

**KANSAS GEOLOGICAL SURVEY
OPEN-FILE REPORT 2000-63**

Identification of Natural and Anthropogenic Sources
of Chloride and Sulfate

by

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Identification of Natural and Anthropogenic Sources of Chloride and Sulfate

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Abstract

Many streams in the U.S. receive substantial concentrations of chloride and sulfate from both natural and anthropogenic sources and processes. The main natural source of high concentrations of chloride and sulfate in surface waters is discharge of ground water that has dissolved evaporite minerals or that is affected by formation brine. Anthropogenic sources of chloride include oil-field brine, road salt, water-softener salt, and various chemical wastes and spills. Loss of irrigation water to evapotranspiration in the Great Plains and western U.S. can cause substantial increases in the concentrations of both chloride and sulfate in surface waters. Identification of the different sources and processes is necessary for proper pollutant allocation and determination of background concentrations for appropriate implementation of TMDL's.

Slide list and explanation

1. Identification of Natural and Anthropogenic Sources of Chloride and Sulfate

Acknowledgment: Partial support of results presented is from the TMDL Program of the Kansas Department of Health and Environment

2. Sources of high chloride contents in surface waters (identify as point and nonpoint sources)

Discharge of natural ground waters that dissolved halite (rock salt – NaCl)

Discharge of natural formation waters that are altered seawater

Formation brines associated with petroleum exploration and production

Natural and accelerated salinization from evapotranspiration concentration

Dissolution of deicing and water-softener salt

Salt mine wastes

Other wastes and chemical leaks and spills (e.g. hydrochloric acid)

3. Sources of high sulfate contents in surface waters (identify as point and nonpoint sources)

Discharge of natural ground waters that dissolved gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) or anhydrite (CaSO_4)

Discharge of natural formation waters that are altered seawater or are associated with volcanism

Weathering of sulfide minerals in rocks

 Natural weathering and discharge of ground waters

 Accelerated weathering after exposure by coal and metal mines

Natural and accelerated salinization from evapotranspiration concentration

Dissolution of gypsum used on soils or in waste wallboard

Other wastes and chemical leaks and spills

4. Natural intrusion of saline ground water into surface water
Dissolution of evaporite minerals (halite, gypsum, and anhydrite)

Chloride up to 200,000 mg/L

Sulfate up to 10,000 mg/L

- Formation brine that is trapped, altered seawater

Chloride can be over 100,000 mg/L

Sulfate usually much lower than chloride

5. Map of natural saltwater intrusion areas in Kansas

South-central Kansas: Intrusion of saltwater from Permian redbeds into High Plains aquifer and alluvium and then into streams and Arkansas River

Central Kansas: Intrusion of saltwater from Wellington Formation into High Plains aquifer and alluvium and then into streams and Arkansas and Smoky Hill rivers

North-central Kansas: Intrusion of Permian saltwater into Dakota aquifer, then into streams or into alluvial aquifers and then into streams and rivers

6. Cross section of Smoky Hill River valley in Salina area

Dissolution of rock salt from Hutchinson Salt Member of Wellington Formation, intrusion of saltwater from Wellington Formation into alluvium and then into Smoky Hill River

7. Salinity from Evapotranspiration

Concentration of dissolved salts in surface waters, soils, and shallow ground waters by loss of water to evaporation and transpiration

Direct increase in chloride and sulfate in surface water and increase in salt concentration of discharge to streams from soils and shallow ground-water

Acceleration by increase in area of surface water in storage bodies and diversion canals

Acceleration by increase in evapotranspiration from irrigation systems

Chloride and sulfate levels can exceed 1,000 mg/L depend on starting contents and degree of concentration

