

Variation of Water Quality Parameters
during Floods and Its Implications
for Sampling Protocols

by

A.G. Bobba and E.D. Ongley

Rivers Research Branch
National Water Research Institute
Canada Centre for Inland Waters
Burlington, Ontario, L7R 4A6

July 1987

NWRI Contribution #87-136

VARIATION OF WATER QUALITY PARAMETERS DURING
FLOODS AND ITS IMPLICATIONS FOR SAMPLING PROTOCOLS

A.G. Bobba and E.D. Ongley

Rivers Research Branch
National Water Research Institute
Canada Centre for Inland Waters
Burlington, Ontario, Canada L7R 4A6

MANAGEMENT PERSPECTIVE

This paper briefly reviews the impact of the major changes in land use on water quality from the perspective of flood events. An overview is presented of water quality transformations that may occur as water moves through the hydrological cycle. The transformations occurring in free water are then reviewed from a number of specific viewpoints. Three specific aspects of water quality are considered in detail to review present approaches to prediction. These aspects are nutrients, inorganic exchange processes and organic transformations.

The problems of data collection from monitoring systems are addressed. Many countries now commit substantial resources to the collection of water quality data, but there are concerns as to the reliability and validity of some of this information. Clear objectives for a monitoring system, and the need to understand the hydrological and biological systems being monitored are essential.

PERSPECTIVES DE GESTION

La présente communication décrit brièvement les effets des principaux changements au niveau de l'utilisation des terres sur la qualité de l'eau dans la perspective de phénomènes comme les inondations. On présente une vue d'ensemble des transformations de la qualité de l'eau qui peuvent se produire à mesure que l'eau se déplace à travers le cycle hydrologique. Les transformations se produisant dans l'eau libre sont ensuite étudiées à partir d'un certain nombre de points de vue particuliers. Trois aspects caractéristiques de la qualité de l'eau sont considérés en détail pour examiner les techniques actuelles utilisées pour les prévisions. Ces aspects concernent les agents nutritifs, les processus d'échange minéral et les transformations organiques.

Les problèmes de la collecte de données à partir de systèmes de surveillance sont abordés. De nombreux pays consacrent maintenant des ressources importantes à la collecte de données sur la qualité de l'eau, mais il y a des doutes quant à la fiabilité et à la validité de certaines parties de cette information. Des objectifs clairs pour tout système de surveillance, et la nécessité de comprendre les systèmes hydrologiques et biologiques surveillés sont essentiels.

TABLE OF CONTENTS

INTRODUCTION

HYDROLOGICAL DISCRIMINATION OF SNOWMELT VERSUS RAINFALL EVENTS

SEDIMENT AND SEDIMENT-ASSOCIATED CHEMICAL TRANSPORT

MAJOR IONS

SAMPLING FOR COMPLIANCE AND LOADINGS

INFERENCES REGARDING NONPOINT AND POINT SOURCE MANAGEMENT

CONCLUSIONS AND RECOMMENDATIONS

ABSTRACT

The intent is to demonstrate the very substantial differences which occur between snowmelt and rainfall induced events. The biogeochemical processes operating on source materials are an important control over stream chemistry. Suspended sediment plays an important role in chemical transport, particularly for phosphorous and organic contaminants. Sediment transport behaves very differently from major ion transport; sediment-associated chemistry is different seasonally and requires different sampling protocols. We will draw conclusions and make recommendations for sampling both for sediment-associated chemistry and for major ions. We demonstrate the utility of these sampling protocols for making meaningful inferences about river basin management.

RÉSUMÉ

Le but est de démontrer les différences notoires entre les phénomènes dus à la fonte des neiges et ceux causés par les pluies. Les processus biogéochimiques qui s'exercent sur les matières à la source constituent des facteurs importants pour la chimie des cours d'eau. Les sédiments en suspension jouent un rôle de premier plan dans le transport des substances chimiques, et particulièrement du phosphore et des contaminants organiques. Le transport des sédiments se fait de façon très différente de celui des principaux ions; la chimie associée aux sédiments varie selon la saison, et requiert différentes méthodes d'échantillonnage. Nous rechercherons des conclusions et ferons des propositions pour l'échantillonnage aussi bien des substances chimiques associées aux sédiments que des principaux ions. Nous démontrons l'utilité de ces méthodes d'échantillonnage pour l'obtention de résultats concluants en ce qui a trait à la gestion des bassins de rivières.

INTRODUCTION

This paper is a comparative survey of the occurrence of changes in water quality arising from variation in discharge within the context of the hydrological cycle. The emphasis here is on storm flow generated by rainfall or snowmelt. Sampling strategies can be optimized and the process validated or better characterized by knowledge of source and conveyance mechanisms; therefore the hydrological cycle can be appropriately conceptualized as a number of interlinked storages or compartments, each of which can be identified with part of the water environment. Such schemes range in complexity from the simplest three compartment structures for the global hydrological cycle to systems comprising many compartments which yet depict only a part of the water environment (e.g. McPherson and Schneider, 1974).

Variations in constituent concentration may be due to a combination of physical, chemical and biological processes. Such processes include dilution (and concentration), nucleation, diffusion, turbulent dispersion, oxidation (and reduction), radioactive decay, nitrification, leaching and biodegradation. These processes can generally be regarded as occurring within the compartments; that is, there is no opportunity for quality change between the output of one compartment and the input of the next. Processes which occur only at the interfaces are identified below.

Physical Processes

Phase changes occur in evaporation from free water, transpiring vegetation and surface soil, and within the pores of unsaturated soils. Volatilization may be significant in such cases as ammonia losses from soil of water, especially at higher pH, which favours the formation of free NH_3 , rather than NH_4 , thus contributing to the ammonia load in the atmosphere. Other important gas transfer phenomena are the solution of oxygen, necessary to sustain aerobic conditions in soil and water, and solution of carbon dioxide. Diffusion processes largely determine the distribution of oxygen and CO_2 within both aqueous and gas phases, and the distribution of salts and nutrients in soil water and free surface waters.

In addition, various adsorption and ion exchange phenomena are important to the ionic constituents within pore water, and play a significant role in the transport and retention of phosphorus and nitrogen in the form of NH_4 . The thermal energy distribution has a profound effect on other processes, especially evaporation and the kinetics of chemical and biological reactions.

Chemical Processes

Viewed simplistically, mineral weathering and soil formation are chemical processes which result in the release of many products, of varying solubility, which affect the constituents in pore water

streams and lakes. Hence both solubility and kinetic relationships for the various constituents in soils and waters are fundamental to any basic study of water quality changes, although direct application of such data is frequently made difficult by the complexity of the matrix and other competing or complementary processes, such as adsorption and ion exchange.

Biological Processes

Whenever organic residues such as vegetation, wastes and dead animal matter are present, the growth of various forms of microorganisms is stimulated; these are accompanied by biodegradation processes which result in the mineralization of many nutrients and their return to the environment. In the presence of molecular oxygen, aerobic bacteria and fungi are the major forms. Where the low solubility and limited diffusion rate of oxygen combine to limit the availability of dissolved oxygen, alternative forms of respiration are encouraged, such as anoxic respiration using, in order, nitrates and sulphates, and finally fully anaerobic action may result. The order in which these forms of respiration are listed corresponds to decreasing energy yield and decreasing redox potential. Thus, many superficially chemical processes in soil and water are in fact biochemically mediated, as an example, hydrolysis, oxidation and reduction. The nutrients released in these microbial processes are

recycle in the growth of primary procedures such as plants and algae, and in the process may significantly contribute to the pool of nutrients potentially available for transport out of the catchment.

Nitrification and the oxidation of reduced sulphur compounds to sulphates are also aerobic processes carried out primarily by autotrophic bacteria which share with plants the use of carbon dioxide as their carbon source. Both processes result in acid production with the potential for reducing pH. In nitrification NH_4 , which is significantly adsorbed in soil systems, is oxidized through the intermediate stage of NO_2 to NO_3 , which is much more mobile and hence prone to leaching and transport by pore water movement. Sulphate (sulphuric acid) production can be a particular problem where sulphides such as feldspars are oxidized - most notably in the drainage waters from many coal and metalliferous mines and their associated tailing dumps (Bobba, 1971). Low pH resulting from such action increases the solubility of heavy metals and potential for leaching and mobilization into surrounding drainage systems.

Overall, the availability of oxygen determines whether aerobic or anaerobic processes prevail, and hence whether oxidizing or reducing conditions occurs. This affects many chemical equilibria and ultimately influences surface water quality.

Storm-Period Response

The study of storm (and snowmelt) runoff generation can be approached in a variety of ways. For example, one may consider only what portion of the runoff water existed in the watershed prior to the runoff event and what portion was added by the runoff-inducing event. Alternatively, one may choose only to examine the manner in which the runoff water travels over the last several meters to the stream. A third approach could be concerned only with the history of the water from its arrival in the watershed to its ultimate delivery to the stream. These three approaches are termed: time aspects, ultimate delivery mechanism aspects and historical aspects, respectively. Each approach can be modelled and each is conceptually linked to surface water quality.

Currently, the most widely accepted theories for storm (and snowmelt) runoff generation stem from the ultimate delivery mechanisms approach to the subject. Each concept attempts to account for both the rapid response of the stream to runoff-inducing events and observed increase in stream discharge. Freeze (1974) has summarized the most popular of these theories as: a) Horton overland flow, b) partial area - overland flow, c) variable source area - overland flows and d) variable source area - subsurface storm flow. The reader is referred to Freeze (1974) for an excellent review and reference list for each mechanism.

