Quantifying contributions to stream salinity using electromagnetic induction and hydrochemistry in a small Texas coastal-plain basin

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Abstract

Airborne, ground, and borehole electromagnetic (EM) induction measurements were combined with surface-water chemical analyses to determine the extent of salinization as well as identify salinity sources and migration mechanisms that elevate total dissolved solids (TDS), Cl⁻, and SO₄²⁻ concentrations in Petronila Creek, a shallow stream that drains a small (1600 km²) basin on the Texas coastal plain. A multifrequency airborne EM induction survey measured apparent electrical conductivity of the ground to depths of a few tens of meters along the axis of the stream and along parallel flight lines within a 150 km² area extending from where the stream is fresh to the estuarine mixing zone. Apparent conductivity sections and maps were analyzed to identify stream segments where high conductivity indicates near-surface salinization and where saline baseflow increases the salinity load. Elevated conductivities at shallow depths beneath the stream lie adjacent to extensive conductive areas in oil fields and along ditches that once carried brine produced from the oil fields. These highly conductive areas delineate salinization that dominantly is caused by past discharge of produced brine into ditches and pits, infiltration into sandy, permeable horizons, lateral subsurface migration, and eventual discharge into the stream. Streamflow measurements and chemical analyses show that the TDS load increased along two highly conductive stream-bed segments upstream from the estuarine mixing zone. Extensive salinization between the ditches and the stream could provide a continuing source of salinity. A third highly conductive segment coincides with the zone of estuarine mixing, where there is geophysical evidence of possible subsurface seawater intrusion.

Multifrequency EM induction spectral images (the sectional depiction of apparent conductivity measured at multiple frequencies) along the stream axis, produced with minimal geophysical processing, helped identify stream segments that receive saline baseflow and guided surface-water sampling that allowed quantification of salinity loads. Apparent conductivity maps helped determine the salinization extent and identify salinity sources and migration mechanisms. Both the stream-axis and gridded airborne EM surveys were effective approaches to investigate salinization and interaction between ground water and surface water in this small basin, but multifrequency stream-axis images are a more practical alternative in larger basins where discrete salinity sources are poorly known.

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1. Introduction

Ground and airborne geophysical methods were combined with hydrochemical analyses along and near Petronila Creek, a small stream on the central Texas coast, USA (Fig. 1), to investigate the extent, intensity, and sources of salinization that degrade water quality in the stream. This study extends investigations of water quality that resulted from the US Environmental Protection Agency’s (EPA) designation of the stream as impaired for some uses by elevated concentrations of total dissolved solids (TDS), Cl\(^-\), and SO\(_4^{2-}\) (EA Engineering, Science, and Technology, Inc., 2002). Results are being used to predict future salinity loads and guide efforts to improve water quality.

Petronila Creek flows generally SE across the western Gulf Coastal Plain physiographic province from its headwaters near Banquete to the Baffin Bay estuarine complex (Fig. 2). The drainage basin is relatively small, encompassing a surface area of about 1600 km\(^2\). Petronila Creek flow rates measured between 2003 and 2005 by EA Engineering, Science, and Technology, Inc. (2002) range from 0 to as much as 42 m\(^3\)/s during storms. The median flow rate during this period was 0.06 m\(^3\)/s; flow for a given measuring event generally increased downstream. The climate is transitional between subtropical subhumid areas to the west and south to subtropical humid to the east and north (Larkin and Bomar, 1983). Average annual evaporation (160 cm; Larkin and Bomar, 1983) greatly exceeds average annual rainfall over the basin (66–76 cm;)
Larkin and Bomar, 1983; Bomar, 1995). The stream flows in a narrow, shallow valley eroded into semi-consolidated, clay-rich and sandy clay strata of the Beaumont Formation (Brown et al., 1975), an upper Pleistocene alluvial complex tens of meters thick that slopes gently gulfward. Thin Holocene alluvium (fine sand to clay) is present within the valley adjacent to Petronila Creek and in the streambed in places atop stiff Beaumont clay strata. On the upland, more recent flood and eolian sediments partly blanket older Beaumont strata.

Chemical analyses of surface water in Petronila Creek, its tributaries, and in ditches indicate that TDS, Cl\(^-\), and SO\(_4\)\(^-\) concentrations are low upstream from US 77 at Driscoll, but increase to levels that commonly fail to meet surface-water-quality standards for the designated contact recreation and aquatic life uses farther downstream (Fig. 2). TDS concentrations increase from freshwater values of 220 mg/L upstream from US 77 to very saline values of 15,100 mg/L or more downstream from US 77 (Fig. 2). TDS concentrations above 500 mg/L, Cl\(^-\) concentrations above 250 mg/L, and SO\(_4\)\(^-\) concentrations above 250 mg/L do not meet National Secondary Drinking Water Regulations established by the EPA. These concentrations also exceed maximum average concentration limits of 4000 mg/L for TDS, 1,500 mg/L for Cl\(^-\), and 500 mg/L for SO\(_4\)\(^-\) set forth in the Texas Administrative Code as required to support aquatic life. Possible causes of the abrupt increase in salinity far upstream from estuarine influence include: (a) the presence of primary saline pore water in Beaumont Formation strata that were deposited in a late Pleistocene coastal plain environment; (b) saline seawater droplets and salt grains transported and deposited by prevailing onshore winds and directly or indirectly carried into the stream; (c) inland flooding of saline gulf and estuarine water during recurrent tropical storms; (d) the formerly allowed practice of surface and near-surface discharge of co-produced saline water during hydrocarbon production, including discharge into brine pits, streams, and ditches and subsequent infiltration; and (e) leaking injection or brine-disposal wells.

