Dissolved Loads of Rivers and Surface Water Quantity/Quality Relationships
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A regional analysis of water quality in major streams of the United States

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ABSTRACT The National Stream Quality Accounting Network (NASQAN), established by the US Geological Survey in 1973, is designed to describe quantitatively the quality of the major rivers of the United States on a systematic and continuing basis. Historical data collected at 88 long-term water quality sites were evaluated relative to their suitability for depicting general areal variability and time trends of major inorganic chemical constituents. Many of these sites are included among the current 517-site NASQAN program. More recent data from this network were used to characterize stream temperatures. Using the 88-site historical data, regression relationships between major inorganic constituent concentrations and specific conductance or discharge were developed, and water quality conditions were related to regional geological features and physiographic provinces. Based upon variation in and distribution of regression coefficients, regional regression equations which provide estimates of water quality of surface waters are presented for major regions of the nation. For selected sites, examples are shown for assessing time trends in historical water quality data.

Analyse régionale de la qualité de l'eau des principales rivières des etats-unis

RESUME Le Réseau national de la qualité des eaux des rivières (NASQAN), établi par le US Geological Survey en 1973 est destiné à décrire quantitativement la qualité des principaux cours d'eau des Etat-Unis de façon systématique et continue. Des données collectées en 88 stations historiques de mesures de la qualité des eaux ont été examinées en vue de définir leur capacité à décrire correctement les variations spatiales et les tendances des principaux constituants chimiques. Beaucoup de ces stations font partie des 517 sites courants du programme NASQAN. Des données récentes de ce réseau ont été utilisées pour caractériser la température des cours d'eau. En utilisant les données des 88 stations historiques des régressions ont été établies entre les concentrations des constituants chimiques, la conductivité ou le débit; la qualité de l'eau a été associée aux caractéristiques géologiques et aux régions géographiques. A partir des coefficients de régression des équations ont été établies qui permettent d'estimer la qualité des eaux de surface pour les principales régions des Etats-Unis. Pour quelques sites choisis, des exemples sont donnés de l'évolution temporelle de la qualité des eaux.

INTRODUCTION

Population growth and economic expansion within the United States have had an impact on, and will continue to alter, the nation's environment. These environmental changes often are visible through their direct and significant effects on water quality of the nation's rivers. Visual inspection of a sediment-laden stream below a developing area or chemical analyses of water from a stream receiving mine drainage or industrial waste discharge are examples that substantiate the need for better understanding of man's influence on water quality in order to properly manage our water resources. Concern for the effect of the environmental changes on water quality on a nationwide basis in the USA is shared by the US Geological Survey (USGS), through its role in the collection and interpretation of hydrological data that are used by federal, state and local agencies, and by the private sector, through development of management plans for the nation's water resources.

State and federal agencies traditionally have conducted hydrological data collection activities with the primary objective of satisfying local interests or needs. Abbreviated periods of station operation, station relocations over time, and variation in water quality variable coverage across the nation associated with local project objectives and interests have limited the usefulness of much of the data available for evaluation and analysis on a regional or nationwide basis. Consequently, the USGS's data base until recent years has been limited in providing information leading to better understanding of the complex physical processes (natural and human-induced) that affect streamflow quality.

In an effort to provide a consistent data base and more relevant water quality information for water resources planning and management on a national and regional scale, the USGS began in January 1973 operation of the National Stream Quality Accounting Network (NASQAN). The accounting concept of the network is fulfilled by siting stations at outflow points from major hydrological accounting units (Ficke & Hawkinson, 1975). The unit boundaries represent a delineation of river basins into hydrological areas that coincide with Water Resources Council (WRC) region and subregion boundaries (US Water Resources Council, 1970). Since January 1973, when 50 stations were initiated, this network has grown to 345 stations in September 1975 and to 517 stations in 1980 (Smith *et al.*, 1982). A broad range of water quality characteristics, including major inorganic constituents, nutrient species, sediment, temperature, trace elements, selected organics, and biological constituents, is provided (Ficke & Hawkinson, 1975). The primary objectives of NASQAN are: (a) to account for the quantity and quality of water moving within and from the USA; (b) to depict areal variability in surface water quality; (c) to detect long-term changes in stream quality; and (d) to lay the groundwork for future assessments of changes in stream quality. Some doubts as to whether present NASQAN operations can effectively achieve these objectives have been raised (Systems Analysis Group, 1979; US General

Accounting Office, 1981). The purpose of this paper is to present an overview of some of the information provided by this national network on regional patterns and time trends in water quality.