SNOWMELT RUNOFF

Snowmelt dominates the hydrologic year in cold temperature and subarctic regions. It generates the greatest flood hazard (often in conjunction with ice jamming), and raises groundwater levels to their highest levels often causing landslides and waterlogging that impede access, building, ploughing and other uses of the land.

Field investigations of snowmelt runoff are difficult and uncomfortable, and therefore runoff processes have received relatively little empirical study. Consequently, there has been little stimulus for the development of models. On the other hand, the more tractable problem of melting at the snowpack surface has been the focus of much fieldwork and theoretical study. Yet runoff processes can have at least as great an influence on peak flows and their timing as do the melt parameters that have received so much study.

Non-Point Source Pollution

Sediment erosion

Sediment is an important component in water quality studies. The close association of heavy metals and toxic hydrophobic organic contaminants with suspended matter is now well known (Förstner and Wittman; Chapman et al., 1982). Less well known are the spatial and

temporal changes which occur under various flow regimes (Ongley, 1987).

Sediment transport in rivers has been studied for years, especially its influence on channel morphology (e.g. Yalin, 1972; Garf, 1971). Sediment moving downstream can be classified into two categories, bed load and suspended sediment load. The bed load is generally considered as those solid particles (sometimes boulders) that move along (roll on) the bottom of the stream or waterway by the force of the moving water. Bed load, although mainly associated with high levels of river discharge, is not considered an important element in chemical transport. Suspended sediment load, also discharge dependent, is comprised of two components. One of these, the sand-size component ($\geq 63 \mu\text{m}$) displays increasing concentrations with depth in the water column, especially in the coarser fractions. This phenomenon is well known and requires depth-integrated sampling for studies of sand transport. Because particles that exceed $63 \mu\text{m}$ in equivalent spherical diameters have a small surface area, such particles are not especially chemically active and therefore do not play an important role in chemical transport. The second component of the suspended load is the wash load, composed of silt and clay-sized material. For water quality purposes, the wash load is important for two reasons: one, the particles comprising wash load have large and chemically active surfaces and, two, the wash load originates from beyond the channel boundaries and therefore reflects the chemistry from source (eroding) areas. Also, wash load in transit scavenges

dissolved metals and certain nutrients and synthetic organic contaminants from the water column. The wash load is, therefore, an important conveyance mechanism in water quality studies. The wash load is not considered to be depth dependent, therefore, depth-integrating sampling is less important than for sand-sized material.

The importance of storm-period flow in sediment transport, including wash load has been widely documented. A study of sediment yield from a Mississippi delta cotton field by Dendy (1981) found erosion rates in the range of 5 to 12 mg/ha.y; with highest sediment concentrations occurring during spring. About 98% of sediment particles exported were less than 16 μm in diameter. A five year study on the island of Oahu by Dooty et al. (1981) indicated 90% of the total suspended sediment load was produced during less than 2% of the time. Applicable state water quality standards did not establish a means of measuring the impacts of short-time activity on suspended sediment production. Some of the highest annual sediment yields reported in the world resulted from a study by Griffiths (1981) of basins of South Island, New Zealand. Geology had little apparent influence on sediment yields, and rainfall was the primary determining variable. McLaren (1981) reported that during 1974 a stream from a small drainage basin (117 km) on the east coast of Mellville Island discharged approximately $1.63 \times 10^7 \text{ m}^3$ water containing $7.08 \times 10^7 \text{ kg}$ suspended sediment. Because nearby basins showed hydrological similarities, the data could be extrapolated to provide an indication of the total suspended sediment discharge to adjacent channels.

Extrapolated values indicated that design criteria must consider typical runoffs to $1.2 \times 10^9 \text{ m}^3$ with peak mean-daily discharges in excess of $9.0 \times 10^6 \text{ m}^3/\text{d}$ and suspended sediment loads of $5.0 \times 10^9 \text{ kg/y}$.

The close association of sediment load and land use practices at source is important in water quality studies. Under the 1972 USA-Canada, Great Lakes Water Quality Agreement, 11 agricultural watersheds, representative of major soil-crop-livestock combinations, were monitored for two years to quantify the agricultural component of Great Lakes drainage basin pollution loads (Coote, D.R. et al., 1982). The data base from these 11 watersheds was used by Wall et al. (1982) to predict sediment yields from cropland and daily fluvial suspended loads to the Great Lakes. It was estimated that agricultural land-use activities contributed over $650 \times 10^6 \text{ kg/ha}$ of suspended sediment to the Great Lakes.

Hamlett et al. (1983) observed increased stream flow, sediment load, and stream channel widening that corresponded with increased row cropping in an Iowa watershed. Roles and Jonker (1985) introduced a statistical method that tested representativity of soil erosion samples and calculated plot data accuracy for different sample sizes. Murphee et al. (1985) reported that in a Mississippi delta watershed, the combined sediment yield for the months of March, April and May was 67% of the average annual yield. A six-year monitoring of three watersheds with three silviculture treatments in north central

Florida suggested that minimum disturbance practices with protective stream management zones may minimize non-point source pollution (Rickert, 1985). Verhoff and Yaksich (1982) analyzed a 26 year record of sediment discharge in the Maumee River at Waterville, Ohio, as affected by land use, hydrology and weather. Only hydrologic and meteorologic parameters were found to be correlated with sediment discharge.

Phosphorus

Phosphorus in streams frequently demonstrates strong associations with discharge and with suspended sediment concentrations. Phosphorus chemistry and the relative amounts of dissolved and sediment-associated phosphorus species are influenced both by point sources (e.g. sewage treatment outfalls) and by urban and rural land use.

Hergert et al. (1981) discovered phosphorus concentrations in tile effluent increased with increasing flow and related this to the effect of salt or calcium (Ca) concentrations upon phosphorus solubility. Sharpley et al. (1981) studied runoff from cropped and grassed watersheds and found a linear inverse relationship between soluble-P and sediment concentrations. In simulated studies they also found sorption of soluble phosphorus added in rainfall occurred during transport. It was concluded that leaching of phosphorus from vegetative cover could contribute significant amounts of soluble

phosphorus to runoff, and that soil material may act as a phosphorus link rather phosphorus source. Logan (1982) reviewed the mechanism by which inorganic phosphate enters the dissolved phase, and the effect of fertility management and conservation tillage on phosphate concentration in drainage waters.

Hubbard et al. (1982) measured and sampled runoff continuously from two small watersheds over a two-year period and found that 70 to 95% of N in runoff and 90 to 98% of P were carried in sediments, except during winter months when up to 80% of the N and 33% of the P were in solution. Miller et al. (1982) reported that about 70% of the total P load (3×10^6 kg/ha) to the Great Lakes was attributable to cropland runoff, 20% to livestock operations, and 10% to a combination of runoff from unimproved land and stream bank erosion. Culley and Bolton (1983) found that storm flow events accounted for 57% of annual discharge, 73% of total phosphorus, and more than 50% of orthophosphate from tile drained fields.

Grobler and Silberbauer (1985) described methods to reduce the uncertainty associated with phosphate loads estimated by means of export coefficients and discussed the significance of a link between the bioavailability of particulate phosphorus and watershed geology with respect to phosphate load estimates. Kunishi and Glotfelty (1985) monitored forms and concentrations of phosphorus in an estuary of the Chesapeake Bay and noted that high P concentrations during summer were related to increased P release from sediments and increased P mineralization by marine organisms because of higher temperature.

Nitrates

Nitrogen species in runoff are influenced by agricultural management practices and land use. White (1981) found that the canopies of corn, oats and soybeans altered nutrient concentrations of precipitation. Oat canopies produced enrichment in $\text{NH}_3\text{-N}$, $\text{NO}_3\text{-N}$, soluble-P, total-P and K. Soybean and corn canopies each produced enrichment of some nutrients and losses of others. Baker and Johnson (1981) fertilized two similar cornfields to different extents. After a delay of two months, NO_3 concentrations in the drainage from the more heavily fertilized plot exceeded the other by a factor of 2 to 4. Timmons and Dylla (1981) found that an irrigated cornfield experienced up to 53% greater leaching losses of NO_3 than a similar nonirrigated field. Extent and dynamics of a thin zone of soil that interacted with rainfall and overland flow in releasing soil chemicals to runoff were studied by Ahula et al. (1981).

Houston and Brooker (1981), in a study of the River Wye in the United Kingdom, observed seasonal changes in concentrations of Si, PO_4 and inorganic N. All species, with the exception of NO_3 , exhibited inverse concentration relationships with flow. Neilson et al. (1982) reported the $\text{NO}_3\text{-N}$ accounted for 75% of the total N load to the Great Lakes. Only 12% of the runoff samples observed in the 11 watersheds had $\text{NO}_3\text{-N}$ concentrations below 0.3 mg/L, whereas 3% of the samples exceeded the drinking water standard of 10 mg/l.

Duda and Finan (1983) demonstrated that the levels of N and P in the stream increased with livestock numbers. Baker et al. (1983) estimated that 2% of the organic and nutrient content of swine manure from a 4000 hog dry lot was transported to a coastal plain stream by surface runoff. The N levels in the stream during low-flow conditions were found to be influenced more by drainage from row crop areas than by the hog dry lot.