There has been significant oil and gas exploration and production activity in the area. Active or once-active fields include the Clara Driscoll, North Clara Driscoll and Luby oil fields (Fig. 2). Records from the Railroad Commission of Texas (RRC) indicate that 900 wells have been drilled within the boundary of the airborne geophysical survey. Cumulative oil production attributed to the Driscoll fields totaled 19.7 million barrels (3.1 x 10\(^6\) m\(^3\)) between 1935 and 1982. Oil production was accompanied by unknown, but likely equal or greater, volumes of formation brines. Discharge of co-produced brine into surface pits presumably ceased with the implementation of the RRC’s no-pit order in 1969. The RRC no longer permitted discharge of produced water to area ditches and streams beginning in 1987 (Shipley, 1991). Water produced from area oil fields is highly saline; Gaither (1986) reports a TDS concentration of 49,300 mg/L and a Cl\(^-\) concentration of 28,904 mg/L in water produced from the Oligocene-age Vicksburg Formation in the Clara Driscoll Oil Field. Shipley (1991) cites Cl\(^-\) concentrations of 36,500–55,700 mg/L in produced brines sampled in the Petronila Creek area.

The past oil industry practice of discharging highly saline produced water at the surface into pits, ditches, and into the stream itself has been shown to have degraded surface-water quality and affected aquatic species in Petronila Creek (Shipley, 1991). In a study covering 7 a (1980–1986) of produced brine discharge directly or indirectly into the stream and one year of monitoring after permitted discharge ceased in 1987, Shipley (1991) showed that (a) stream salinities remained high after discharge ceased; and (b) pore-water salinities in stream-bottom sediments along the affected segment also remained high, despite flushing storm events. Further, Shipley (1991) interpreted produced water as the dominant salinity source because the relative concentrations of major ions in saline Petronila Creek water more closely matched those of produced water than those of Baffin Bay estuarine water downstream.

In addition to surface-water sampling and chemical analysis, geophysical instruments can be used to noninvasively estimate the electrical conductivity of the ground to identify salinized areas that might contribute to Petronila Creek salinity. The measured conductivity of the ground is the combined effect of electronic (ohmic), electrolytic, and dielectric current flow that is influenced by fluid (water content and dissolved species), sediment or rock (porosity and permeability), and mineral properties (including mineral-grain conductivity and cation-exchange capacity) (McNeill, 1980a; Telford et al., 1990). In most natural settings, electrical conductivity of the ground is dominated by electrolytic flow of ions in pore water (McNeill, 1980a; Schlumberger, 1989). Because the salinity of water is strongly
correlated to its electrical conductivity (Robinove et al., 1958; Hem, 1985) the electrical conductivity of soil and sediment is also strongly influenced by pore-water salinity, particularly at very high salinities such as those at Petronila Creek. As salinity increases, so does the electrical conductivity of the ground. Ground conductivity is thus a useful proxy for ground salinization.

Geophysical methods, particularly electromagnetic (EM) induction, have proven to be very effective in locating salinized areas, mapping the extent and intensity of salinization, and locating potential salinity sources in support of drilling, sampling, and analysis. Early geophysical instruments used to estimate soil salinity indirectly included in situ transducers and electrode arrays to measure soil conductivity (Enfield and Evans, 1969; Halvorson and Rhoades, 1974). During the late 1970s and early 1980s, investigators began developing and using EM instruments to measure ground conductivity noninvasively and estimate soil and water salinity (De Jong et al., 1979; McNeill, 1980a,b; Rhoades and Corwin, 1981; Corwin and Rhoades, 1982, 1984; Williams and Baker, 1982; Williams and Braunach, 1984; Williams and Fidler, 1985). Statistical techniques have been developed to predict soil salinity and monitor temporal changes by combining EM and soil sampling (Lesch et al., 1995, 1998). Ground-based EM methods continue to be used widely in salinity mapping (McKenzie et al., 1997; Banerjee et al., 1998). The EM method is popular because it can be rapidly and noninvasively applied. It is effective because a large increase in electrical conductivity typically accompanies the introduction of extremely conductive saline water (several hundred to several thousand millisiemens/m; Hem, 1985) into soil and rock that generally have low natural conductivities (a few tens to a few hundred millisiemens/m; McNeill, 1980a).

Airborne EM surveys have been widely applied to delineate soil and groundwater salinization arising from natural, agricultural, and oil-field causes, particularly in Australia and the United States (Smith et al., 1992, 1997; Street and Roberts, 1995; Paine et al., 1997; Coppa et al., 1998; Brodie, 1999; Paine, 2003; Paine and Minty, 2005). Wider application has been hindered by the relatively high cost of flying closely spaced lines over geographically large areas. Both curvilinear stream-axis and grid-style surveys were flown to evaluate whether the axial surveys might be a useful lower-cost alternative where size of the affected area might preclude grid surveying.

2. Methods

Ground, airborne, and borehole EM induction measurements of the electrical conductivity of the ground were integrated with surface-water chemistry data to better characterize and quantify salinization at Petronila Creek. The approach was to use ground-based instruments to acquire reconnaissance conductivity data that would (a) supplement water-quality data, (b) establish background, non-salinized conditions, and (c) determine the general extent of salinization. Results from the ground measurements guided design of an airborne geophysical survey that encompassed key Petronila Creek areas, including the oil fields, a nonsalinized upstream segment of Petronila Creek, and the ditches that received produced water from area oil fields for decades. The airborne survey was intended to delineate the extent and assess the intensity of salinization by measuring apparent ground conductivity at multiple exploration depths simultaneously. Finally, salinization patterns evident from airborne survey data were combined with chemical analyses of surface water to interpret likely salinity sources and transport mechanisms that continue to produce high concentrations of TDS, Cl⁻, and SO₄²⁻ long after permitted discharge ceased. This approach to quantifying stream salinization should be applicable in similar sedimentary settings where baseflow is an important streamflow component.

2.1. Ground and borehole EM

Frequency-domain EM induction was used to measure the electrical conductivity of the ground. Frequency-domain EM methods employ a changing primary magnetic field created around a transmitter coil to induce current to flow in the ground, which in turn creates a secondary magnetic field that is sensed by the receiver coil (Parasnis, 1986; Frischknecht et al., 1991; West and Macnae, 1991). The strength of the secondary field is a complex function of EM frequency and ground conductivity (McNeill, 1980b), but generally increases with ground conductivity at constant frequency.