Statistical analyses and interpretation of data presented herein are not necessarily dependent upon data collected since inception of the network in January 1973. Most of the historical data at NASQAN-designated stations consist primarily of major inorganic constituents, stream temperature and specific conductance. For example, Leifeste (1974) used dissolved solids data for 54 coastal river basins for the 1966-1969 period to estimate dissolved solids loads contributed to the oceans from the conterminous USA. Many of these same stations have been incorporated into the NASQAN program. Steele *et al.* (1974) utilized historical long-term water quality records from 88 stations nationwide (Fig.1) in an effort to describe and to apply statistical approaches for evaluating areal variations and temporal changes in stream temperature and selected chemical quality variables. Results of regression analysis of selected major inorganic constituents, specific conductance, temperature, and trace metals during the 1974 and 1975 water years have been provided by Hawkinson *et al.* (1977) and Briggs & Ficke (1978). Recent trend analysis studies using NASQAN data have been made by Hirsch *et al.* (1982) and Smith *et al.* (1982).

APPROACH

Statistical data summaries (Steele *et al.*, 1974) and regression analyses relating concentrations of major inorganic constituents or

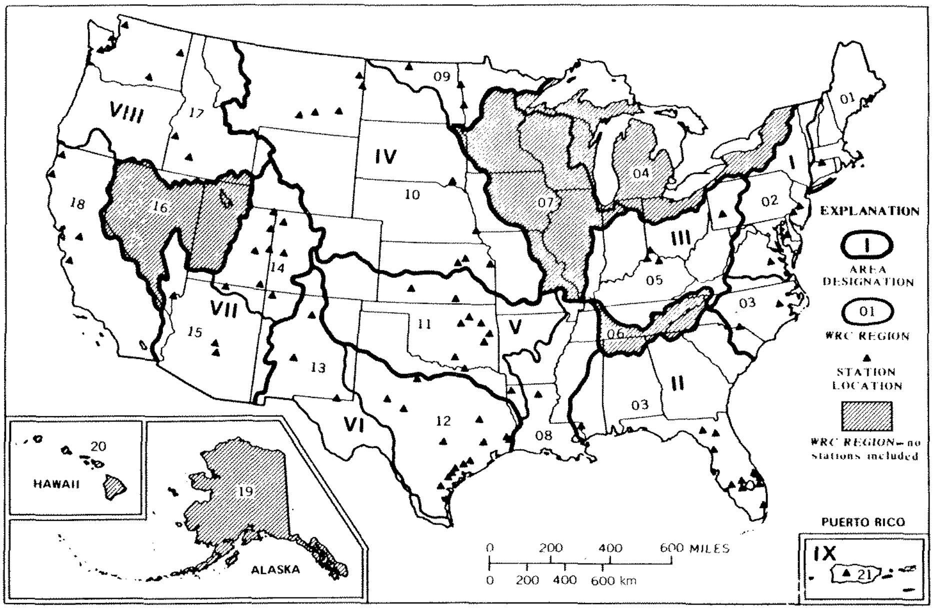


FIG.1 Location of selected historical stations used in the assessment and delineation of areas for regional analysis.

dissolved solids to specific conductance, and dissolved solids or specific conductance to stream discharge (Steele & Hawkinson, in review) provide the basis for a preliminary regional analysis for inorganic water quality characteristics in major drainage basins of the USA. The physiographic divisions of the USA as described by Fenneman (1928) provide a means for regionalization. The divisions are based on similar geographical and topographical features (Table 1), with sequence (numbered) codes representing the study site(s) within each division. Site locations used in the study are shown in Fig.2.

