quercus alba* L.); however, using an electron microprobe they found consistently higher concentrations of chloride and sulfur in ray tissue than in nonray tissue, within both heartwood and sapwood.

Element Concentrations Within Sapwood Rings

The sapwood is the outer series of rings conducting transpirational flow and in which storage cells remain living and element translocations sometimes occur. With time the innermost sapwood converts to heartwood and becomes nonfunctional [Bamber and Fukazawa, 1985]. The 15–20 sapwood rings of study trees appear lighter in hue than the darker-colored heartwood.

Tree WP-4 was the oldest known wetland tree and the only chemically analyzed specimen that died during the course of this study. The concentrations of chloride in sapwood rings of tree WP-4 ranged from 213 to 950 $\mu\text{g/g}$ but only from 83 to 197 $\mu\text{g/g}$ in heartwood rings (Figure 5). Chloride was most highly concentrated in the narrow ring series that formed during the 1990s, just before the tree died. Chloride concentrations in rings nearest the bark were 183 and 324 $\mu\text{g/g}$ in trees WP-7 and 11, respectively, exceeding the largest chloride concentrations within their heartwood rings by at least a factor of 2. It seems unlikely that the high concentrations of chloride in the outermost rings relative to earlier formed rings have resulted solely from chloride translocation from earlier formed rings. Rather, the large concentrations of chloride within the outermost sapwood suggest that chloride availability has increased recently in the vicinity of the three central-area trees. Additionally, the maximum chloride concentration in the sapwood of tree WP-4 is greater than that detected in hundreds of rings that we have analyzed at the U.S. Geological Survey, with the exception of baldcypress trees growing in a saltwater-intruded estuary [Yanosky et al., 1995].

Tree WP-2 contained sapwood concentrations of chloride that are similar to those in some heartwood rings, although concentrations were greater within the sapwood than within the outer heartwood. However, the concentration of chloride in the outermost analyzed sapwood was less (174 $\mu\text{g/g}$) than