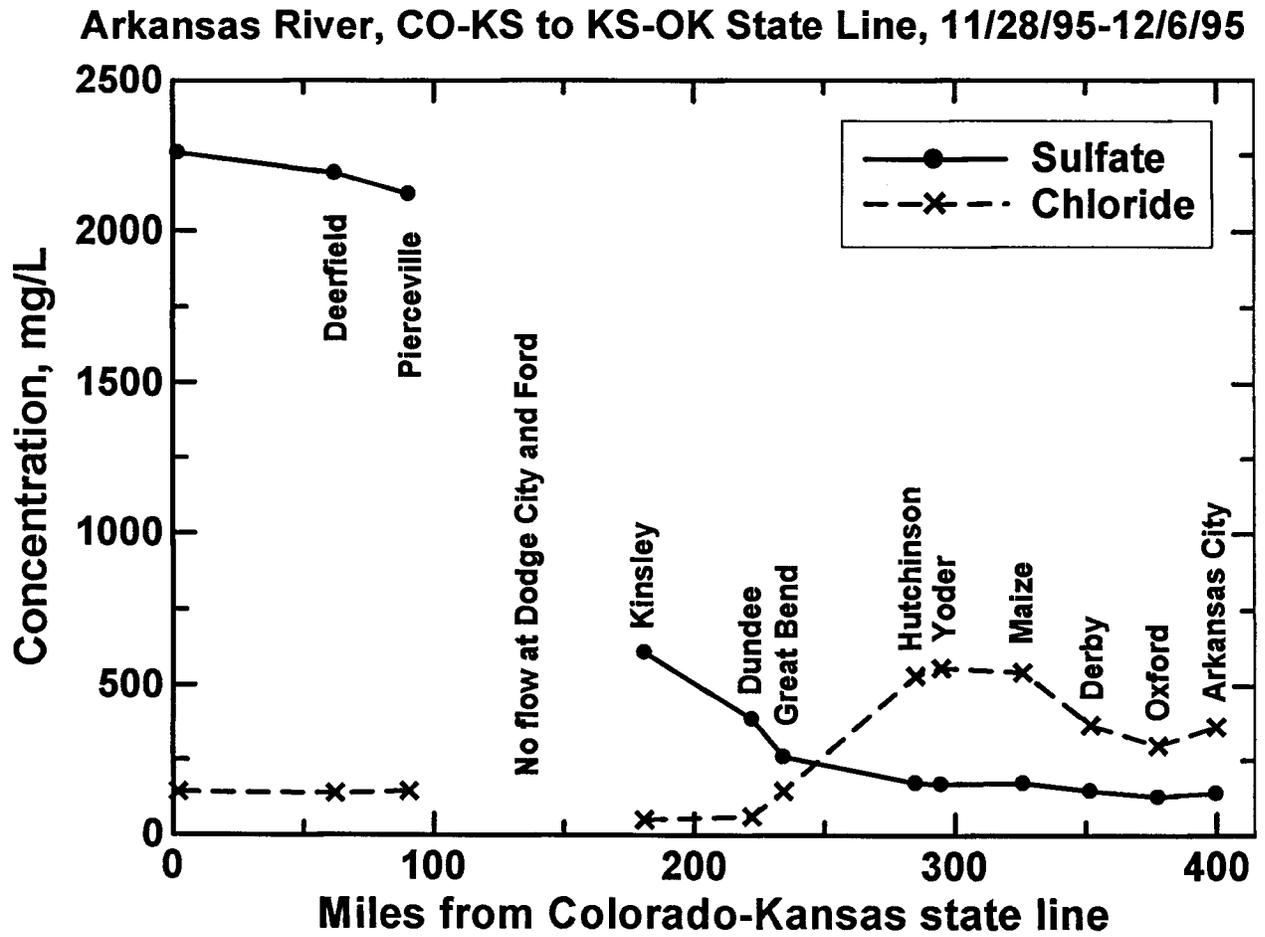
Problem in more arid areas

8. Map of Kansas with evapotranspiration vs precipitation dominant areas

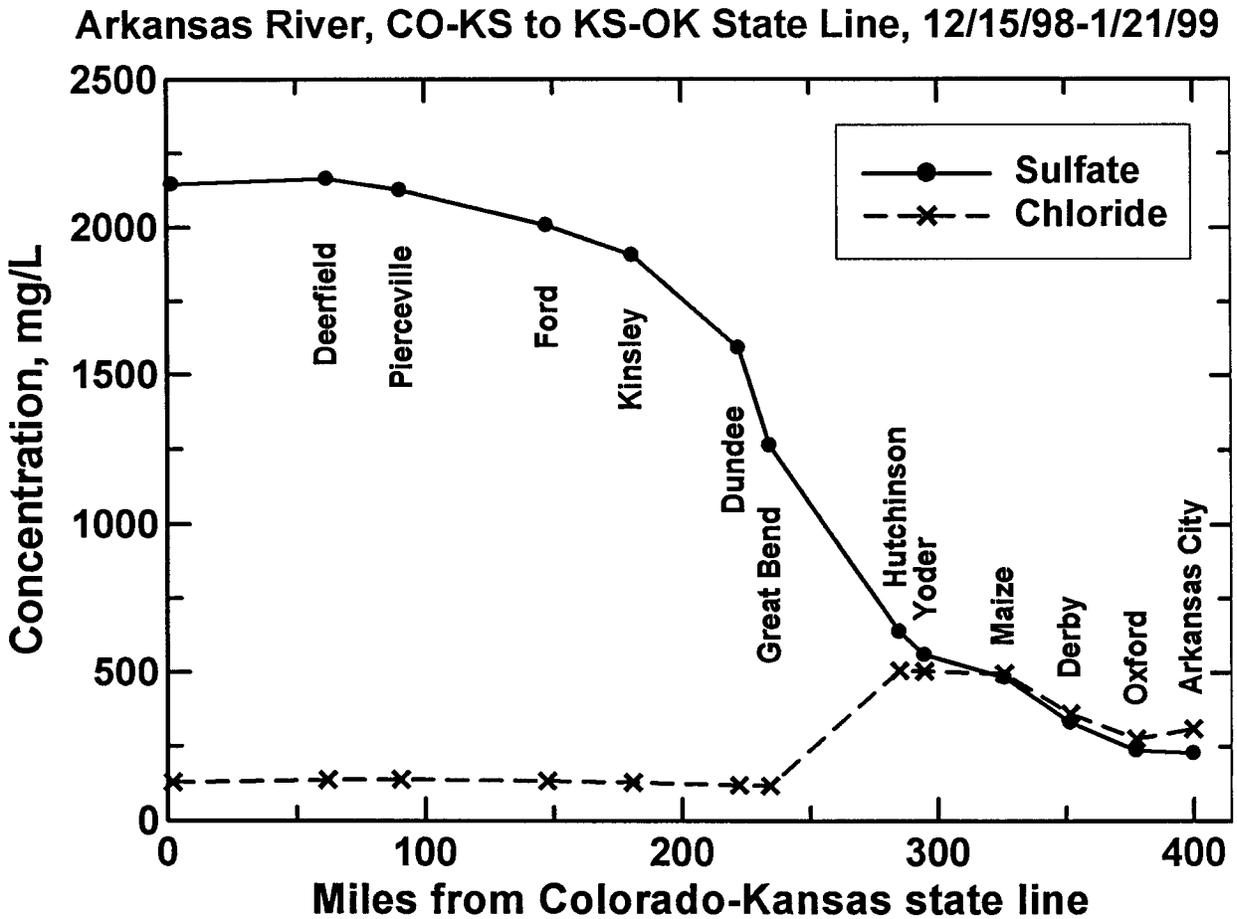
Mean potential evapotranspiration exceeds precipitation in western two-thirds of Kansas

9. Map of Arkansas River basin in Kansas

10. Graph of Cl and SO₄ for Arkansas R when flow is not continuous through Kansas



11. Graph of Cl and SO₄ for Arkansas R when flow is continuous through Kansas



12. Saltwater/Mineralized Water Pollution

Disposal of waste saltwater and salt

Oil and gas brine (high chloride, low sulfate)

Conventional water-softener discharge (high chloride, low sulfate)

Salt mining and processing (high chloride, low to moderate sulfate)

Salt applied to roads for deicing (high chloride, low sulfate)