The regional evaluation and comparison in this study involves two aspects. First, mean levels and variability of selected inorganic constituents are used to describe the general condition of major streams within the various physical divisions. Secondly, regression relationships are presented that permit estimates of inorganic chemical quality (in this case, dissolved solids, chloride, and hardness concentrations from specific conductance) within physical divisions or groups of divisions. A simplified regional analysis is also made of stream temperature characteristics for a set of NASQAN stations along the eastern coast of the USA. Finally, some examples of trend-analysis techniques for specific conductance-stream discharge relationships and stream temperatures are described.

RESULTS

Regionalization

Based on data obtained during the 1966-1972 water years, the distribution of mean specific conductance values for the 87 historical stations in relation to the physical divisions of Fenneman (1928) is shown in Fig.2. Using specific conductance as an overall indicator of major inorganic chemical quality, the lowest concentrations of dissolved materials were found to exist along the Atlantic coast above Florida and along the Pacific coast. These areas coincide with the following regions of Fenneman (1928): Appalachian Highlands, the Pacific Mountain System, and the northern portion of the Atlantic Plain. Rock types in these regions include the sedimentary types of sandstone, shale and limestone and the metamorphic types of gneiss, schist, and some quartzite in the mid-Atlantic area. Highest mean concentrations and greatest variability in dissolved solids (based on specific conductance as an indicator) occur predominately in the Central Lowland and Great Plains provinces (J and L) of the Interior Plains located in the central USA from North Dakota to Texas, and in the Colorado Plateaus and Basin and Range provinces (P and R) of the Intermontane Plateaus which comprise the Colorado River basin of the southwestern USA. Mean chloride concentrations at 90% of 87 stations having data were less than the 250 mg l^{-1} recommended drinking water standard (National Academy of Sciences-National Academy of Engineering, 1973) for public water supplies. Highest concentrations (>500 mg l^{-1}) generally occurred in the southern part of the Central Lowland Province (Oklahoma and northwestern Texas).

Excessively hard waters (concentrations greater than 300 mg l^{-1} as $CaCO_3$) tended to be associated with provinces J, L, and P (Central

TABLE 1 Physical divisions of the USA and stations located within each

Letter designation[*]	*Region*	*Province*	*Stations within province*[†]
A	*Appalachian Highlands*	*New England*	*1*
B	*Appalachian Highlands*	*Valley and Ridge*	-
C	*Appalachian Highlands*	*Appalachian Plateaus*	*20*
D	*Appalachian Highlands*	*Blue Ridge*	-
E	*Appalachian Highlands*	*Piedmont*	*2, 3, 5, 7*
F	*Atlantic Plain*	*Coastal Plain*	*4, 6, 8-19, 47-52, 56-62*
G	*Interior Plains*	*Interior Low Plateaus*	*21, 23*
H	*Interior Highlands*	*Ozark Plateaus*	*42, 43*
I	*Interior Highlands*	*Ouachita*	*44*
J	*Interior Plains*	*Central Lowland*	*22, 24-26, 32, 33, 35, 36, 38-41, 45, 46, 53, 55*
K	*Laurentian Upland*	*Superior Upland*	-
L	*Interior Plains*	*Great Plains*	*27-31, 34, 37, 54*
M	*Rocky Mountain System*	*Northern Rocky Mountains*	*84*
N	*Rocky Mountain System*	*Southern Rocky Mountains*	*63*
O	*Rocky Mountain System*	*Middle Rocky Mountains*	-
P	*Intermontane Plateaus*	*Colorado Plateaus*	*66, 67, 70-75*
Q	*Intermontane Plateaus*	*Columbia Plateaus*	*85-87*
R	*Intermontane Plateaus*	*Basin and Range*	*64, 65, 76, 77*
S	*Pacific Mountain System*	*Cascade-Sierra Mountains*	-
T	*Pacific Mountain System*	*Pacific Border*	*78-83*
U	*Rocky Mountain System*	*Wyoming Basin*	*68-69*