A Geonics EM31 ground conductivity meter was used to measure the apparent conductivity of the ground at 165 locations along Petronila Creek, tributaries, and ditches and across adjacent upland fields. This instrument has a 3.7-m transmitter–receiver coil separation, operates at a frequency of 9.8 kHz, and measures apparent conductivity to
nominal depths of about 3 m (horizontal dipole [HD] orientation) and 6 m (vertical dipole [VD] orientation) (McNeill, 1980b).

One borehole was drilled, sampled, and logged using a Geonics EM39 induction probe. The EM39 has a 50-cm transmitter–receiver coil separation, an operating frequency of 39.2 kHz, and a maximum penetration radius of about 1 m (McNeill, 1986). Conductivity measurements were taken at 2.5-cm intervals in the borehole.

In addition to logging, borehole sediment samples were homogenized from a 15-cm depth range at 30-cm depth intervals from the surface to 7.2 m. Samples were analyzed for sand, silt, and clay content using sieve and pipette methods, water content using the gravimetric (repeated weighing and drying) method, and Cl$^-$ and SO$_4^{2-}$ concentration in soil extracts using ion chromatography.

2.2. Airborne EM survey

An airborne implementation of the frequency-domain EM method was used to measure apparent electrical conductivity of the ground along the axis of Petronila Creek and within a corridor centered on the stream (Fig. 2). Geophex, Inc. provided the survey crew, a GEM-2A instrument, and a helicopter.

The GEM-2 A employs a single pair of transmitter and receiver induction coils in horizontal coplanar (vertical dipole) orientation that operates at multiple effective frequencies (and exploration depths) simultaneously (Won et al., 2003). Five primary frequencies (450, 1350, 4170, 12,810, and 39,030 Hz) were chosen that yield exploration depths ranging from a few meters to several tens of meters. Because the exploration depths of these instruments decrease as either frequency or ground conductivity increases, coils operating at different primary frequencies will measure different apparent conductivities over ground where the actual conductivity varies with depth. Exploration depth for a given frequency and half-space conductivity is commonly approximated by “skin” depth, which is defined as the depth at which the field strength generated by the transmitter coil is reduced to $1/e$ times its original value (Telford et al., 1990). Apparent ground conductivity ranges and averages measured with the Geonics EM31 were used over the entire study area (Table 1) to estimate average exploration depths reached with each airborne-instrument frequency. Estimated exploration depth (Fig. 3) over the most conductive ground (607 mS/m) is the shallowest, increasing from about 3 m at the highest frequency (39,030 Hz) to 30 m at the lowest frequency (450 Hz). Exploration depths are greatest over the least conductive ground (95 mS/m), ranging from about 8 m at 39,030 Hz to 77 m at 450 Hz. Increasing conductivities with depth, weak induced ground currents, and cultural noise can all reduce the actual exploration depth achieved.

EM calibration included recording ambient noise at the chosen frequencies and pre- and post-flight checks of instrument phase and amplitude response. Instrument response and drift were compensated by raising the instrument above 300 m at the beginning and end of each flight to minimize the instrument’s response to the ground. The helicopter flew at a
nominal height of 60 m, towing the instrument at a height of about 30 m. The final sampling rate for EM and magnetic field data was 10 Hz. Average flight speeds of 106–130 km/h translate to an approximate on-the-ground sample spacing of 3–4 m. The diameter of the sensed footprint – approximated by the instrument manufacturer as twice the radius at which the vertical magnetic field becomes half its value directly beneath the transmitter (I.J. Won, pers. comm., 2006) – is about 30 m.

Geophex acquired airborne EM data along a total flight distance of more than 879 km over two days in February 2005. This distance included (a) a single curvilinear path 38 km long that followed the axis of Petronila Creek, and (b) 841 km along evenly spaced, parallel lines within a 6×25 km corridor centered on Petronila Creek (Fig. 2). Thirty-one NW–SE main lines were flown spaced 200 m apart and 11 NE–SW tie lines spaced 2 km apart to provide dense spatial coverage of the survey block.

Geophex processed the data to calculate apparent conductivities and centroid depths along the flight lines for each frequency using a half-space model algorithm (Sengpiel, 1988; Geophex, 2005). Apparent conductivity images were produced at each frequency along the stream axis and multifrequency spectral images were generated along the stream axis, considering distance along the stream as one variable and apparent conductivity at each frequency as the other variable. These spectrograms require only minimal processing to depict the lateral extent of ground salinization along the stream axis and indicate whether apparent conductivities increase (deep salinity source) or decrease (shallow salinity source) with depth. For the block survey, apparent conductivity was gridded from the 214,081 measurement locations using a 25-m cell size to produce apparent conductivity maps for each frequency.

2.3. Surface-water sampling, analysis, and flow estimates

Surface-water sampling and analyses were completed during and shortly after the airborne geophysical survey, both by the authors and by EA Engineering, Science, and Technology, Inc. (2002). Nine stream samples and one produced-water sample were collected for laboratory analysis of ionic concentrations. The produced water sample was collected from a tank battery in the Clara Driscoll Oil Field (Fig. 2) that contained commingled brine produced from wells draining Vicksburg Formation (Oligocene) reservoirs. For anion analyses, water was passed through a 0.45 mL Whatman syringe filter and collected in a bottle. For cation analyses, water was passed through a 0.45 mL filter and HCl was added to maintain metals in solution. All samples were analyzed at the Kansas Geological Survey laboratory as described below (D. Whittemore, pers. comm., 2005). Alkalinity (HCO$_3^-$) and pH were determined using a titrimeter. Colorimetric methods on segmented-flow spectrophotometers were used to measure concentrations of SO$_4^{2-}$, Cl$^-$, NO$_3^-$, and Br$^-$. Specific conductance was used to determine the dilution for the optimum concentration range for Cl$^-$ and SO$_4^{2-}$, determinations. The sample dilutions based on Cl$^-$ and SO$_4^{2-}$ were used to optimize Br$^-$ determination. The HCO$_3^-$ and SO$_4^{2-}$ concentrations were used to estimate the ranges in Ca and Na contents for optimal determination of cations, silica and B with an inductively coupled plasma mass spectrometer. Inorganic I and IO$_3^-$ concentrations were determined using colorimetric methods on a segmented-flow spectrophotometer and used in the correction of apparent Br$^-$ to true values. TDS concentration was calculated from the sum of concentrations of silica, Ca, Mg, Na, K, Sr, CO$_3^{2-}$, HCO$_3^-$ (multiplied by 0.4917), SO$_4^{2-}$, Cl$^-$, NO$_3^-$, Br$^-$, and B. The factor of 0.4917 times the HCO$_3^-$ concentration was used to better approximate the TDS value that would be obtained by evaporating a sample to dryness (Hem, 1985).