Pesticides and herbicides

Perhaps the clearest documentation of the interaction between hydrologic processes and nutrient, sediment and pesticide levels in streamflow has been the attempts by Donigian and Crawford (1976) to simulate all the relevant processes on small agricultural watersheds. This modelling gave improved insights into the most sensitive factors affecting the quality and quantity of agricultural runoff. Tillage operations affect the total sediment loss and peak concentrations and therefore pesticide loss in sediments. The time of application of pesticide relative to the occurrence of a major storm also greatly affects pesticide loss. Mechanisms of pesticide attenuation are therefore critical, together with the hydrologic variables such as soil moisture and infiltration characteristics, land surface treatment and sediment transport.

Gaynor and Volk (1981) found that herbicide losses in runoff from agricultural lands could be greatly affected by soil adsorption

properties as well as by pesticide solubility. Toxaphene and sediment yields from a cotton field in Mississippi were studied by McDowell et al. (1981). They found a linear relationship between these two parameters in runoff. Approximately 0.5 to 1% of applied toxaphene was accounted for in runoff, and over 90% was attached to transported sediments. Both toxaphene and sediment yields were greatest during the spring, but toxaphene concentrations in runoff and sediment were highest during the summer application period.

Frank et al. (1982) studied the 11 agricultural watersheds and revealed that 81 pesticides were applied to rights-of-way during 1975. Wu et al. (1983) measured the yield of atrazine and alachlor in watershed runoff and found that atrazine was significantly more mobile during the three year study. A laboratory column study showed that tightly bound pesticides such as DDT and Paraquat may be leached through the soil profile when attached to finely dispersed clay particles (Zinten et al., 1983). The occurrence of atrazine in shallow groundwater in Nebraska and the mechanism of its dispersion and degradation were reported by Wehje et al. (1983).

McDowell et al. (1984) found that pesticide losses in runoff seemed affected only by the amount of rainfall. Mayewx et al. (1984) showed that runoff concentrations of picloram in runoff dissipated with distance and successive rainfall events. A transport model developed by Smith and Carsel (1984) predicted greater pesticide losses from soil than from leaves. The model results agreed well

with field data when 90% of the pesticide was supplied. Hall et al. (1984) observed that conservation tillage systems lost less cyanazine than conventional systems, presumably because runoff and sediment losses were reduced. Glotfelty et al. (1984) found that atrazine and simazine were delivered to the Wye River estuary through runoff. Emmerich et al. (1984) reported that only 0.47% tebuthiuron was lost in rangeland runoff. The bulk of tebuthiuron persisted in the soil.

Adsorption of pesticides to organic colloids of soil particles can be an important transport mechanism. Corwin and Farmer (1984) determined that adsorption-desorption isotherms of bromacil conformed to a set of Freundlich equations. Wijayartne and Means (1984) demonstrated an affinity of atrazine for estuarine humics, desorbing from soils to bind to the colloids. In contrast, Reinert and Rodgers (1984) concluded that sorption was not an important transport pathway for the herbicide endothall. Acid-catalysed hydrolysis seemed to be the major transformation of atrazine in acid soils, and was unaffected by conservation tillage practices.

Wauchope and Meyers (1985) determined atrazine and linuron adsorption-desorption rates in sediment-water slurries and concluded that adsorption-desorption equilibrium can be assumed to be a reversible process for input into the non-point source pollution models.

Generally, the occurrence in water of highly chlorinated and persistent pesticides tend to be controlled by their affinity with

five suspended sediments (organic and mineral). Hence, erosion and sediment transport are important determinants in developing water quality sampling program for agricultural area. Other pesticide groups such as the phenoxy acid herbicides are much more soluble; their occurrence, transport and fate may be quite independent of sediment transport.

Industrial Organic Contaminants

Work by Chapman et al. (1982) shows that 95% of the Class I and II "priority pollutants" are preferentially associated with sediments and biota. Conventional water sampling is, therefore, frequently ineffective in determining presence of low levels of organic contaminants. Organic contaminants emanating from sewage or industrial outfalls are either prohibited or limited by permit. These may show inverse relationships with discharge due to dilution by storm runoff. Contaminants migrating from waste disposal sites or those associated with contaminated surfaces in industrial complexes may be expected to show a runoff effect when these are mobilized and transported by surface and subsurface runoff. Industrial spills are stochastic in nature and have no predictable relationship with discharge. Alternative sampling strategies may be required (discussed below). The kinetics of transport of pesticides and industrial compounds involve a complex interaction between volatilization, photolysis and bioaccumulation and biotransformation which is poorly

understood for many chemical compounds, but, surprisingly, sampling programs cannot hope to achieve a high degree of resolution of chemical compounds nor of spatial and temporal patterns. Similar comment applies also to the myriad of synthetic organic contaminants released intentionally or accidentally into river.

Water Quality-Flow Relationships

Recent research (Ongley, unpublished) suggests that hydrophobic inorganic (metals) and organic contaminants are stored in the river channel during downstream transport. This implies that information is "lost" in the downstream direction (Ongley, 1987); and thus limits the utility of fixed-site sampling programs. The spatial dimensions of information loss varies with discharge and places severe restrictions on the ability of fixed site monitoring programs to resolve upstream causes as well as downstream implications. Drainage from land surfaces, when natural or modified by man's activities, such as agriculture, are regarded as nonpoint (diffuse) systems; the collection, treatment and discharge of industry and urban effluents are characterized as point sources. The relationship between discharge and concentrations of naturally occurring constituents and of pollutants has been presented by Manczak and Florczyk (1971); they proposed three types of relationships between concentration C and waterflow Q , as presented schematically in Figure 1. In contaminated rivers (Type I), the main factor influencing the shape of the curve is the dilution of the waste water with increasing discharge. In

clean rivers, represented by Type II, the concentration increases with Q as a result of runoff in the drainage area and of stirring up and transport of the river sediments. The concentration can be represented by a linear, second power or an exponential function of Q. For intermediately contaminated rivers, Type III, the dilution of the wastewater determines the shape of the curve for low Q, and runoff at high Q.

The adoption of intensive storm period sampling programmes in a growing number of studies (e.g. Ongley, Bynoe and Percival, 1981; Miller and Drever, 1977; Reid et al., 1981) has not only highlighted the complexity of solute behaviour during storms at particular stations but has also demonstrated considerable intra- and intercatchment variability in detailed solute response (Foster, 1979; Webb and Walling, 1983). In some cases such as the study of K concentrations in small, undisturbed forested watersheds of southwestern British Columbia, Canada (Feller and Kimmins, 1979), the response during individual storms may vary markedly from storm to storm. An example of the latter phenomenon is provided by an examination of NO_3 responses observed in the River Dart, a tributary of the Exe Basin in Devon (Walling and Webb, 1983, Fig. 2). A delayed increase in NO_3 concentration is typical of summer and autumn storms in this watershed, but rapid dilution of NO_3 levels is more characteristic of flood events during the winter and spring period. There is further variation between storms in the timing of dilution

troughs, which may lead, coincide with or lag the discharge peak. These contrasts in storm-period behaviour are thought to reflect the influence of several factors, including variations in rates of mineralization and nitrification, storm hydrograph characteristics and antecedent moisture levels.

Storm-period sampling has also highlighted the contrasting behaviour of different solute parameters during flood events (Cleaves et al., 1970; Douglas, 1972; Foster, 1978). Responses of individual ions will differ in their detailed character because particular chemical species have varying origins, are stored at different locations within the vegetation, soil and rock of a drainage basin, and are accessed to different extents by runoff from various sources. These controls are evident in the moorland Glendye watershed of northeast Scotland (Reid et al., 1981) where dissolved species derived from chemical weathering, including Ca, Mg, Na, SiO₂ and HCO₃, have highest concentrations in baseflow draining from the lower mineral soil horizons but are strongly diluted during storm events by waters which originate in the upper organic and organo-mineral layers of the soil (Fig. 3). Dilution is, however, less pronounced for the cations because these are displaced from organic colloidal material by H⁺ ions in percolating rainfall. In contrast, runoff from surface horizons of the soils exhibit enriched concentrations of total organic carbon and of complexed Fe, so that these parameters show an increase during flood events (Fig. 3). Concentrations of Fe peak relatively early

during the storm because these elements are mobilized in the gleyed soils by reduction processes and are flushed into the stream with displaced soil water at an early stage in a flood event. Although K concentrations also increased during stream rises in the autumn months (Fig. 3), this ion was unaffected by storm events at other times of the year; Reid et al. (1981) argue that this behaviour is related to the leaching of potassium from decomposing plant litter.

A particularly important facet of storm-period solute behaviour is the occurrence of hysteresis whereby variations in solute concentrations are not linearly related to discharge during storm events; generally, concentrations are markedly different at the same level of discharge on the rising and falling limbs of the hydrograph (Fig. 4). This phenomenon has often been investigated in terms of a looped trend in the relationship between solute concentration and discharge for specific storm events (e.g. Hendrickson and Krieger, 1964; Collins, 1979). The frequent occurrence of hysteresis severely limits the explanatory and predictive powers of simple rating lines when they are applied to storm periods. Basic clockwise and anticlockwise hysteretic loops were recognized in relatively early studies of streams in Kentucky and Georgia, U.S.A. (Hendrickson and Krieger, 1960; Toler, 1965). A wide range of causes often involving more than one factor for any one stream, have been proposed to account for this phenomena. Miller and Drever (1977), for example, suggest that solution of material in the soil zone, dilution of base flow,

selective weathering of ferromagnesium minerals and leaching of biological materials, all contribute to a marked hysteresis effect in water chemistry during a storm event in the North Fork of the Shoshone River, Wyoming, U.S.A. (Fig. 5).