[*] *See Fig.2.*

[†] *Numbers represent station sequence code from Fig.2.*

Lowlands, Great Plains and Colorado Plateaus). The excessively hard waters tended to coincide with the river basins containing waters categorized as a calcium-magnesium, sulphate-chloride type by Rainwater (1966, pl. 2). Dominant rocks in these basins are sedimentary and of Cretaceous and late Palaeozoic ages.

Regression coefficient equations for dissolved concentration (DS)-specific conductance (SC) relationships were analysed regionally. Preliminary efforts involved the grouping of all stations located in the provinces within a region such as the Appalachian Highlands or Interior Plains. The weighted DS-SC regression relationships, based on station records representing each region, are presented in Table 2. Similarity in DS-SC regression relationships is evident for the dilute surface waters of the Appalachian Highlands and Pacific Mountain System regions. The effect of the relatively greater range in salinity conditions in the Interior Plains and Intermontane Plateaus regions is evidenced by the occurrence of greater slope coefficients and larger negative intercepts in comparison with these regression coefficients for other regions. The regional DS-SC equations (Table 2) gave estimates of dissolved solids concentrations that were generally within about 15% of those obtained using the equation based solely on individual station data. Favourable results of a similar regional analysis have been reported in the Susquehanna River basin (Lystrom *et al.*, 1978).

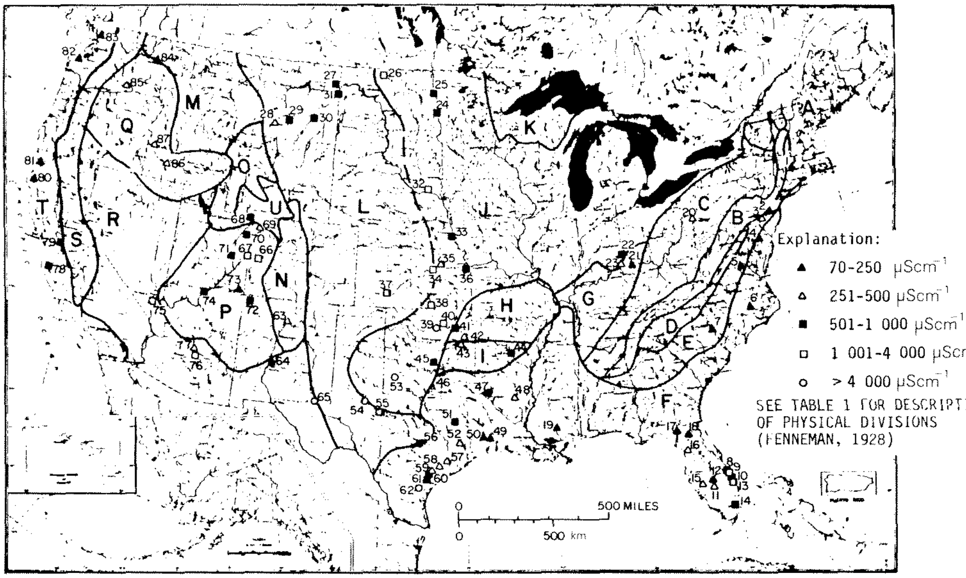


FIG.2 Variation of mean specific conductance with respect to physical divisions of the USA.