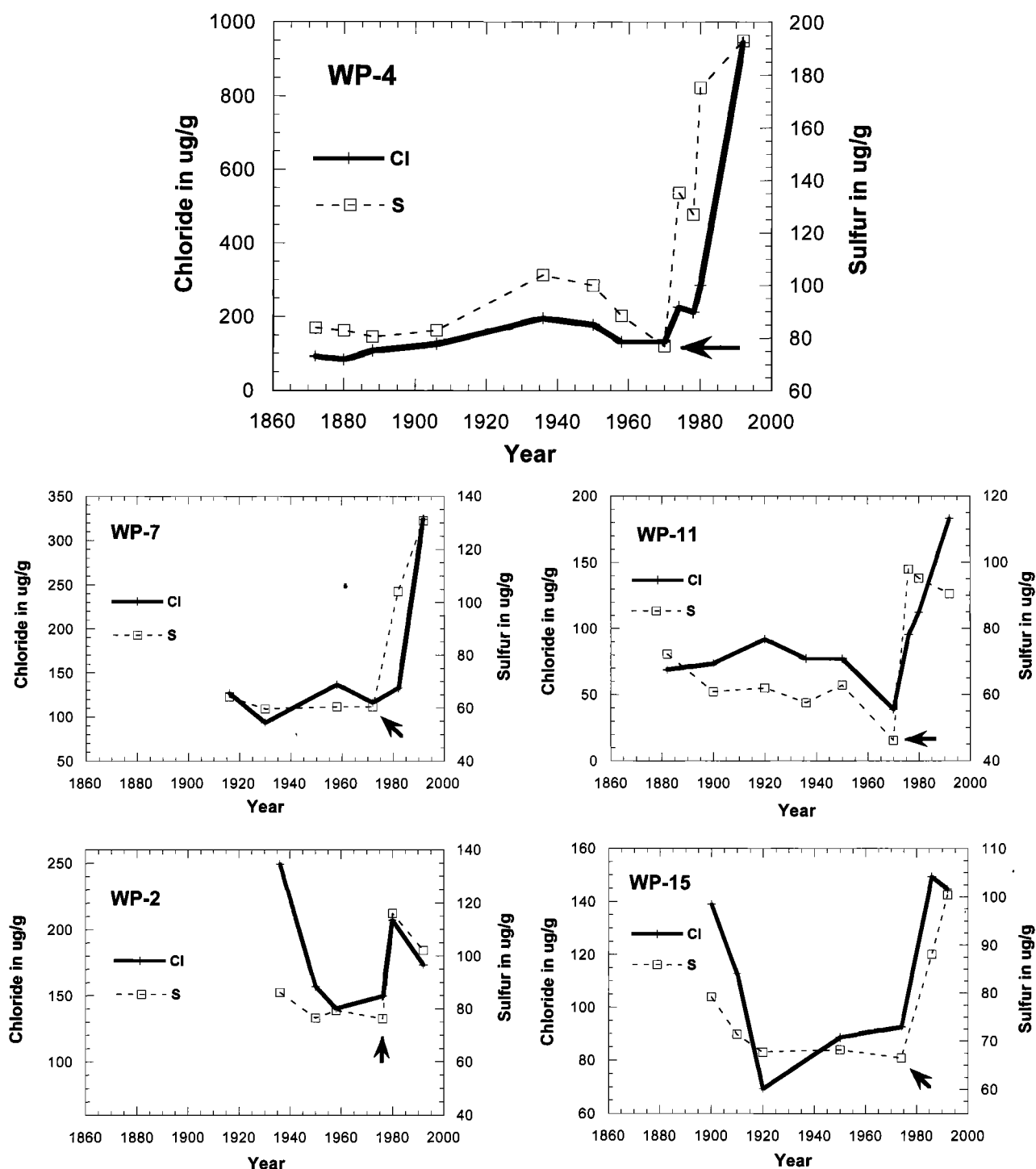


Figure 5. Concentrations of chloride and sulfur in rings of three trees from the central part of the wetland (WP-4, 7, and 11) and one each from the southern (WP-2) and northern (WP-15) parts. Arrows indicate the outermost (youngest) heartwood; rings to the outside (right) of arrows are in the sapwood. Note the y axis scale of chloride, tree WP-4.

that in the innermost analyzed sapwood (207 $\mu\text{g/g}$). Similarly, tree WP-15 contained nearly the same concentration of chloride in the innermost (145 $\mu\text{g/g}$) and outermost (150 $\mu\text{g/g}$) analyzed sapwood, and these concentrations were comparable to those of at least some heartwood rings. In contrast, chloride was 2–4 times more highly concentrated in the outermost than inner sapwood of central-area trees. Additionally, the ratio of

chloride in the outermost sapwood rings to that of the average heartwood concentration was 7.3 in tree WP-4, 2.6 in tree WP-11, and 2.7 in tree WP-7, but only 1.0 and 1.4 in trees WP-2 and 15, respectively. Thus chloride availability apparently has not increased recently near trees WP-2 and 15, which grow considerably south and north, respectively, of the central area.

The sapwood concentrations of sulfur in each tree exceeded

those of all respective heartwood rings. Sulfur is essential to plant growth [Kabata-Pendias and Pendias, 1984], and thus concentrations in the sapwood might be maintained at least in part by translocation. Trees with the highest sapwood concentrations of chloride (trees WP-4 and 7) also contained the highest sulfur concentrations, including five of the six highest concentrations within all wetland trees. The ratio of sulfur in the outermost sapwood rings to that of the average heartwood concentration was 2.2 and 2.1 for trees WP-4 and 7, respectively, and 1.5, 1.3, and 1.4 for trees WP-11, 2, and 15, in turn. It seems possible, therefore, that the availability of sulfur may have increased recently within part of the central region of the wetland.