Several factors may influence the form and timing of storm period chemographs and, in turn, generate hysteretic behaviour. In particular, a "flushing effect" has been noted in many rivers (e.g. Hendrickson and Krieger, 1960; Edwards, 1973; Walling, 1974; Walling and Foster, 1975) by which soluble material accumulated during the pre-storm is mobilized and transported to the stream where it influences solute concentrations during the early stages of a storm event. Solute accumulation before a flood event will be affected by evaporation of soil moisture, capillary rise and the buildup of dry fallout deposits, leaf residues and dead plant material. Flushing effects are particularly pronounced in autumn storms following solute accumulation over the summer period, and Klein (1981) has demonstrated that solute concentrations in overland and subsurface flows are systematically related to the length of the dry period preceding storm.

Hysteresis has also been widely documented for suspended sediment concentrations (Walling and Webb, 1983) both in storm period response and for intra and inter seasonal response. Rapid depletion of sediment available for transport (sediment exhaustion) is considered to be the principal causal variable. Although peaks in suspended

sediment concentrations usually precede the discharge peak (Fig. 10A), this relationship can be reversed in long rivers due to the more rapid migration of the flood crest downstream relative to the velocity of the water particles and their associated sediment load.

IONIC RUNOFF DUE TO SNOWMELT

Spring snowmelt can profoundly influence streamwater chemistry. Data from Turkey Lakes Watershed (northern Ontario) have been used to illustrate processes in natural (unmodified by man) watersheds. The snowpack water equivalent (mm) and chemical ions content (H, NH₄, SO₄, NO₃ in meq.m⁻²) are shown in Figures 6 and 7 for 1981 and 1982 together with important precipitation events. Note that the frequency of snowpack sampling was much shorter in 1982 than in 1981 (Jeffries and Semkin, 1983; Lam et al., 1987; Bobba and Lam, 1987).

The greater variability in snowpack content present in Figure 7 compared to Figure 6 can be attributed, in part, to the shorter sampling frequency used in 1982. The frequency of sampling in 1982 was suitable for detecting small losses and additions to the water equivalent of the snowpack in response to changing meteorological conditions. The major differences between the two years were the approximately 1.5 fold greater accumulation of materials and the much later date of major melting in 1982. Despite these differences, there are some strong similarities in the behaviour of individual ionic species across the two years of this study.

All anions were quickly removed from the snowpack with the beginning of the major melting periods in both years. A lesser but significant loss of ions (particularly H) was associated with the earlier mid-March melt in 1982 and it is probable that a similar loss occurred in mid-February 1981. The differential release of ions compared to water is often strongly influenced by rain. Rain supplies both the heat and the liquid carrier agent required to enhance the movement of materials through snowpack. Almost all of the chemical ions deposited in the heavy rains that occurred from March 28 to April 1, 1981 were immediately released from the snowpack since there was virtually no increase in ion or water content over this time period except for NH_4 (Fig. 6).

The chemical concentrations of $\text{Ca}+\text{Mg}$, SO_4 , alkalinity, NO_3 , and H^+ ($\mu \text{ eq.L}^{-1}$) in streamwater are shown in Figures 8 and 9 due to snowmelting. Each of the parameters exhibited roughly the same response to snowmelt in both 1981 and 1982. The year to year differences which do exist may be attributed to the varying meteorological and hydrological conditions.

Pollutant Transport from Agricultural Watersheds

Baker's (1985) intensive study of pollutant transport from agricultural watersheds of Lake Erie reveals a typical pattern for agricultural pollutant transport in the region's river system. Stream

discharge increases rapidly during the rising stage of the hydrograph and decreases more slowly during the falling stage (Fig. 10). The concentrations of sediment and sediment-bound pollutants, such as particulate P, increase rapidly at the beginning of the event and peak well in advance of the peak discharge. In contrast, nitrate concentration peak during the falling portion of the hydrograph. In the watershed, nitrate enters streams primarily in tile drainage system discharges which lags surface runoff. Herbicides in this study leave fields primarily as dissolved material in runoff water rather than in adsorbed form. Peak concentrations of soluble herbicides, such as atrazine, occur about the same time as peak discharge. The concentration patterns for such herbicides differ from the concentration patterns of both suspended solids and nitrates.

The general pattern of discharge and pollutant concentrations is common for most runoff events at stream gauging stations in the Honey Creek Watershed. The actual discharges and concentrations vary widely at individual stations, depending primarily on rainfall amounts, intensities, snowmelting and seasons. Also, systematic differences in discharge and pollutant concentrations occur, depending upon watershed size, soil types and land use pattern in the watershed.

Variations in Concentration of Dissolved Chemical with Discharge

The inverse trend between solute constituents of base flow and discharge, which has been described for many rivers, is to be expected

if all the other factors affecting river chemistry are constant. Base flow, which is usually relatively rich in solutes, is diluted by interflow and overland flow, which have shorter residence times in the watershed and hence a shorter period in which solution reactions can take place.

Hem (1970) has shown an hyperbolic relationship between discharge and solute concentration. The relationship between concentration and discharge is as follows:

$$C_1Q_1 + C_2Q_2 = (Q_1 + Q_2) C_3 \quad (1)$$

where Q_1 is the discharge before dilution, C_1 is the concentration of solute before dilution, Q_2 is the discharge of dilutant, C_2 is the concentration of solute in diluting water and C_3 is the resultant concentration. The three terms in this equation represent concentration of solute, and an inflow-outflow balance is assumed (no change in storage). If C_1Q_1 is constant (α) as assumed for the model, and if the concentration of diluting water (C_2) is zero, then

$$C_3 = \frac{C_1Q_1}{(Q_1 + Q_2)} = \frac{\alpha}{(Q_1 + Q_2)} \quad (2)$$

If expressed in logarithmic form thus becomes

$$\log C_3 = \log \alpha - \log (Q_1 + Q_2) \quad (3)$$

Equation 3 has the form of straight line with slope-1. (Q_1+Q_2) is the river's total discharge (Q), the form of equation 3 is:

$$\log C = \log \alpha - \beta \log Q \quad (4)$$

The degree of linear association between C and Q was ascertained by using the product moment correlation coefficient and the regression lines fitted by the method of least squares.

Osborne et al. (1980) and Edwards (1973) have shown the relationship between concentration flow and discharge by applying equation (4). Osborne et al. (1980) collected the hydrogeochemical data of River Wye (Great Britain) for three years (1975-1977) at different locations in the watershed. Similarly, Edwards (1973) determined the different hydrogeochemical parameters in different watersheds. Figure 11 shows the regression equation exponents of alkalinity, TDS, NO-N, PO₄-P, SiO₂, Na, K, Ca, Mg and HCO₃ for different stations in the watershed and different seasons.

A positive exponent indicates that as flow increases, the concentration of solute or nutrient also increases (so called "runoff" effect). An exponent of zero indicates that the concentration is independent of flow. (This indicates that, on average, the added flow contains the same concentration as the stream. When this is the case, a linear relationship exists between flow and load, and use of average flow and concentration to compute load is a satisfactory procedure). Finally, a negative exponent indicates that the incoming flow dilutes and reduces the concentration (dilution effect).

In Figure 11, the region above zero represents runoff effects and the negative region is dilution. Nitrates and SiO nearly always display increased concentration with flow. Magnesium, calcium, bicarbonate and orthophosphate are usually diluted. The sodium and potassium, probably derived from chlorides, fall into an intermediate category, though potassium concentration increases at the beginning of most storm events. Although these data have similarities to data of Miller and Drever (1977) in Figure 5, there is no universality in solute-discharge relationships as demonstrated for nitrate in Figure 2.

Sampling Frequency to Determine Water Quality Parameters

While long-term regular monitoring may facilitate detection of trends in concentrations, a knowledge of the relationships between flow and quality is required if accurate loads of soluble or suspended material transported by the river are to be determined. Stream load determination is often the most critical quality characteristic, particularly when the quality of downstream reservoirs, lakes and estuaries is of concern.

Major Ion Constituents

The importance of flow variability in affecting soluble ionic concentrations of river systems is well documented (Osborne et al.,

1980; Hem, 1959). The sampling frequency necessary to obtain accurate integration of concentration with flow depends upon variability of concentration and stability of the relationship between flow and concentration.

Techniques for calculating loads of soluble constituents using flow-concentration relationships have been developed for some time (Hall, 1970) but the complexities of these relationships are becoming increasingly apparent (O'Connor, 1976; Walling and Foster, 1975). Where there is pronounced hysteresis in the flow concentration relationship, frequent monitoring during all storms may be required if accurate loads are to be calculated for those variables which change significantly during runoff. Nonetheless, in comparison with sediment associated variables, major ions do not critically change over orders of magnitude during storm flow. Hence, errors in local calculation using intensive sampling data generated by weekly or monthly sampling progress may produce reasonable results in river management programs (Ongley and Walborg, research in progress).

Nutrients and Sediments

High frequency sampling during storm events is critical for nutrient (especially for total phosphorus) and sediment load determination as the concentrations of these variables not only increase with increasing flow rate but may change over several orders

of magnitude. This results in a large percentage of the annual load occurring in short periods of high flow. Walling (1974) has indicated errors up to +900% in monthly and +280% in annual suspended loads using average sediment flow relationships. Whipple and Hunter (1977), in discussing non-point source pollution, strongly argue that storm event and hydrograph analysis are indispensable for small catchment studies because discharge loadings are complex and dependent on storm characteristics and time of year.

Heavy Metals

Heavy metals are often concentrated in the sediment loads of the first flush of storm runoff in urban areas. Annual heavy metal loadings from small catchments therefore require accurate sediment load determination on a storm by storm basis. Moreover, long-term metal loads of major river systems are usually dominated by particulate sources during flood flows (Presley et al., 1980) or by particulate scavenging at any time that sediment concentration increases.