The ability of alternative forms of regression functions to provide

TABLE 2 Summary of dissolved solids-specific conductance regression equations

Region	Provinces[*]	Number of stations in region[†]	Slope[§] (b)	Intercept[§] (a)	Range in SC ($\mu S\ cm^{-1}$) (independent variable)	Standard error of estimate ($mg\ l^{-1}$)
Appalachian Highlands	A, C, E	6	0.557	6.07	45-706	6.7
Atlantic Plain	F	27	0.562	-5.38	28-39 400	39.4
Interior Plains	G, J, L	26	0.718	-69.6	103-66 100	91.8
Interior Highlands	H, I	3	0.541	17.9	94-1280	11.7
Rocky Mountain System	M, N, U	4	0.681	-19.1	61-1060	12.3
Intermontane Plateaus	P, Q, R	15	0.725	-63.8	125-41 000	30.6
Pacific Mountain System	T	6	0.576	7.64	33-1620	7.2

[*] No stations included in the study represented provinces B, D, K, O, and S (see Table 1 and Fig.1).

[†] Puerto Rico (station 88, Fig.1) is not represented.

[§] Regression relationship: $DS = a + b(SC)$, when DS = dissolved-solids concentrations, SC = specific conductance, and a and b are regression coefficients.

an adequate means of predicting certain chemical constituents is summarized in Fig.3. Both specific conductance (SC) and stream discharge (Q) have been suggested for use as indicator variables in estimating concentrations of major ions or dissolved solids. However, Steele (1970) demonstrated the preferred use of specific conductance for this purpose. Such a preference is confirmed by the regional analysis results shown in Fig.3, where much greater explained variances are achieved using solute concentration-specific conductance relationships relative to the use of stream discharge as an indicator variable for the same set of data.

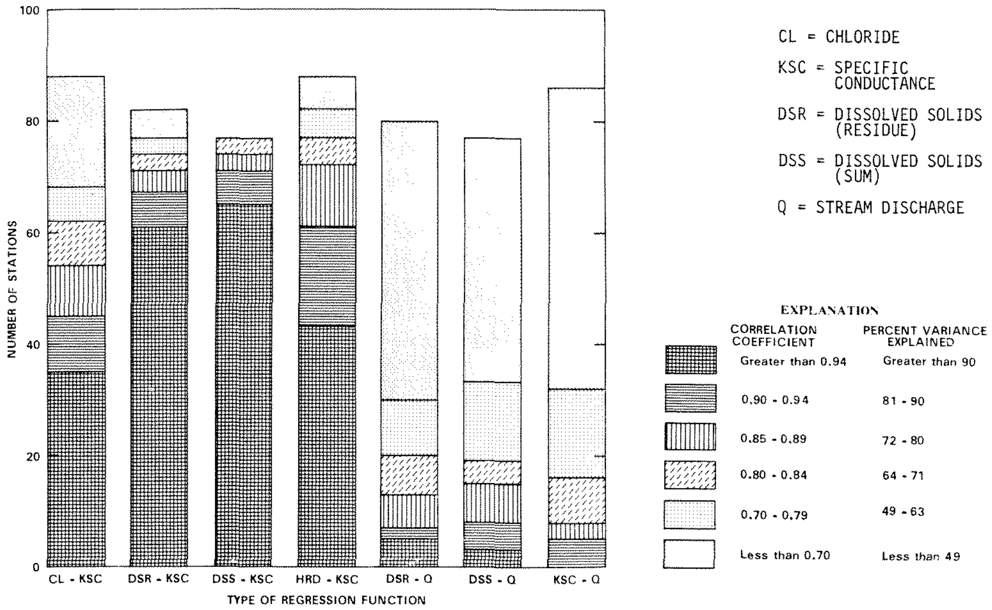


FIG.3 Distribution of the explained variance of the various regression functions used in the regional analysis for 88 sampling stations.

As an example of regional analysis of water temperature characteristics, daily records of water temperature at 14 NASQAN stations along the US eastern coast were analysed using a harmonic function depicting seasonal variability (Hawkinson *et al.*, 1977; Briggs & Ficke, 1978). The harmonic analysis techniques are described by Steele (1974). Average mean and amplitude harmonic coefficients for 2 years of data at each station were plotted as a function of station latitude (Fig.4). Quite consistent regional relationships were exhibited for these two water temperature harmonic coefficients. Similar case studies on a smaller areal scale have been reported using this regional analysis procedure in the states of Indiana and Georgia, where the range of station elevation was minimal.