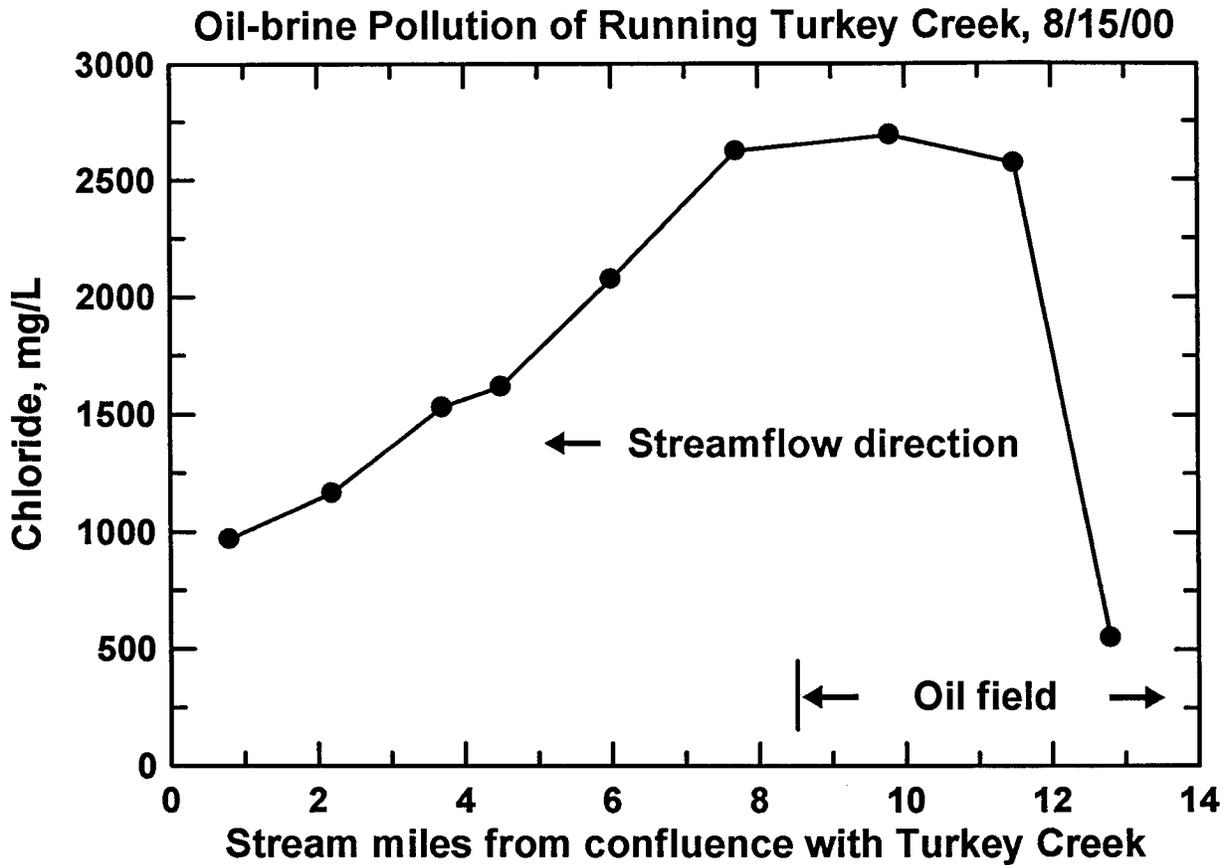
Other wastes

Landfill leachate (moderate chloride and sulfate)

Chemical leaks and spills (e.g., hydrochloric acid)

13. Oil and gas map of Kansas

14. Graph of Cl versus stream miles showing oil-brine contamination of Running Turkey Creek



15. Cl source identification for upper Little Arkansas River basin for Feb 2000 flow conditions

Chloride Source Identification for the Upper Part of the Little Arkansas River Basin for February 21, 2000 Conditions.

Stream site	Turkey Creek near Alta Mills	Little Arkansas River near Alta Mills
Measured chloride concentration	624 mg/L	300 mg/L
Estimated oil-brine source	55-60% (~360 mg/L)	55-65% (~180 mg/L)
Estimated natural sources	15-20% (~110 mg/L)	30-35% (~100 mg/L)
Estimated wastewater sources (primarily water-softener salt)	20-30% (~154 mg/L)	5-10% (~20 mg/L)

16. Weathering of sulfide minerals in rocks

Natural weathering and discharge of ground waters

Slow, small additions to surface waters

Accelerated weathering after exposure by coal and metal mining

Sulfate concentrations can exceed 10,000 mg/L in mine waters

Can increase sulfate concentrations by over 1,000 mg/L in streams

High sulfate/chloride ratios

17. Salinity Source Identification Methods

Chloride and bromide, and usually sulfate, are conservative during mixing of different waters

Bromide/chloride and sulfate/chloride ratios range widely in different salinity sources

Identify sources based on changes in ratios with change in chloride or sulfate concentration

Can differentiate and estimate contributions from multiple sources in some mixtures.

18. Examples of saltwater differentiation – intrusion of natural saltwater

19. Br/Cl vs Cl concentration for GMD5, mixing of freshwater with halite-dissolution brine

See Figure 1 in Whittemore, 1995, Environmental Geosciences 2: 15-31.

20. Examples of saltwater differentiation – oil and gas brine contamination

21. Br/Cl vs Cl concentration for Blood Orchard area in Wichita

In principle, similar to Figures 3 and 4 in Whittemore, 1995, Environmental Geosciences 2: 15-31.

22. Examples of saltwater differentiation – salinization from evapotranspiration concentration

23. SO_4/Cl vs Cl concentration for mixing of upper Ark R waters with lower Ark R waters

Mixing of upper Arkansas River water of high SO_4/Cl from southwest Kansas with lower Arkansas River water of much lower SO_4/Cl ; chemistry of mixture relative to upper Arkansas water chemistry and mixing curve between freshwater and Permian saltwater intrusion in south-central Kansas allows estimation of chloride and sulfate sources

24. Examples of saltwater differentiation – contamination from dissolution of rock salt

25. Br/Cl vs Cl concentration for Turkey Creek - mixing of freshwater with oil brine and water-softener salt sources

Intersections of multiple mixing curves based on different end points of contamination sources progressively downstream allows estimation of chloride from different sources

26. Conclusions

Concentrations of chloride and sulfate exceeding drinking-water standards in a surface water can originate from multiple sources

Origins of high chloride and sulfate include natural and anthropogenic sources and processes

Sources can be identified and often quantified based on mixing relationships involving bromide/chloride and sulfate/chloride ratios