Streamflow was measured at selected stations by EA Engineering, Science, and Technology, Inc. using a Marsh-McBirney flow meter at discrete water depths along the stream cross section, following the procedure outlined in Texas Commission on Environmental Quality (2003).

3. Reconnaissance ground conductivity measurements

Ground measurements made before the airborne survey show that apparent conductivities in the shallow subsurface are high across the Petronila Creek area (Table 1). In the horizontal dipole (HD) instrument orientation, where the measured value represents the apparent conductivity to a depth of no more than 3 m (and perhaps shallower; Callegary et al., 2007), conductivity ranged from 95 to 1065 mS/m and averaged 370 mS/m (Table 1). Measurements taken along the stream and away
from it depict a general trend of increasing apparent conductivity toward the coast. The lowest conductivities (188 mS/m or less) are found only in the NW half of the study area. Virtually all measurements higher than 272 mS/m were located on the coastal side of US 77.

Measurements taken in the vertical dipole (VD) orientation, which represents apparent conductivity to a depth of no more than 6 m, are also high across the area (Table 1). These measurements average 294 mS/m, lower than the HD average. Apparent conductivity measured in the VD orientation also generally increases toward the coast. Lowest values (185 mS/m or less) are all located in the NW half of the study area. The highest values (343 mS/m or greater) are all located SE of US 77.

Moderate to high background apparent conductivities measured throughout the area are likely the combined result of (a) the presence of clayey Beau- mont Formation sediments at or near the surface (Brown et al., 1975); (b) high moisture content in area soils; and (c) high soil and sediment salinities caused by original depositional salinity, salt recently deposited by prevailing winds or storm inundation, or discharge and migration of saline water produced from area oil and gas operations. The general gulfward increase in apparent conductivity suggests that regional influences (increasing clay content, syndepositional salinity, and modern aerosol or inundation) control the overall trend, whereas oil- and gas-field sources of produced saline water might explain local, very large increases in ground conductivity (beyond those attributable to clay content and regional salinity trends) along and near Petronila Creek.

4. Airborne survey results

Ground-based investigations confirmed the presence of significant ground salinization and defined its geographic extent. The affected area was large enough to justify an airborne survey (Fig. 2), allowing better characterization of ground salinization by rapidly measuring ground conductivities at multiple exploration depths and at high spatial resolution.

4.1. Stream-axis EM data

Results from the curvilinear flight line that approximately followed the axis of Petronila Creek were used to identify highly conductive streambed segments caused by ground salinization. Stream-axis data consist of apparent conductivity measurements for five frequencies along 38 km of Petronila Creek (Fig. 4). Average apparent conductivities were high, ranging from 553 to 1304 mS/m for all frequencies (Table 2). Similar to the ground measurements, conductivities were highest for the higher, shallow-exploring frequencies.

Relatively low conductivities were measured at all frequencies upstream from US 77 (Fig. 4). Further downstream, apparent conductivity trends differ according to location and frequency. At the deepest-exploring frequencies, significant conductivity highs are located in the Concordia and Luby areas (Fig. 4b). The shallowest-exploring frequencies (12,810 and 39,030 Hz) recorded the highest conductivities in the Concordia area (Fig. 4a).

4.2. Petronila creek block EM data

Measurements from the closely spaced lines of the block survey were used to produce apparent conductivity maps at each frequency (two are shown in Fig. 5) that depict the lateral extent of salinization and aid in identifying source areas and migration routes to the stream. Average conductivities over the block ranged from 378 to 1477 mS/m for all frequencies, similar to the values along the stream axis (Table 2). Highest apparent conductivities were measured at the highest (shallowest-exploring) frequency.

General conductivity trends in the Petronila Creek block are similar to those evident in the stream-axis data (compare Figs. 4 and 5). Apparent conductivities are low at all frequencies near Petronila Creek upstream from US 77 (Fig. 5). Similarly, at all but the highest (shallowest-exploring) frequency, high conductivities are measured over a broad area extending downstream from Farm-to-Market Road 70 (F.M. 70) at the southeastern part of the survey block. This is particularly well expressed at the two lowest (deepest-exploring) frequencies (Fig. 5b). This area includes the southern part of the Luby Oil Field.

A broad zone of generally high conductivity is evident at all frequencies south of Petronila Creek between Driscoll and water sampling location E (Fig. 5a and b). This area includes the Clara Driscoll Oil Field and all or part of two major drainage ditches that cross the oil field. Higher conductivities are less extensive north of Petronila Creek, but are evident in some areas, such as along the stream between sampling locations D and E on the intermediate- to high-frequency maps (Fig. 5a).
Fig. 4. Apparent conductivity measured at (a) 12,810 Hz and (b) 1350 Hz along the axis of Petronila Creek. Also shown are the Driscoll, Concordia, and Luby highly conductive areas (red rectangles) and stream and tributary TDS and Cl\(^{-}\) concentrations at the time of the airborne survey. The 12,810-Hz frequency explores from the land surface to an average depth of about 5 m. The 1350-Hz frequency explores from the land surface to an average depth of about 16 m. Ditches that discharge into Petronila Creek are shown as light lines. Water-quality data provided by EAEST.
5. Highly conductive areas

Block and stream-axis EM data allow delineation of three areas of generally elevated apparent ground conductivity along the stream. From upstream to downstream, these are the Driscoll, Concordia, and Luby areas (Figs. 4 and 5). These areas enclose the stream segments most likely to be receiving highly saline water that degrades Petronila Creek water quality.