The outermost sapwood of central-area trees also contained larger concentrations of iron (24–57 $\mu\text{g/g}$) than did trees WP-2 (10 $\mu\text{g/g}$) and 15 (15 $\mu\text{g/g}$). The concentration of calcium in the outermost sapwood of tree WP-4 was 1,170 $\mu\text{g/g}$, compared to a range of 622–701 $\mu\text{g/g}$ within the remaining sapwood; no other study tree contained more than 471 $\mu\text{g/g}$ within outermost sapwood rings. Generally, calcium concentrations in conifers decline from the pith to the outermost rings [Bondietti *et al.*, 1989]. Calcium was more highly concentrated in brackish waters irrigating the wetland than in adjacent fresh waters (Table 1).

The high concentrations within rings of calcium, chloride, and sulfur, and the abrupt growth decline followed by death, suggest that tree WP-4 grew within a part of the central area where ionic stress was greatest or first began to limit the recent growth of trees. Trees WP-7 and 11 are more distant than tree WP-4 from springs irrigating the wetland (Figure 2) with brackish flow, contain large concentrations of chloride in the outer sapwood relative to inner sapwood and heartwood (Figure 5), and, as defined earlier, show a recent growth suppression (tree WP-11) or growth decline (tree WP-7) (Figure 4). It seems likely that both trees will succumb to deteriorating conditions within the wetland, as may all central-area trees.

Element Concentrations Within Heartwood Rings

The conversion of a sapwood ring to heartwood may be accompanied by the depletion or enrichment of some elements during the conversion process. After a sapwood ring converts to heartwood, its element composition does not change unless the heartwood/sapwood boundary is susceptible to diffusion. For example, phosphorus and potassium in many tree species are translocated out of heartwood-converting rings and into the remaining sapwood [Bamber and Fukazawa, 1985]. Thus concentrations of these elements are lower in heartwood than in sapwood even if element availabilities remain constant. In contrast, reverse translocation sometimes occurs if an element is concentrated in excess of physiological requirements. For example, Vroblesky *et al.* [1992] found that tuliptrees typically translocated potassium from inner to outer rings, but that trees growing over a potassium-contaminated aquifer contained greater concentrations of potassium in heartwood than in sapwood rings. Apparently, concentrations of potassium in excess of metabolic requirements were translocated from outer to inner rings and thus into permanent storage within heartwood.

Inspection of the concentrations of chloride near the heartwood-sapwood boundary of the five study trees suggests that chloride may be translocated to some extent from inner to outer rings during the conversion of sapwood to heartwood. However, even though the element composition of heartwood rings may change since the rings were produced by the cam-

bium, an element “signal” useful for historical interpretations of element availability may nevertheless sometimes be preserved [Yanosky *et al.*, 1995]. Most, if not all, heartwood rings analyzed by PIXE probably converted from sapwood to heartwood before the cessation of mining in 1988 and thus would be expected to contain only locally derived chloride rather than also some from the upper valley. If wetland irrigation increased shortly after the onset of mining, as suggested by the ring-area growth of the oldest trees, it seems reasonable that heartwood rings might preserve a record of chloride- and sulfur-containing flows derived from the lower valley but driven by hydraulic forces originating in the upper valley. The extent to which the timing of increased element concentrations coincides with that of documented mining practices would be expected to depend on the degree to which ring-element compositions have been modified by translocation or multiring transpirational flow. However, the purpose of the element analysis of heartwood rings was to determine if, rather than when, flow quality changed during the 70 years following the onset of mining. Interpretations of heartwood-element concentrations were based on relative concentrations within each tree rather than on absolute concentrations among trees.