Pesticides and Industrial Organic Contaminants

Although pesticide runoff from different land uses has been widely reported, little is known of the downstream pathways of pesticide runoff. With the exception of certain other synthetic

organic contaminants such as PCB's, dioxin, chlorophenols, etc., the same comments apply to the majority of the same 60,000 chemicals found in basin environmental compartments. Because residues are usually low and processes of metabolization, volatilization, degradation, land adsorption of the unknown, downstream continuity of target organic contaminant concentrations (i.e. parent compounds) may be difficult to determine. Therefore, optimal sampling strategies in time and space are poorly developed and infrequently applied in any systematic manner.

Further complications arise due to the opportunistic presence of many pesticides in flowing waters resulting from the juxtaposition of pesticide application with rainfall. Industrial and municipal sources may discharge intermittently or unevenly in time. All of these lead to highly misleading sampling results from the usual fixed interval monitoring program. Errors are compounded if multimedia (water, sediment, biota) sampling is not employed due to the preferential associating of different chemical groups with different substrates.

Finally, one must weigh the costs of some form of regular monitoring for determination of ambient conditions and trends, relative to the potential for randomly occurring spills which may not only vastly outweigh "normal" contaminant levels but also cause the greatest ecological damage. These factors can be reasonably evaluated through an appraisal of program costs relative to a clear statement of program objectives.

Our work to date in Canada suggests that contaminant sampling in water and suspended sediment using high flow versus low flow effectively discriminates between nonpoint (high flow period) and point source (low flow) impacts. Thus flow separation technique tends to capture the chemistry associated with runoff and erosion during high flow (partial contributing area is larger) on the one hand, and chemistry dominated by point source input during low flow when the land surface is not contrasting to river chemistry.

Length of Water Quality Studies and Load Estimation

While short-term intensive sampling programs may accurately define water quality loads during the study period, they may be severely limited in value if they have not included a relatively wide range of yearly conditions (Foster, 1980). However, manual sampling programmes provide the basis for many studies of solute transport and it is important to recognize the potential problems associated with sampling frequency and load calculation procedures (Ongley et al., 1977).

The discussion on temporal variations in solute transport presented previously has clearly demonstrated that solute concentrations may vary considerably through time. Infrequent samples are unlikely to provide a meaningful representation of the pattern of variation, and estimates of such simple statistics as the annual mean

are unlikely to provide a meaningful representation of the pattern of variation, and estimates of such simple statistics as the annual mean concentrations based on a small number of samples may involve significant errors. As we noted above, however, the error can become very large for the substances which vary substantially during a discharge event. Such variation tends to be smallest for major ions and larges for suspended sediment. Coliforms are not considered here.

Considering methods which have commonly been used to estimate annual solute loads from infrequent grab samples, it is possible to distinguish the two basic approaches of interpolation and extrapolation. Interpolation procedures (Table 1) effectively involve the assumption that the concentration of load associated with an instantaneous sample is representative of the time period between samples, whereas rating curve techniques and the load interval procedure described by Verhoff et al. (1980) may be viewed as extrapolation techniques. The extrapolation procedures that are employed involve a simple logarithmic rating between concentration and flow and the load interval method. El-Shaarawi and Esterby (1987) proposed numerical integration techniques to estimate the total load at a specific site and applied to Niagara River.

CONCLUSIONS

From the literature review, we conclude that, on balance, weekly sampling is adequate for geochemical mass balance studies provided a continuous record of discharge is available. The reliability of the

results is improved if sufficient storm event samples are analyzed to allow compensation for changes in river chemical concentration through storms. Hourly sampling is a minimal requirement for studying behaviour during storm events and elucidation of transport mechanisms. Shorter sampling intervals may be necessary for small catchments. It is advisable to sample at high frequency through storm events until concentration trends have been established for the chemical species interest. For detailed studies of changes in chemical composition with time through precipitation events, the variability of precipitation (rain and snow) composition with time and for larger watersheds, over the catchment should not be overlooked.

For chemicals which display pronounced runoff effects and especially for sediment and sediment-associated chemistry, sampling programs that fail to characterize storm flow will be highly inaccurate for loading purposes. Sediment concentration (and associated chemistry) is both nonlinear and irregularly related to discharge. This generally requires a pilot program to establish the rough dimension of flow dependency. For metals this relationship is easily established and can be extrapolated in space. For organic contaminants and in the absence of gross pollution, most monitoring programs are effectively limited to presence/absence information. Lack of spatial and temporal consistency and unknown biogeochemical pathways usually precludes any higher level of interpretation of concentration values of organic contaminants.

REFERENCES

- Ahula, L.R. et al. 1981. The depth of rainfall-runoff-soil interactions as determined by phosphorus-32. *Water Resour. Res.*, Vol. 17, pp. 969.
- Baker, J.L. and Johnson, H.P. 1981. Nitrate-nitrogen in tile drainage as affected by fertilization. *J. Environ. Qual.*, Vol. 10, pp. 519.
- Baker et al. 1983. The concentrations and transport of pesticides in northwestern Ohio rivers - 1981. U.S. Army Corps Engs., Buffalo, N.Y., 33 p.
- Baker, D.B. 1985. Regional water quality impacts of intensive row crop agriculture. A Lake Erie Basin case study. *J. of Soil and Water Conservation*. Vol. 40, pp. 125.
- Bobba, A.G. and Lam, D.C.L. 1987. Application of hydrological model to the acidified Turkey Lakes Watershed. Paper submitted for publication in *Can. J. Fish. Aquatic Science*.
- Bobba, A.G. 1971. Temperature survey of coal mines producing acid water. Masters Thesis, Ohio University, Athens, Ohio.
- Chapman, P.M. et al. 1982. Design of monitoring studies for priority pollutants. *J. Wat. Pollut. Control Fed.*, Vol. 54, pp. 292.
- Chapra S.C. et al. 1983. Effectiveness of treatment to meet phosphorus objectives in the Great Lakes. *J. Water Pollut. Control. Fed.*, Vol. 55, pp. 81.

- Cleaves, E.T. et al. 1970. Geochemical balance of a small watershed and its geomorphic implications. Geological Society of America Bulletin, Vol. 81, pp. 3015.
- Collins, D.N. 1979. Hydrochemistry of meltwater draining from an alpine glacier. Arctic and Alpine Research, Vol. 11, pp. 307.
- Coote, D.R. et al. 1982. Agricultural and water quality in the Canadian Great Lakes Basin: I. Representative agricultural watersheds. J. Environ. Qual., Vol. 11, pp. 473.
- Corwin, D.L. and Farmer, W.J. 1984. Nonsingle-valued adsorption-desorption of bromicil and diquat by freshwater sediments. Environ. Sci. Technol., Vol. 18, pp. 507.
- Culley, J.L.B. and Bolton, E.F. 1983. Suspended solids and phosphorus loads from a clay soil: watershed study. J. Environ. Qual., Vol. 12, pp. 498.
- Davis, J.S. and Zobrist, J. 1978. The interrelationships among chemical parameters in rivers - analyzing the effect of natural anthropogenic sources. Prog. Wat. Tech., Vol. 10, pp. 65.
- Dendy, F.D. 1981. Sediment-yield from a Mississippi delta cotton field. J. Environ. Qual., Vol. 10, pp. 482.
- Dooty, R.D. et al. 1981. Suspended sediment production from forested watersheds on Oahu, Hawaii. Water Resourc. Bull., Vol. 17, pp. 399.
- Donigian, A.S. and Crawford, N.H. 1976. Modelling pesticides and nutrients on agricultural lands. Report EPA-600/2-76-043, U.S. Environmental Protection Agency, Office of Research and Development, 317 pp.

- Douglas, I. 1972. The geographical interpretation of river water quality data. *Progress in Geography*, Vol. 4, pp. 1.
- Duda, A.M. and Finan, D.S. 1983. Influence on non-point source nutrient levels of streams. *Trans. Am. Soc. Agric. Eng.*, Vol. 26, pp. 1710.
- Edwards, A.M.C. 1973. The variation of dissolved constituents with discharge in some Norfolk rivers. *Jour. of Hydrology*, Vol. 18, pp. 219.
- El-Shaarawi, A.H. and Esterby, S.R. 1987. Spacing of measurements: Applications to the estimation of loading. *EOS, Transaction, American Geophysical Union*, Vol. 681, pp. 315.
- Emmerich, W.E. et al. 1984. Fate and effectiveness of tebuthiuron applied to rangeland watershed. *J. Environ. Qual.*, Vol. 13, pp. 382.
- Feller, M.C. and Kimmins, J.P. 1979. Chemical characteristics of small streams near Haney in southwestern British Columbia. *Water Resources Research*, Vol. 15, pp. 247.
- Förstner, U. and Wittmann, G.T.W. 1981. Metal pollution in the aquatic environment. *Springer-Verlag, Berlin*.
- Foster, I.D.L. 1979. Intra-catchment variability in solute response, An East Devon example. *Earth Surface Processes*, Vol. 4, pp. 381.
- Foster, I.D.L. 1980. Chemical yields in runoff and denudation in a small arable catchment, East Devon, England. *J. of Hydrology*, Vol. 47, pp. 349.