Time trends

Several examples of time trends in historical long-term water quality

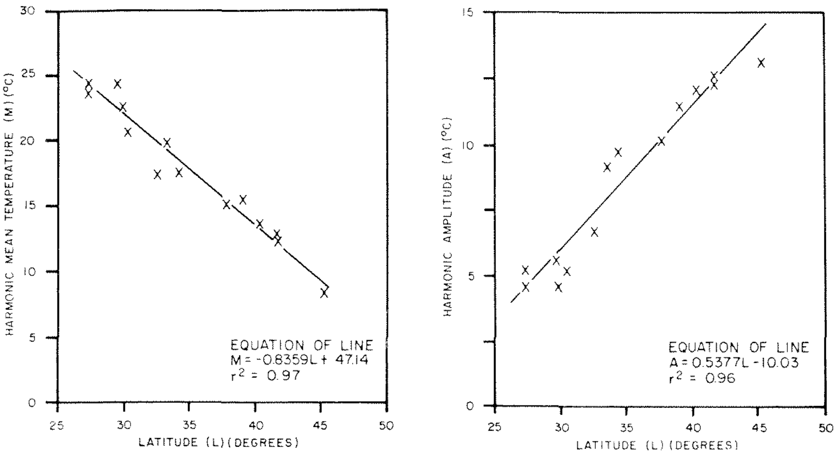


FIG.4 Regional analysis of water temperature harmonic coefficients, eastern coast of the USA (data provided by Hawkinson et al., 1977 and Briggs & Ficke, 1978).

data are shown in Fig.5. In these case studies, attention is directed to masking out the effects of annual flow variability and to evaluating the net effects of water quality changes as depicted by specific conductance. In the first case study for the Delaware River, no significant change has affected the specific conductance-stream discharge relationship. However, segmenting the period of record and using a nonparametric test for significant changes (Kendall's tau ranking test, Conover, 1971), reveals that streamflows have declined and specific conductances correspondingly increased over the historical period studied, even though the functional relationship was unchanged (Steele *et al.*, 1974). In the second and third case studies (Fig.5), significant shifts in the specific conductance-stream discharge relationships have occurred. For the Green River, degradation in water quality, reflected by increased specific conductance levels, has occurred as a result of an upstream impoundment. For the Canadian River, water quality conditions have improved, due primarily to the elimination of brines discharging into this river during the mid-1950's.

The harmonic analysis technique discussed previously has been useful in documenting significant changes in water temperature seasonal variability (Steele *et al.*, 1974). Several examples are given in Fig.6, where the seasonal variability in water temperature and, in some cases, the mean water temperature has been reduced as the result of upstream impoundments (Steele, 1982). In each case, the significance of these observed changes can be evaluated by Kendall's tau procedure (Conover, 1971) applied to the annual series of harmonic coefficients for the period of record.

DISCUSSION

Several procedures for regionalizing information on water quality conditions in streams have been demonstrated, using historical long-term data and data provided from the National Stream Quality