Eight irradiations were performed within the heartwood of tree WP-4, the oldest and most intensely sampled tree (Figure 5). Three irradiations performed on the ring series that formed from about 1870 to 1886 yielded chloride concentrations of 94, 83, and 108 $\mu\text{g/g}$, respectively. However, concentrations were 127, 197, and 179 $\mu\text{g/g}$, respectively, in three irradiations performed within part of the suppressed ring series that formed from the early 1890s until just before 1960. Two of these irradiations were of about 10 rings simultaneously, the centers of which formed in the late 1900s and the mid-1930s, respectively. Two irradiations performed on rings that formed after the start of the late-1950s growth enhancement contained only 133 and 135 $\mu\text{g/g}$, respectively. The concentration pattern along the heartwood-core radius of tree WP-4 suggests that the availability of chloride increased after the onset of mining and decreased after the cessation of surface-injection mining practices, but it seems unlikely that chloride burdens within the wetland contributed significantly to growth suppressions or enhancements. Modification of heartwood-chloride concentrations either has not occurred or has not been great enough to obscure a detectable signal of long-term variations in chloride availability within the wetland. Thus the chloride-concentration trend in tree WP-4 supports the earlier hypothesis that mining altered wetland hydrology after 1890 and again after 1960.

The range of chloride concentrations in heartwood rings of tree WP-11 was 39–92 $\mu\text{g/g}$. However, the concentration of chloride increased slightly from the early 1880s (69 $\mu\text{g/g}$) to a maximum of 92 $\mu\text{g/g}$ in a complex of narrow rings that formed in the 1920s, decreased somewhat thereafter, and was least concentrated (39 $\mu\text{g/g}$) in the post-1960 outer heartwood. Thus the trend of chloride concentrations along the heartwood core radius of tree WP-11 somewhat resembles that of tree WP-4, even though a set of rings common to both trees was not irradiated, and the range of variability of pre-1960 concentrations was less than that of tree WP-4.

Chloride concentrations in heartwood rings of tree WP-7 ranged from 94 to 137 $\mu\text{g/g}$, suggesting that chloride availability might have been fairly uniform from about 1915 to 1970. Unlike trees WP-4 and 11, however, tree WP-7 became established after the onset of mining, and thus the extent to which

chloride concentrations are "elevated" is unknown. Absolute concentrations of chloride in the heartwood of tree WP-7 were greater than those of tree WP-11 but somewhat smaller than those of tree WP-4.

The greatest concentration of chloride in tree WP-2 was within the innermost heartwood ($249 \mu\text{g/g}$). Although tree WP-2 is not among those with extensive growth suppression prior to 1960 (Figure 4), the innermost-heartwood irradiation was performed on the second and third rings (1936 and 1937) of a 10-year juvenile series that was moderately suppressed (areas less than 4 cm^2) compared to the initial juvenile growth of trees WP-1, 13, 16, and 17. The decline in the concentrations of chloride from the late 1930s to 1960 is similar to that detected in trees WP-4 and 11 during the same period and suggests that the three trees may preserve a common signal of past-chloride availability.

Tree WP-15, like tree WP-2, contained the greatest heartwood concentration of chloride ($139 \mu\text{g/g}$) within the innermost rings. Concentrations declined in rings formed in about 1910 ($113 \mu\text{g/g}$) and 1920 ($69 \mu\text{g/g}$) but increased somewhat thereafter. The chloride-concentration trend of tree WP-15 does not resemble that of any other study tree, although concentration data suggest that chloride availability has been variable during the tree's lifetime. Tree WP-15 may grow where drainage-flow patterns differ from those of more southerly parts of the wetland, as also suggested by a sustained growth enhancement beginning in the mid 1980s rather than in approximately 1960 or just thereafter.

Concentration trends of sulfur within heartwood rings of the study trees generally resembled those of chloride, but absolute concentrations were smaller and less variable. The average chloride concentration in all heartwood rings of the five study trees was $117 \pm 45 \mu\text{g/g}$ (coefficient of variation (cv) = 0.38), compared to an average sulfur concentration of $73 \pm 13 \mu\text{g/g}$, cv = 0.18. Combining the 27 element-data pairings from all five trees into a single set, a positive correlation was found between the concentrations of chloride and sulfur ($R^2 = 0.47$, $F = 22.55$, $P < 0.01$), despite that only sulfur is unquestionably essential for plant growth. Thus it seems likely that the concentrations of chloride and sulfur within heartwood rings resulted in part from similarities in their availability, uptake, and subsequent mobility and storage.