- Frank, R. et al. 1982. Agriculture and water quality in the Canadian Great Lakes Basin: V. Pesticide use in 11 agricultural watersheds and presence in stream water, 1975-1977. J. Environ. Qual., Vol. 11, pp. 447.
- Freeze, R.A. 1974. Streamflow generation. Rev. Geophysics Space Physics, Vol. 12, pp. 627.
- Garf, W.H. 1971. Hydraulics of sediment transport. McGraw Hill Book Co., New York.
- Gaynor, J.D. and Volk, V.V. 1981. Runoff losses of atrazine and terbuthyn from unlined and lined soil. Environ. Sci. and Technol., Vol. 15, pp. 440.
- Glotfelty, D.E. et al. 1983. Atrazine and simazine movement to Wye River estuary. J. Environ. Qual., Vol. 13, pp. 105.
- Griffiths, G.A. 1981. Some suspended sediment yields from south island catchments, New Zealand. Water Resourc. Bull., Vol. 17, pp. 662.
- Grobler, D.C. and Silbervauer, M.J. 1985. The combined effect of geology, phosphate sources and runoff on phosphate export from drainage basins. Water Res., Vol. 19, pp. 975.
- Hall, F.R. 1970. Dissolved solids-discharge relationships. 1. Mixing models. Water Resources Research, Vol. 6, pp. 845.
- Hall, J.K. et al. 1984. cyanazine losses in runoff from no-tillage corn in living and dead mulches versus unmulched conventional tillage. J. Environ. Qual., Vol. 13, pp. 115.

- Hamelett, J.M. et al. 1983. Channel morphology changes and sediment yield from a small agricultural watershed in Iowa. Trans. Am. Soc. Agric. Eng., Vol. 26, pp. 139.
- Hem, J.D. 1950. Quality of water in Gila River Basin above Coolidge Dam, Arizona. U.S. Geol. Survey Water-Supply Paper 1104, pp. 1.
- Hem, J.D. 1970. Study and interpretation of the chemical characteristics of natural water. U.S. Geological Survey Water Supply Paper No. 1473.
- Hendrickson, G.E. and Krieger, R.A. 1960. Relationship of chemical quality of water to stream discharge in Kentucky. Report of 21st International Geological Congress, Copenhagen, Vol. 1, pp. 66.
- Hendrickson, G.E. and Krieger, R.A. 1964. Geochemistry of natural waters of the Blue Grass Region, Kentucky. U.S. Geological Survey Water Supply Paper No. 1700.
- Hergert, G.W. et al. 1981. Phosphorus concentration-water flow interactions in tile effluent from manured land. J. Environ. Qual., Vol. 10, pp. 338.
- Hergert, G.W. et al. 1981. Effects of dairy manure on phosphorus concentrations and losses in in tile effluent. J. Environ. Qual., Vol. 10, pp. 345.
- Houston, J.A. and Brooker, M.P. 1981. A comparison of nutrient sources and behaviour in two lowland subcatchments of the River Wye. Water Res., Vol. 15, pp. 49.
- Hubbard, R.K. et al. 1982. Movement of diffuse source pollutants in small agricultural watersheds in the Great Lakes Basin. J. Environ. Qual., Vol. 11, pp. 117.

- Jeffries, D.S. and Semkin, R.G. 1983. Changes in snowpack, stream and lake chemistry during snowmelt in the Turkey Lakes watershed. Proceedings of International Symposium on Acid Precipitation, LINDAU, FRG.VDI-Berichte 500.
- Klein, M. 1981. Dissolved material transport - the flushing effect in surface and subsurface flow. Earth Surface Processes and Landforms, Vol. 6, pp. 173.
- Kunish, H.M. and Glotfelty, D.E. 1985. Sediment, season and salinity effects on phosphorus concentrations in an estuary. J. Environ. Qual., Vol. 14, pp. 292.
- Lam, D.C.L., Bobba, A.G., Jeffries, D.S. and Craig, D. 1987. Modelling stream chemistry for Turkey Lakes Watershed: Comparison to 1981-1984 Data. Paper submitted for publication in Can. J. Fish. Aquatic Science.
- Logan, T.J. 1982. Mechanism for release of sediment-bound phosphate to water and the effects of agricultural land management on fluvial transport of particulate and dissolved phosphate. Hydrobiologia, Vol. 92, pp. 519
- Manczak, H. and Florczyk, H. 1971. Interpretation of results from the studies of pollution of surface flowing waters. Water Research, Vol. 5, pp. 575.
- Mayewx, H.S. et al. 1984. Dissipation of picloram in storm runoff. J. Environ. Qual., Vol. 13, pp. 44.
- McDowell, L.L. et al. 1981. Texaphene and sediment yields in runoff from a Mississippi delta watershed. J. Environ. Qual., Vol. 10, pp. 120.

- McDowell, L.L. et al. 1984. Methyl parathion and EPN washoff from cotton plants by simulated rainfall. Environ. Sci. Technol., Vol. 18, pp. 423.
- McLaren, P. 1981. River and suspended sediment-discharge into Byam Channel, Queen Elizabeth Islands, N.W. Territories, Canada. Arctic, Vol. 34, pp. 141.
- McPherson, M.B. and Schneider, W.J. 1974. Problems in modelling urban watersheds. Water Resour. Res., Vol. 10, pp. 434.
- Miller, W.R. and Drever, J.I. 1977. Water chemistry of a stream following a storm, Absavoka Mountains, Wyoming. Geological Society of America Bulletin, Vol. 88, pp. 286.
- Miller, M.H. et al. 1982. Agriculture and water quality in the Canadian Great Lakes Basin: III. Phosphorus. J. Environ. Qual., Vol. 11, pp. 487.
- Murphee, C.E. et al. 1985. Sediment yield from a 259-ha flat lands watershed. Trans. Am. Soc. Agric. Eng., Vol. 28, pp. 160.
- Neilson, G.H. et al. 1982. Agriculture and water quality in the Canadian Great Lakes Basin. IV. Nitrogen. J. Environ. Qual., Vol. 11, pp. 493.
- Osborne, A.C. et al. 1980. The chemistry of the River Wye. J. of Hydrology, Vol. 45, pp. 233.
- O'Connor, D.J. 1976. The concentration of dissolved solids and river flow. Wat. Resour. Res., Vol. 12, pp. 279.
- Ongley, E.D. et al. 1977. Sediment and nutrient loadings to Lake Ontario: methodological arguments. Can. J. Earth Science, Vol. 14, pp. 1555.

- Ongley, E.D., Bynoc, H.C. and Percival, J.B. 1981. Physical and geochemical characteristics of suspended solids, Willow Creek, Ontario. *Can. Jour. Earth Sci.*, Vol. 18, pp. 1365.
- Ongley, E.D. 1987. Scale effects in fluvial sediment-associated chemical data. *Hydrological Processes*, Vol. 1, pp. 171.
- Presely, B.J. et al. 1980. Heavy metal inputs to Mississippi Delta sediments - A historical view. *Water, Air and Soil Pollution*, Vol. 13, pp. 481.
- Reid, J.M. et al. 1981. Factors affecting the chemistry of precipitation and river water in an upland catchment. *J. of Hydrology*, Vol. 15, pp. 129.
- Reinert, K.H. and Rodger, J.H. 1984. Influence of sediment types on the sorption of endotoxin. *Bull. Environ. Contam. Toxicol.*, Vol. 32, pp. 557.
- Rickert, H. 1985. Water quality effects of pine flatwoods silviculture. *J. Soil Water Conserv.*, Vol. 40, pp. 306.
- Roles, J.M. and Jonker, P.J. 1985. Representativity and accuracy of measurements of soil loss from runoff plots. *Trans. Am. Soc. Agric. Eng.*, Vol. 28, pp. 1458.
- Sharpley, A.N. et al. 1981. The sorption of soluble phosphorus by soil material during transport in runoff from cropped and grassed watersheds. *J. Environ. Qual.*, Vol. 10, pp. 211.
- Sharpley, A.N. et al. 1981. The release of soil phosphorus to runoff in relation to the kinetics of desorption. *J. Environ. Qual.*, Vol. 10, pp. 386.

- Smith, C.N. and Carsel, R.F. 1984. Foliar washoff of pesticides (FLOWP) model: Development and evaluation. J. Environ. Sci. Health, B19, pp. 323.
- Timmons, D.R. and Dylla, A.S. 1981. Nitrogen leaching as influenced by nitrogen management and supplemental irrigation level. J. Environ. Qual., Vol. 10, pp. 421.
- Toler, L.G. 1965. Relation between chemical quality and water discharge in Spring Creek, southwestern Georgia. U.S.G.S. Professional Paper, No. 525-C.
- Verhoff, F.H. et al. 1980. River nutrient and chemical transport estimation. Proceedings ASCE, Jour. of the Environmental Engineering Division, Vol. 106, pp. 591.
- Verhoff, F.H. and Yaksich, S.M. 1982. Storm sediment concentrations as affected by land use, hydrology and weather. J. Environ. Qual., Vol. 11, pp. 72.
- Wall, G.J. et al. 1982. Agriculture and water quality in Canadian Great Lakes Basin: II. Fluvial sediments. J. Environ. Qual., Vol. 11, pp. 42.
- Walling, D.E. 1974. Suspended sediment and solute yields from a small catchment prior to urbanization. In: Fluvial Processes in Instrumented Watersheds (Eds. K.J. Gregory, and D.E. Walling), Insitute of British Geographers Special Publication No. 6, pp. 169.
- Walling, D.E. and Foster, I.D.L. 1975. Variations in the natural chemical concentration of river water during flood flows, and the lag effect: Some further comments. J. of Hydrology, Vol. 26, pp. 237.