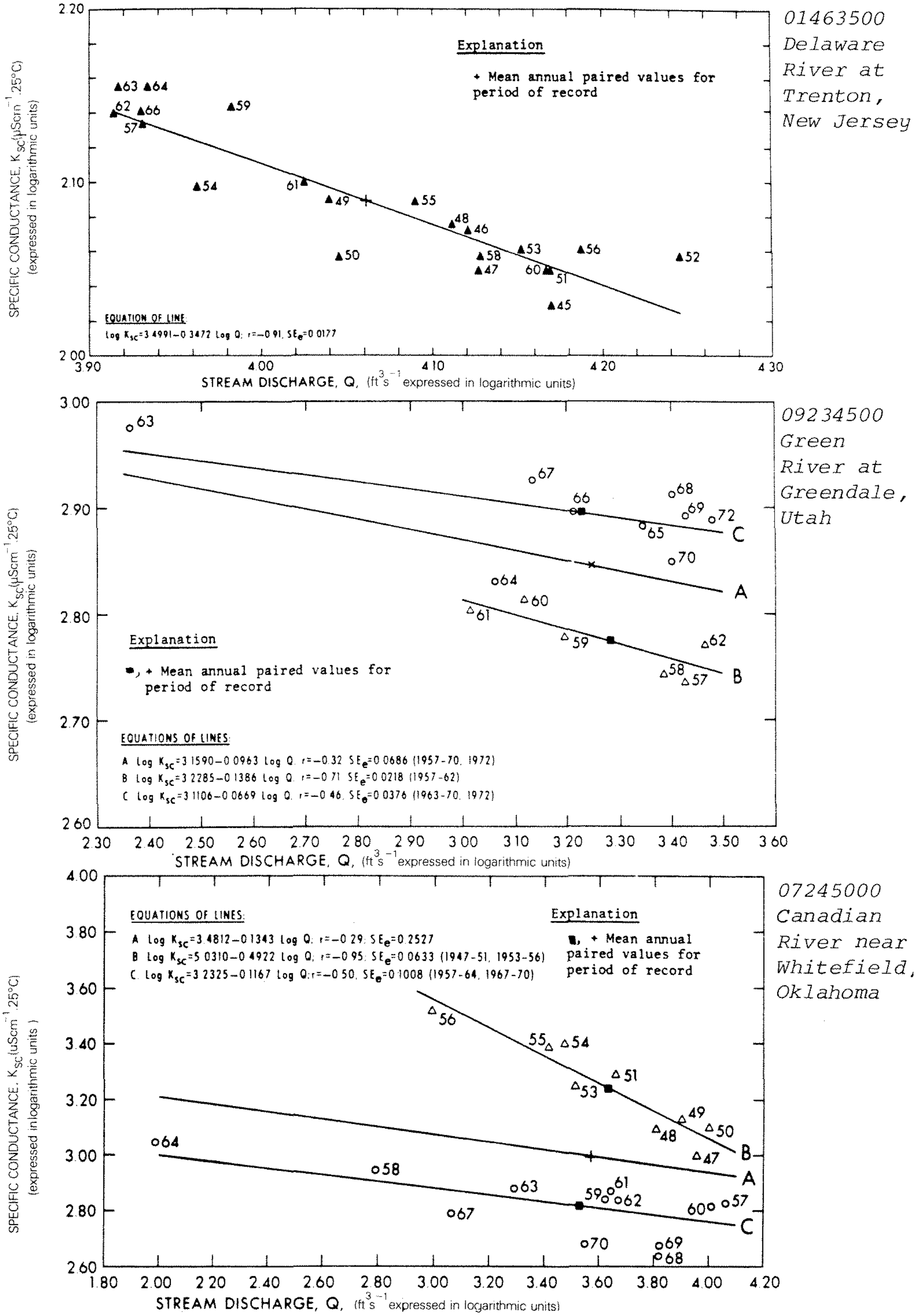
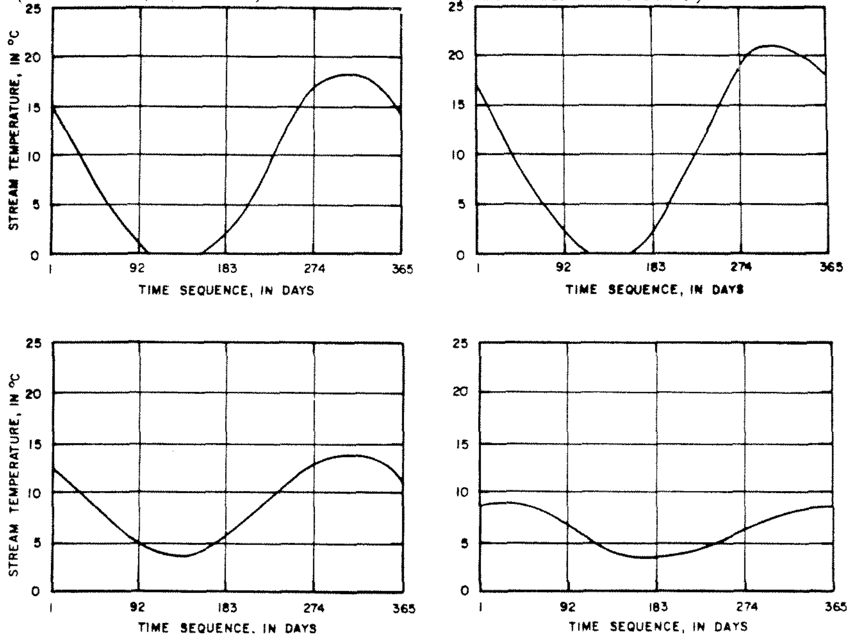