The lowest conductivities measured in the airborne EM survey are found upstream from US 77 (Figs. 4 and 5). Average conductivities in this relatively nonsalinized area range from 181 to 403 mS/m and represent the lowest average conductivity at each frequency (Table 2). In further contrast to the high-conductivity areas downstream, the lowest conductivities in this background area were measured at the highest (shallowest-exploring) frequencies.

### 5.1. Driscoll area

The most upstream of the highly conductive streambed segments is in the Driscoll area, extending about 8 km downstream from US 77 (Figs. 4 and 5). The stream passes between the Clara Driscoll and North Clara Driscoll oil fields. One of the two ditches that enter Petronila Creek from the north drains an area that includes the North Clara Driscoll Oil Field.

Average stream-axis conductivities show the greatest increase over background values at the two highest frequencies, increasing from 282 to 720 mS/m at 12,810 Hz and 181 to 1294 mS/m at 39,030 Hz (Table 2). Smaller increases were measured at lower frequencies. Stream-axis conductivities depicted on maps (Fig. 4) and on a spectral conductivity image along the stream constructed from all frequencies (Fig. 6a) confirm that near-surface ground conductivity increases downstream. Elevated high-frequency (near-surface) conductivities begin just downstream from US 77 and become more laterally extensive downstream between the ditch confluences (4–9 km, Fig. 6a). EM data from the block survey depict high apparent conductivities of the stream at all frequencies (Fig. 5). These high conductivities are located within and SE of the Clara Driscoll Oil Field, extending far enough south to intersect a ditch along County Road 18 (Co. Rd. 18) that drains part of the oil field.

Elevated apparent conductivities at the shallowest-exploring frequencies are consistent with near-surface salinization along the Driscoll segment of Petronila Creek that increases in extent and intensity downstream. Shallow ground salinization along this segment coincides with an increase in Petronila Creek TDS, Cl<sup>−</sup>, and SO<sub>4</sub><sup>2−</sup> concentrations measured at the time of the airborne survey (Figs. 4 and 5). TDS concentration increased from 2460 mg/L at US 77 (station B) at the upstream end of the segment to 15,100 mg/L near the downstream end of the segment (station C). Major cation (Na, Ca, and Mg) and anion (Cl<sup>−</sup> and SO<sub>4</sub><sup>2−</sup>) concentrations in creek waters increase substantially from station A to the downstream end (station C) of the Driscoll segment (Fig. 7a and c). Ionic proportions also change radically from fresh, Ca- and HCO<sub>3</sub>-dominated water upstream from Driscoll (station A, Fig. 7b and d) to highly saline, Na- and Cl- dominated water downstream from the Driscoll area (station C). Extremely high Na and Cl<sup>−</sup> concentrations require either a seawater or produced water salinity source. Shipley (1991) observed that higher concentration of Ca than Mg better matches the reported chemistry of produced water (Fig. 7b) than that of seawater or compositionally similar Baffin Bay estuarine water, which have higher concentrations of Mg than Ca. If seawater were the source, cation exchange with shallow soils might account for the relative increase in Ca concentration in stream water (D. Whittemore, pers. comm.). Conversely, the relative abundance of SO<sub>4</sub><sup>2−</sup> over HCO<sub>3</sub>− in stream water better matches reported seawater abundances (Fig. 7d). If produced water were the source of salinity, additional SO<sub>4</sub><sup>2−</sup> might have been derived from (a) dissolution of gypsum (a minor constituent in area soils, Franki et al., 1965), (b) oxidation of dissolved sulfide in the produced waters, or (c) produced waters with higher SO<sub>4</sub><sup>2−</sup> concentration.
Highly saline water has been sampled repeatedly (this study; EA Engineering, Science, and Technology, Inc., 2002) at the eastern margin of the Clara Driscoll Oil Field near where the Co. Rd. 18 ditch drains into Petronila Creek (35,400 mg/L TDS concentration at station H at the time of the airborne survey. Water-quality data provided by EAEST.

Fig. 5. Apparent conductivity measured at (a) 12,810 Hz and (b) 1350 Hz in the Petronila Creek airborne survey block. Also shown are stream and tributary TDS and SO$_4^{2-}$/CO$_3^{2-}$ concentrations at the time of the airborne survey. Water-quality data provided by EAEST.
As part of the ground survey, apparent conductivity was measured in the floor of the ditch from US 77 eastward for a distance of about 4 km. Apparent conductivities measured in the HD and VD orientations have similar moderate values at the upstream end of the profile (from US 77 to a distance of about 1.6 km downstream, Fig. 8). Along this segment and farther downstream, the deeper VD values remain near 400 mS/m. In contrast, the shallower HD values show a gradual increase from 300 mS/m near US 77 to 470 mS/m 1.6 km downstream, followed by a steeper increase to a peak value exceeding 1000 mS/m about 2.8 km downstream along the ditch. The downstream end of the profile shows lower, but still elevated values. The abrupt increase in apparent ground conductivity evident at 1.6 km from US 77, accompanied by no change in soil substrate type, marks the western limit of highly saline ground in the ditch. Anomalously high HD values suggest that the salinization is restricted to the shallow zone and that downward migration is inhibited by the clay-rich, poorly permeable Beaumont Formation substrate.

Elevated apparent conductivities across the Clara Driscoll field at all airborne-instrument frequencies suggests that oilfield-related, near-surface salinization exists in this area, probably arising largely from decades-long discharge of produced water into pits and ditches. Assuming that there has been no significant surface discharge of produced water since the permitted practice ended in 1987, the most likely mechanism for infiltration of highly saline water into this stream segment is (1) infiltration of produced water into the shallow subsurface beneath pits and along ditches; (2) lateral migration of saline water through sandy Beaumont Formation channels such as those exposed along some ditches; and (3) discharge as local, shallow-source baseflow into Petronila Creek along the conductive segment. Oil field areas with low apparent conductivities,
such as the North Clara Driscoll Oil Field, represent areas where extensive infiltration and migration has not occurred, due to either lack of discharge (later field development) or lack of extensive infiltration horizons at the surface or along drainage ditches.