- Walling, D.E. 1975. Solute variations in small catchment streams: some comments. Transactions Institute of British Geographers, Vol. 64, pp. 141.
- Walling, D.E. and Webb, B.W. 1983. The dissolved loads of rivers: a global overview. In: Dissolved Loads of Rivers and Surface Water Quantity/Quality Relationships, International Association of Hydrological Sciences Publication No. 141, p. 3.
- Walling, D.E. and Webb, B.W. 1983. Patterns of sediment yield in background to paleohydrology. Gregory, K.J. (Ed.), Wiley, New York, pp. 69.
- Wauchope, R.D. and Meyers, R.S. 1986. Adsorption-desorption kinetics of atrazine and linuron in freshwater-sediment. aqueous slurries. J. Environ. Qual., Vol. 14, pp. 132.
- Webb, B.W. and Walling, D.E. 1983. Stream solute behaviourism in the River Exe Basin, Devon, U.K. IAHS Publ. No. 141, pp. 153.
- Wehje, G.R. et al. 1983. Biological significance and fate of atrazine under aquifer conditions. Weed Sci., Vol. 31, pp. 610.
- Weiss, C.M. 1969. Relation of phosphates to eutrophications. J. Amer. Water Works, Vol. 11, pp. 42.
- Whipple, W. and Hunter, J.V. 1977. Non-point sources and planning for water pollution control. Journal WPCF, Vol. 13, pp. 15.
- White, E.M. 1981. Nutrient contents of precipitation and canopy throughfall under corn, soybeans and oats. Water Resourc. Bull., Vol. 17, pp. 708.

- Wijayartne, R.D. and Means, J.C. 1984. Affinity of hydrophobic pollutants for natural estuarine colloids in aquatic environments. Environ. Sci. Technol., Vol. 18, pp. 121.
- Wu, T.L. et al. 1983. Herbicide runoff from experimental watersheds. J. Environ. Qual., Vol. 12, pp. 330.
- Yalin, M.S. 1972. Mechanics of sediment transport. Pergammon Press.
- Zinten, A.J.A. et al. 1983. Vertical transport of pesticides into soil when adsorbed on suspended particles. J. Agric. Food Chem., Vol. 31, pp. 62.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the permission given by various journals and authors to use numerous figures given in this report. E.J. McCurdy and W.D. Finn are thanked for the assistance provided in the preparation of the manuscript.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the permission given by various journals and authors to use numerous figures given in this report. E.J. McCurdy and W.D. Finn are thanked for the assistance provided in the preparation of the manuscript.

FIGURE CAPTIONS

- Figure 1 Different relationships between discharge (Q) and concentration (after Manczak and Florczyk, 1971).
- Figure 2 Varying nitrate responses to storm events in the River Dart at Bickleigh (after Webb and Walling, 1983).
- Figure 3 Variation in discharge and concentrations of sodium, magnesium, calcium, bicarbonate, silica, DOC, iron and Potassium during a storm event in September 1978 (after Reid et al., 1981).
- Figure 4 Variation of gauge height of flow with specific conductance for storm runoff (after Miller and Drever, 1977).
- Figure 5 Variation in chemical composition and gauge height of flow of North Fork of Shoshone River (after Miller and Drever, 1977).
- Figure 6 Chemical ion concentration in snowpack at Turkey Lakes Watershed, 1981 (after Jeffries and Semkin, 1983)
- Figure 7 Chemical ion concentration in snowpack at Turkey Lakes Watershed, 1982 (after Jeffries and Semkin, 1983)
- Figure 8 Chemical ion concentration in streamwater at Turkey Lakes Watershed, 1981 (after Jeffries and Semkin, 1983)
- Figure 9 Chemical ion concentration in streamwater at Turkey Lakes Watershed, 1982 (after Jeffries and Semkin, 1983)
- Figure 10 Chemical ion concentration in stream discharge at Honey Creek Watershed, Ohio, U.S.A. (after Baker, 1985)
- Figure 11 Regression equation exponents between flow and chemical ion concentration.

Table 1. Load Interpolation Procedures

$$A. \quad \text{Total load} = \alpha \left(\sum_{i=1}^n \frac{C_i}{n} \right) \left(\sum_{i=1}^n \frac{D_i}{n} \right)$$

$$B. \quad \text{Total load} = \alpha \left(\sum_{i=1}^n \left(\frac{C_i D_i}{n} \right) \right)$$

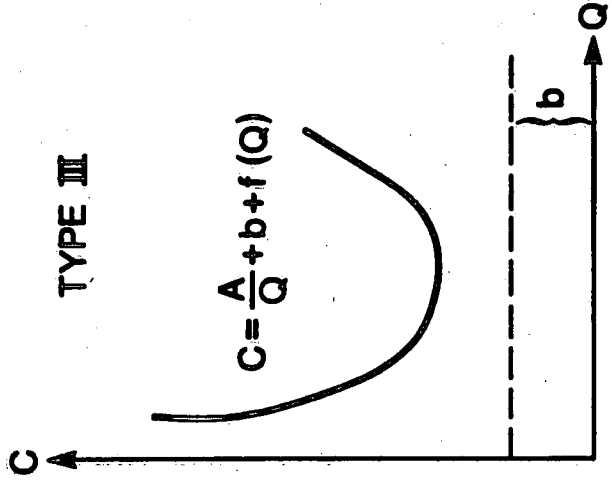
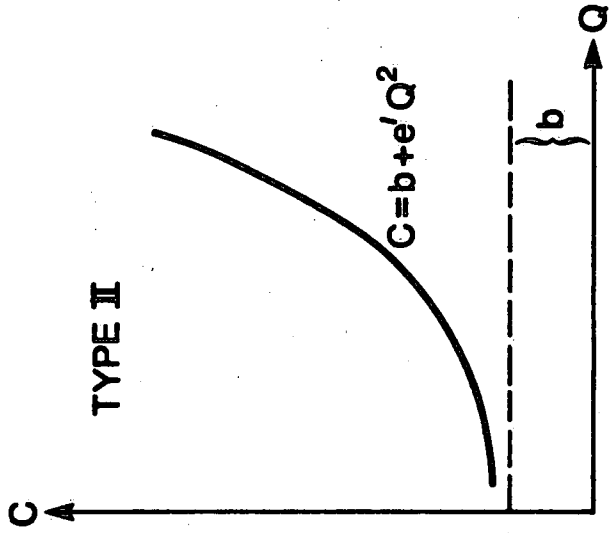
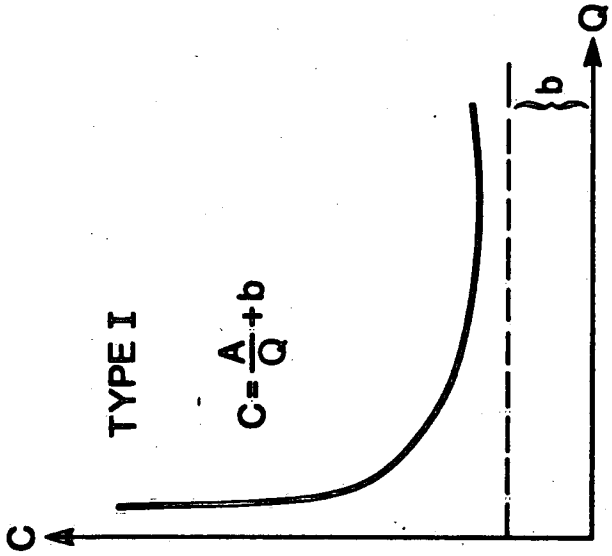
$$C. \quad \text{Total load} = \frac{\alpha \left(\sum_{i=1}^n \left(\frac{C_i D_i}{n} \right) \right) \bar{D}_r}{\sum_{i=1}^n \frac{D_i}{n}}$$