FIG.5 Examples of trend analysis of specific conductance stream discharge relationships (after Steele et al., 1974).

San Juan River near Archuleta,
New Mexico
(STATION 09355500)

Green River near Greendale,
Utah
(STATION 09234500)



Green River at Jensen,
Utah
(STATION 09261000)

Colorado River at Lees
Ferry, Arizona
(STATION 09380000)

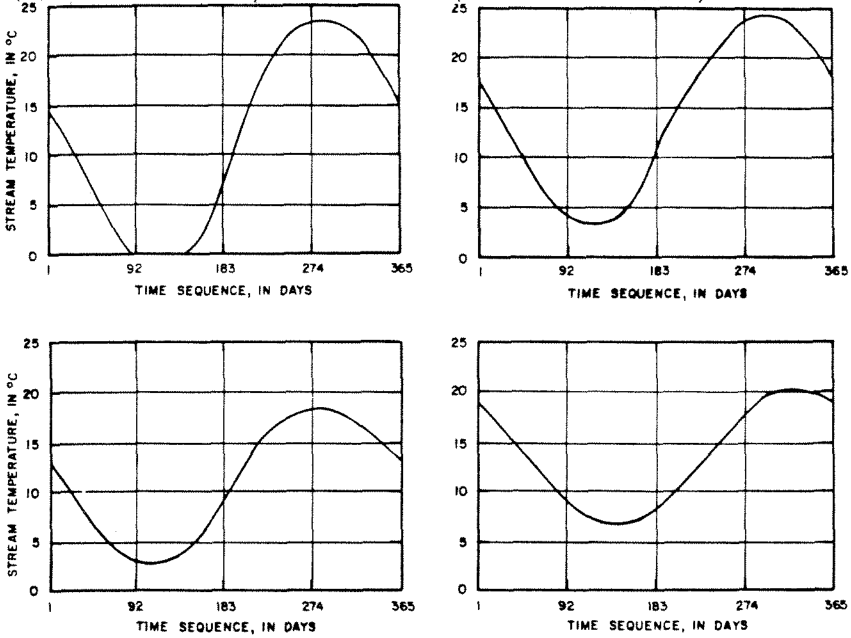


FIG.6 Examples of changes in seasonal stream temperature patterns before and after upstream reservoir development (after Steele, 1982).

Accounting Network (NASQAN). Moreover, a trend-analysis evaluation, as exhibited in several case studies in this paper, is useful in assessing impacts of economic development or allocations of fiscal resources for water pollution control. Such simplified procedures would appear to be readily understood by resource planners and managers to aid them in evaluating trade-offs inherent in their decision making. Of comparable importance may be the value of these procedures in the design, operation, and evaluation of stream quality networks. The effectiveness of nationwide as well as localized water quality data collection programmes can be assessed, and useful information is derived from the basic data. In certain instances, such techniques provide a means to fill in information not provided directly by the data. These procedures might be applied to improving existing nationwide or global estimates of solute levels discharging to the ocean (Durum *et al.*, 1960; Leifeste, 1974; Martin & Meybeck, 1979).

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