Conclusions

For a century or more the study wetland has been irrigated by freshwater springs driven by local precipitation and by sulfur- and chloride-enriched brackish springs flowing from bedding-plane fractures. During summers and in drought years, discharge was less from freshwater springs than from brackish springs fed by the more extensive bedrock aquifer. Solution-mining practices at the south end of Tully Valley reportedly used injections of large volumes of water into the bedrock and possibly the glacial-aquifer systems, increasing head pressures upvalley and probably increasing brackish discharge in areas downvalley, including this wetland. Saturated conditions within the wetland probably persisted longer into the growing season and thus suppressed the growth of the trees (Figure 6). Ring-element concentrations of chloride and sulfur increased modestly in some trees in response to increased brackish flow, but growth suppression apparently was caused primarily if not exclusively by prolonged soil saturation.

Tree-growth remained suppressed during the entire interval

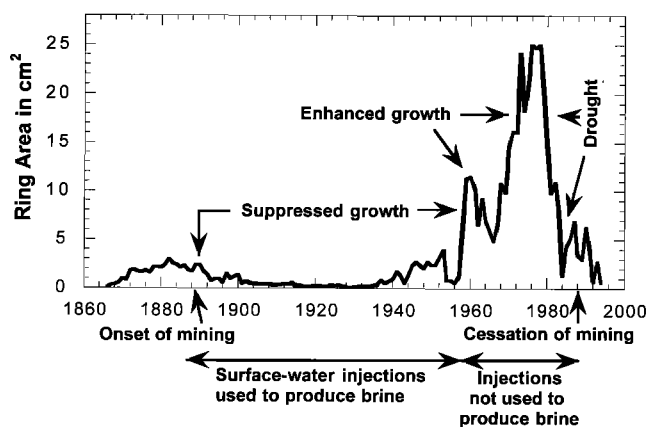


Figure 6. General summary of the relation between documented mining activities within the Tully Valley and ring-area growth of the oldest study tree (WP-4). Growth was suppressed from the early 1890s until the late 1950s due to mine-induced overwatering of the wetland and was enhanced thereafter when overwatering ceased. The tree died in 1995 as the result of an influx of chloride-enriched flow into the wetland following the cessation of mining in 1988.

of injection-mining practices. Beginning in the late 1950s, salt was mined only from the partially collapsed caverns on the western side of the valley. Hydraulic gradients reversed because saturated brine was removed but the caverns were no longer injected, thus lowering head pressures downgradient from the brine fields. Brackish flow into the wetland must have decreased quickly and remained low thereafter because the radial growth of most trees increased abruptly and synchronously (Figure 6). The primary source of wetland irrigation probably was the seasonally variable discharge from freshwater springs. Enhanced tree growth beginning in about 1960 suggests that conditions within the wetland may have become more mesic than at any time during the lives of the oldest trees. Concentrations of chloride and sulfur were less in some rings that formed just after than just before the cessation of injection practices, although alterations in the rate of radial growth probably were more dependent upon the quantity than quality of irrigating flows.

Following the cessation of mining in the late 1980s, however, head pressures increased in the upper valley and drove greater groundwater flows into the wetland. Unlike high flows coinciding with the interval of injection mining, flows contained high concentrations of chloride derived directly from the collapsed brine-mined caverns. Growth declined in central-area trees nearest the brackish springs, and four trees died (Figure 6). Evidence supporting the inferred relation between decreased tree vigor and recent hydrologic alteration includes anecdotal information from residents concerning increases in the amount and quality of flow near the wetland and the high concentrations of chloride in the outermost rings of some trees.

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