To verify the existence of salinized ground between the Driscoll Oil Field and Petronila Creek, a core from borehole NU-0501 on the upland surface in the Driscoll area was acquired and analyzed. A conductivity log of the borehole (Fig. 9), located about 160 m SW of Petronila Creek (Figs. 4 and 5), shows extremely high apparent conductivity at all depths below about 1 m, suggesting the presence of highly saline pore fluid throughout the section. Soil analyses confirmed the abundance of Cl⁻ in pore water at concentrations as great as 13,150 mg/L. Poorly permeable silty clay, contain-

Fig. 7. Major cation and anion concentrations in Petronila Creek samples taken upstream and downstream from the Driscoll (incoming: station A; outgoing: station C, Figs. 4 and 5), Concordia (incoming: station C; outgoing: station E), and Luby highly conductive areas (incoming: station F; contributing tributary/ditch: station I) at the time of the airborne survey. Values are given as actual cation (a) and anion (c) concentration (in milliequivalents/L) and as relative percentages among the three cation (b) or anion (d) concentrations shown. Also shown are relative ionic concentrations reported for seawater (Hem, 1985; Drever, 1997) and water produced from area oil fields (Shipley, 1991). The seawater composition closely matches that reported for Baffin Bay estuarine water sampled in 1980 (Shipley, 1991). Sample locations are shown in Figs. 4 and 5.

Fig. 8. Apparent ground conductivity profile along the Co. Rd. 18 drainage ditch downstream from US 77. HD values are those measured with the ground conductivity meter coils in the horizontal dipole orientation. VD values were measured in the vertical dipole coil orientation.
ing minor amounts of pedogenic carbonate nodules and small gypsum blades, was recovered from the surface to a depth of about 5 m. Below this is a wet, sandy horizon that is more than 1 m thick; the elevation of this horizon overlaps the elevation of the floor of nearby Petronila Creek. Similar sandy stratigraphic intervals were observed near the base of the ditch along Co. Rd. 18. The sandy horizon overlies a poorly permeable stiff clay, both in the borehole and at the floor of the ditch. Laterally extensive, sandy horizons such as these within the Beaumont Formation likely served as produced-water infiltration points along ditches, lateral transport pathways, and discharge horizons along the stream. Dissolution of pedogenic gypsum crystals (CaSO\textsubscript{4} · 2H\textsubscript{2}O), identified in the soil core and noted in a soil survey at 1–2% by volume in the Victoria Clay, the dominant mapped soil unit in the study area (Franki et al., 1965), is a likely source for the Ca and SO\textsubscript{4}\textsuperscript{2−} enrichment in stream water relative to local produced water.

5.2. Concordia area

The Concordia area encloses a 11.5-km-long segment of Petronila Creek (Figs. 4 and 5) that receives discharge from the saline ditch along Co. Rd. 18 about 2 km from the upstream end of this segment. Average conductivities calculated from stream-axis EM data show that the Concordia area encloses the most conductive segment of Petronila Creek (Table 2). Conductivities at the two highest frequencies are particularly high, implying highly conductive near-surface strata beneath the stream. The most conductive segment extends 6 km from the upstream limit of the Concordia area (Figs. 4 and 6b).

Block survey maps most clearly depict elevated Concordia conductivities at the highest frequencies (Fig. 5a), but apparent conductivities are also high at lower frequencies in the same general area on the south side of Petronila Creek (Fig. 5b). Each image also reveals high apparent conductivities associated with a ditch roughly parallel to and a few kilometers south of the Co. Rd. 18 ditch. These high-conductivity lobes trend generally northeastward from this ditch toward Petronila Creek (Fig. 5b), intersecting the stream near high-salinity water sampling sites (stations D and E).

Elevated conductivities between 0 and 9 km along the Concordia segment at the high, shallow-exploring frequencies indicate significant near-surface salinization. Decreasing conductivities observed at lower frequencies (and greater exploration depth) indicate near-surface rather than deep sources of salinity. Elevated surface-water salinities measured at the time of the airborne survey include 35,400 mg/L TDS at station H in the Co. Rd. 18 ditch, 16,200 mg/L at station D on Petronila Creek, and 17,000 mg/L farther downstream on Petronila Creek at station E. There is a small downstream increase in major-ion concentrations (Fig. 7a and c), but relative concentrations of major dissolved constituents remain nearly constant from station D to E and are similar to those at the Driscoll station C (Fig. 7b and d). This suggests that produced oil-field water similar to that responsible for increasing Petronila Creek salinity along the Driscoll segment is also discharging into the Concordia segment.

Produced water from sparse oil and gas wells within the Concordia area could not account for the extensive near-surface salinization evident in that area, nor could the minimal flow measured in the tributary ditches. The two ditches that carried water produced from wells farther west cross the Concordia area south of Petronila Creek are associated with local conductivity highs that extend from the ditches and terminate at Petronila Creek.

Fig. 9. Apparent conductivity measured in borehole NU-0501 in the Driscoll highly conductive area. The borehole is on the upland 160 m SW of Petronila Creek (Fig. 4). Sampled intervals and generalized soil descriptions are also shown.
Based on the conductivity data and elevated stream salinities, the lobes of elevated conductivity south of Petronila Creek are interpreted as representing relatively shallow accumulations of saline produced water that was discharged into the ditches and entered the subsurface where the ditches intersect sandy Beaumont Formation strata. This water has migrated laterally toward Petronila Creek, providing saline baseflow.

5.3. Luby area

The Luby area is the most downstream highly conductive area surveyed (Figs. 4 and 5). The upstream limit of the Luby segment of Petronila Creek coincides with the upstream limit of estuarine mixing from the Baffin Bay-Laguna Madre estuarine system (Shipley, 1991). Petronila Creek crosses the southern part of the Luby Oil Field along the upper 4 km of this segment. A tributary stream connects with a network of ditches that cross the Luby Oil Field.

Average stream-axis conductivity peaks at lower frequencies in this segment than in the Driscoll and Concordia segments (Table 2). Stream-axis maps show a pronounced conductivity high at low frequencies (Fig. 4b), but little evidence of extensive areas of elevated conductivity at the shallowest-exploring frequency. The multifrequency image (Fig. 6c) shows only minor, local areas of elevated conductivity near the Luby Oil Field tributary at the highest frequencies. More notable is an extended length of elevated conductivity best expressed in measurements at 1350 Hz (Fig. 6c) that reaches at least 7 km downstream. Apparent conductivity patterns in the block survey are also striking, depicting a front of high conductivity at the lowest frequencies (Fig. 5b) that extends about 7 km downstream to the SE boundary of the survey area.

Elevated near-surface conductivities are present locally and are associated with water samples having elevated TDS concentration (17,400 mg/L at station F), but are not as extensive as in the Driscoll and Concordia areas. Major-ion concentrations in Petronila Creek at the upstream end of the segment (station F) are similar to those leaving the Concordia segment (station E; Fig. 7a and c). Water sampled from the Luby Oil Field tributary (station I) also has ionic ratios similar to those for Petronila Creek water in the Driscoll and Concordia areas, but has a slightly higher SO\textsubscript{4}\textsuperscript{2-}: Cl\textsuperscript{-} ratio (Fig. 7b and d).

There is relatively little evidence for shallow salinization along the Luby segment despite the possibility of estuarine mixing. Minor near-surface salinization near the Luby Oil Field may be attributed to produced water reaching this segment along ditches. More pronounced is deeper salinization indicated by elevated conductivity at the lower frequencies. These data are interpreted to suggest that this area marks the upstream limit of subsurface intrusion of saline coastal water.

6. Chloride/bromide mixing models

To further confirm whether elevated salinity in Petronila Creek in the Driscoll and Concordia areas is consistent with the addition of brine produced from area oil fields, a sample of brine produced from Vicksburg Formation reservoirs in the Clara Driscoll Oil Field was acquired and chemically analyzed. Conservative hydrochemical mixing models use the high solubility of Cl\textsuperscript{-} and Br\textsuperscript{-} to demonstrate the potential that water samples with significant differences in salinity have mixed to produce water of intermediate salinity (Richter, 1993; Whittemore, 1995). Chloride and Br\textsuperscript{-} are conservative in that they tend to remain in solution while other common ionic species (Ca\textsuperscript{2+}, Mg\textsuperscript{2+}, Na\textsuperscript{+}, HCO\textsubscript{3}\textsuperscript{-} and SO\textsubscript{4}\textsuperscript{2-}) are more prone to participate in chemical reactions or other complexing behavior that affect their concentration in solutions through precipitation as solids or adsorption to electrically charged particulate matter (clay). The concentration of non-conservative ionic species in a mixture may not be the simple sum of the relative contributions from each of the end-member waters, but the concentration of conservative species will more faithfully reflect the proportions of the component end-members.

Hydrochemical models (Fig. 10) were constructed that mixed varying proportions of highly saline water, including brine from the Clara Driscoll Oil Field (Cl\textsuperscript{-} concentration 63,590 mg/L) and water sampled from the Co. Rd. 18 ditch (station H, Cl\textsuperscript{-} concentration 14,780 mg/L), with relatively fresh water from Petronila Creek upstream from the Driscoll area (Cl\textsuperscript{-} concentrations 19 or 838 mg/L, stations A or B). The Petronila Creek samples (Fig. 10) have similar Br\textsuperscript{-}:Cl\textsuperscript{-} ratios over a wide range of Cl\textsuperscript{-} concentrations, suggesting that the samples are hydrochemically similar despite large changes in salinity. Petronila Creek samples become more saline downstream; the increasing...
salinity is accompanied by a small increase in Br⁻:Cl⁻ values. This suggests that the samples represent varying degrees of mixing between relatively fresh, upstream creek water (lowest Cl⁻ concentrations) and waters with higher Br⁻:Cl⁻ ratios than any of the uncontaminated stream samples. Two possible highly saline sources include seawater and brines similar to those produced from the Clara Driscoll Oil Field (Fig. 10).

Despite the passage of several decades since large volumes of produced water were discharged to the ditches, pits, and streams and the possibility that the chemical signature of produced water acquired today from one reservoir might differ from that produced in the past from the same or different reservoirs, Petronila Creek samples fall near, but below, a mixing line that employs creek water from the Driscoll area (station B, samples B₁ or B₂) as a fresh end-member and produced water from the Clara Driscoll Oil Field (station J) as the other end-member. Although not as saline, seawater has a Br⁻:Cl⁻ ratio that is similar to that of the produced brine and provides a similarly good fit as a possible saline end-member for Petronila Creek samples. Because of this, it is not possible distinguish between seawater and recently produced brine as possible salinity sources.

Interestingly, the best mixing-line fit to Petronila Creek samples (Fig. 10) is obtained when highly saline water collected from the Co. Rd. 18 ditch (station H, Figs. 5 and 6) is mixed with relatively fresh water from the Driscoll area (station B, sample B₁). This sample has a lower Br⁻:Cl⁻ ratio than either seawater or brine produced in 2005 from the Clara Driscoll Oil Field, and does not fall on any mixing line between either of these highly saline waters and fresher Petronila Creek samples. This observation supports an interpretation that saline water seeping into the Co. Rd. 18 ditch more closely matches an original, slightly lower Br⁻:Cl⁻ ratio of produced water that was discharged into the ditch during historical oil-field activities than it does Br⁻:Cl⁻ ratios of seawater or brine produced today. It is concluded from this that historical produced water is the most likely dominant source of Petronila Creek salinity in the Driscoll and Concordia areas.

7. Stream salinity loading

The significance of the highly conductive areas as stream salinity sources was verified by combining surface-water analyses and streamflow measurements to estimate salinity loading along Petronila Creek in each of the highly conductive areas. If saline water is flowing into the stream along these segments, salinity loads should increase along each segment.

At the upstream end of the Driscoll area (station B, Figs. 4 and 5), streamflow at the time of the airborne survey was 2.8 L/s at a TDS concentration of 2460 mg/L. The calculated incoming TDS load was 600 kg/day (Table 3 and Fig. 11). At the downstream end of the Driscoll conductive segment (station C), flow increased to 15.9 L/s and TDS concentration increased to 15,100 mg/L. This translates to an outgoing salinity load of 20,800 kg/day, an increase of about 20,200 kg/day. Chloride and SO₄²⁻ loads increased similarly (Table 3). Due to the lack of significant tributary inflows, this loading is attributed dominantly to local-source baseflow containing brine that was once produced in the Driscoll Oil Field, discharged at the surface into pits and ditches, infiltrated into shallow sandy strata, dissolved pedogenic gypsum, migrated laterally, and became diluted down-gradient (northward and eastward) in the shallow subsurface, and discharged into the streambed.

TDS loading at the upstream end of the Concordia segment is represented by the 20,800 kg/day value calculated at station C (Figs. 4, 5 and 11). In the upper part of the segment (station D), flow increased to 35.5 L/s and TDS concentration increased to 16,200 mg/L TDS. The TDS load was 49,700 kg/day at this intermediate location, an increase of about 29,000 kg/day above the value at
the upstream end of the segment (Table 3). At the downstream end of the segment (station E), higher streamflow (55.9 L/s) and TDS concentration (17,000 mg/L) yield a TDS load of 82,100 kg/day (Table 3 and Fig. 11). Total loading increase along the Concordia segment was thus more than 61,000 kg/day. This increase, and similar large increases in Cl⁻ and SO₄²⁻ loading (Table 3), are interpreted as showing domination by a local source, shallow baseflow from produced water that was once discharged into the two ditches that cross the area, entered the shallow subsurface along the ditches, and migrated toward the stream along sandy subsurface Beaumont Formation strata.

Insufficient data are available to estimate TDS loading changes in the Luby area, the downstream, estuarine-influenced segment of Petronila Creek. At the upstream end of the segment (station F, Figs. 4 and 5), combining measured streamflow of 22.3 L/s with a TDS concentration of 17,400 mg/L translates to an incoming load of 33,500 kg/day (Table 3). The reduction in TDS load of more than 48,000 kg/day between the Concordia and Luby segments is caused by the loss of surface flow.

8. Conclusions

Airborne, ground, and borehole electrical conductivity measurements and hydrochemical analyses were integrated to delineate the extent and intensity of salinization and identify possible salinity sources in a small coastal-plain basin. These sources cause increases in TDS, Cl⁻, and SO₄²⁻ concentrations in Petronila Creek, the principal stream in the basin.

Multifrequency apparent conductivity spectrograms and single-frequency apparent conductivity maps constructed from airborne EM data were used to identify three high-conductivity areas where ground salinization contributes to the salinity load of Petronila Creek. These highly conductive segments are part of larger areas of elevated conductivity (and ground salinization) that extend hundreds of meters to several kilometers from the stream. At the most upstream conductive area, the stream passes between oil fields where produced water was once discharged into pits, ditches, and the stream. Farther downstream, brine discharge into ditches that cross the area allowed produced water to infiltrate the shallow subsurface through permeable sandy horizons, where it migrated laterally toward the stream and contributes highly saline base flow to the stream. Significant TDS, Cl⁻, and SO₄²⁻ load gains occur along these stream segments. The most downstream salinized segment coincides with the zone of estuarine mixing. Salinity sources inferred here include subsurface intrusion of seawater and near-surface salinization associated with discharge of produced water in an adjacent oil field.

Table 3
TDS, chloride, and sulfate loading estimates based on flow and water-quality data collected by EA Engineering, Science, and Technology, Inc. (2002) at the time of the airborne survey

<table>
<thead>
<tr>
<th>Location</th>
<th>Flow (L/s)</th>
<th>TDS (kg/day)</th>
<th>Chloride (kg/day)</th>
<th>Sulfate (kg/day)</th>
</tr>
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<tr>
<td><strong>Driscoll area</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Incoming (station B)</td>
<td>2.8</td>
<td>600</td>
<td>230</td>
<td>100</td>
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<tr>
<td>Outgoing (station C)</td>
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<td>20,800</td>
<td>10,000</td>
<td>1790</td>
</tr>
<tr>
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<td>+13.1</td>
<td>+20,200</td>
<td>+9770</td>
<td>+1690</td>
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<tr>
<td><strong>Concordia area</strong></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Incoming (station C)</td>
<td>15.9</td>
<td>20,800</td>
<td>10,000</td>
<td>1790</td>
</tr>
<tr>
<td>Contributing (station H)</td>
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<td>8700</td>
<td>4700</td>
<td>860</td>
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<tr>
<td>Intermediate (station D)</td>
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<td>23,600</td>
<td>3990</td>
</tr>
<tr>
<td>Outgoing (station E)</td>
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<td>6760</td>
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<td>+61,300</td>
<td>+32,500</td>
<td>+4970</td>
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<tr>
<td><strong>Luby area</strong></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Incoming (station F)</td>
<td>22.3</td>
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<td>16,000</td>
<td>3,080</td>
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<tr>
<td>Contributing (station I)</td>
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<td>12,900</td>
<td>7400</td>
<td>1290</td>
</tr>
</tbody>
</table>

Station locations are shown in Figs. 4 and 5.

Fig. 11. Petronila Creek TDS loading estimates for the Driscoll, Concordia, and Luby areas. Estimates are based on stream and tributary flow data and salinity concentrations at the time of the airborne survey. Italicized stations indicate incoming loads from ditches or tributaries. Streamflow and water-quality data provided by EA Engineering, Science, and Technology, Inc. (2002).
Multifrequency conductivity images acquired along the stream axis provide a continuous, rapid, and relatively low-cost means to identify salinized streambed segments where saline baseflow degrades surface-water quality. These data help determine optimal stream sampling locations and set gridded survey boundaries that minimize the area to be flown at higher resolution. Apparent conductivity maps constructed from gridded survey data are necessary to quantify the intensity and extent of salinization, discriminate among possible salinity sources, and evaluate remediation options.

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References