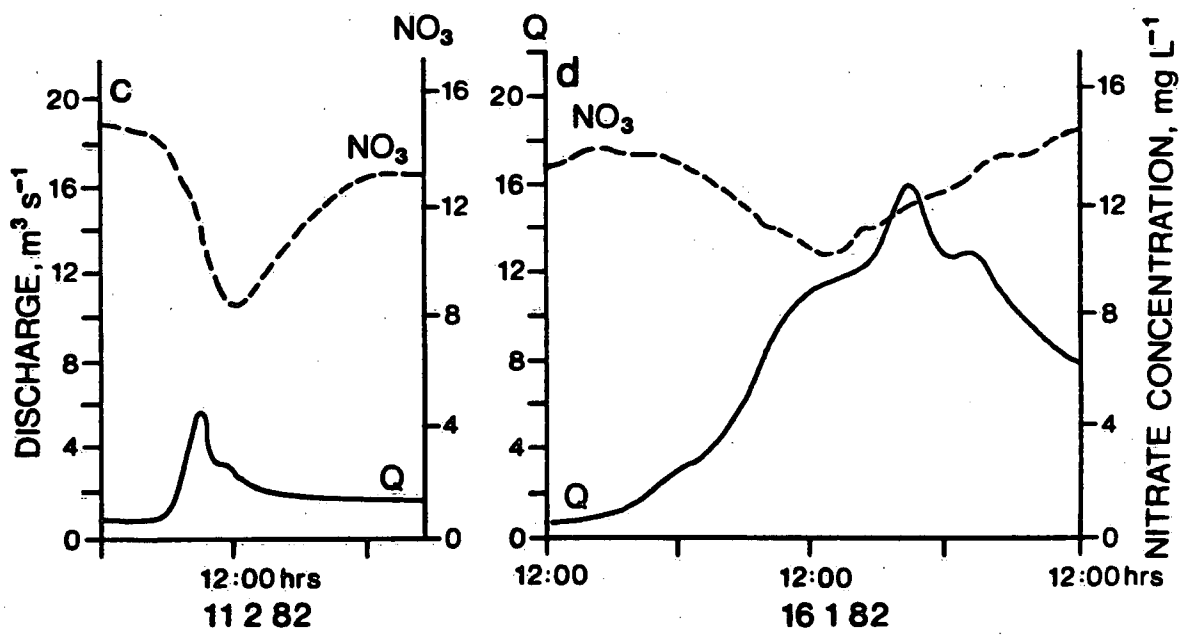
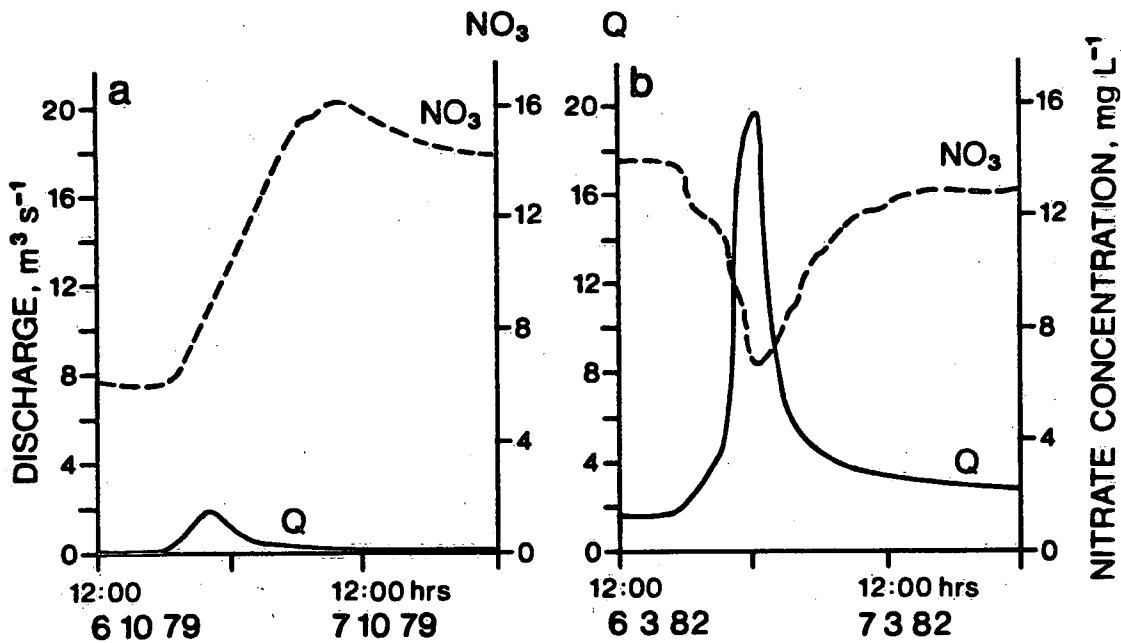
$$D. \quad \text{Total load} = \alpha \bar{D}_r \left(\sum_{i=1}^n \frac{C_i}{n} \right)$$

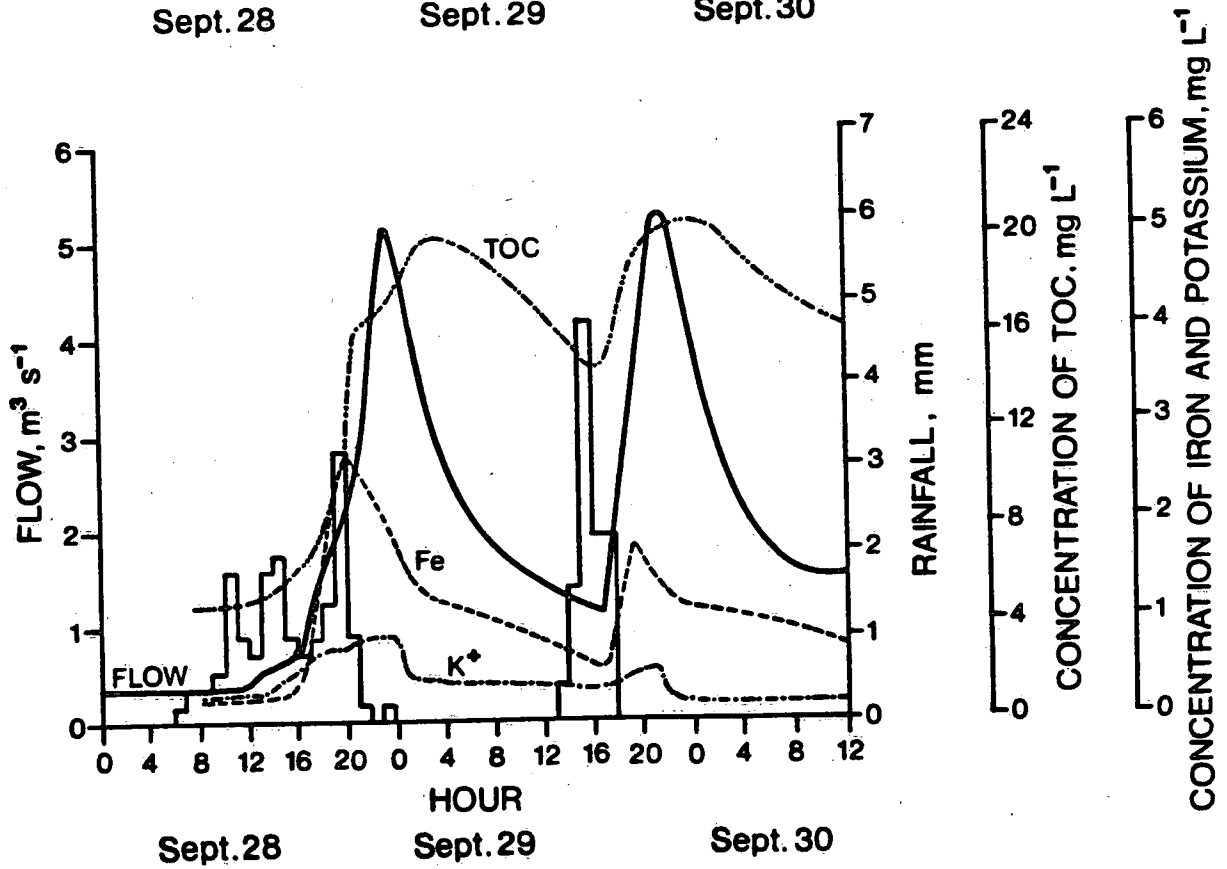
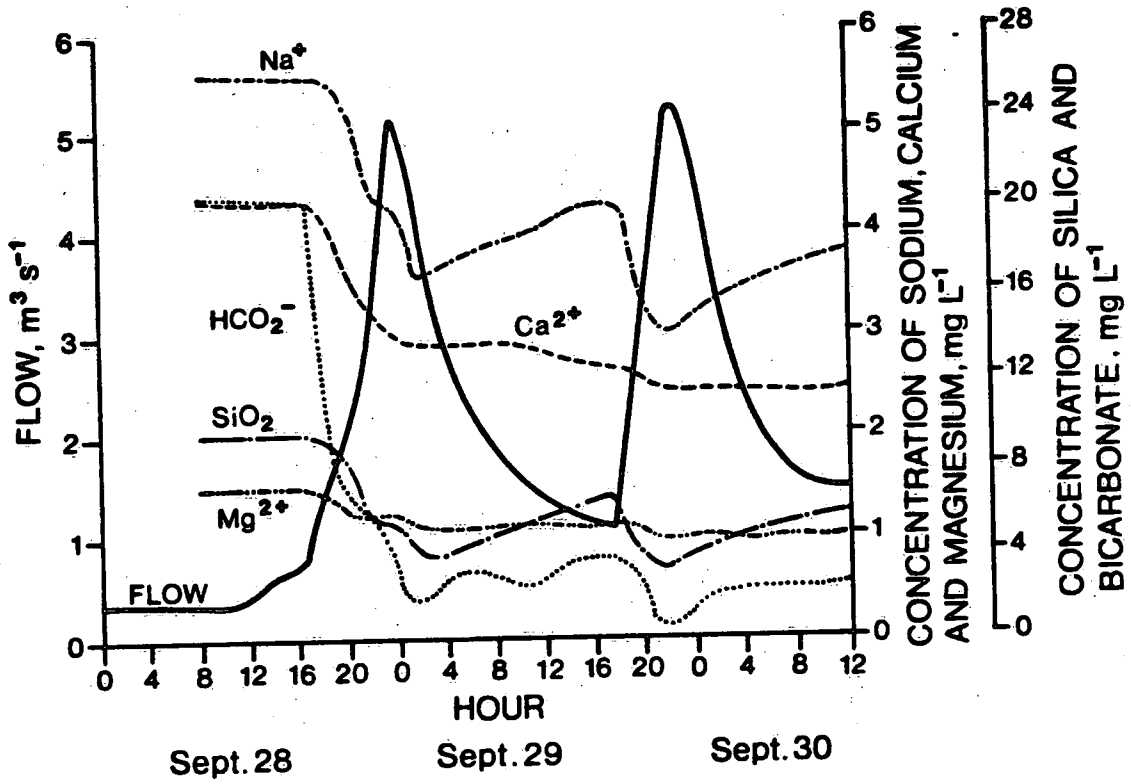
$$E. \quad \text{Total load} = \alpha \left(\sum_{i=1}^n \right) \left(C_i \bar{D}_{pi} \right)$$

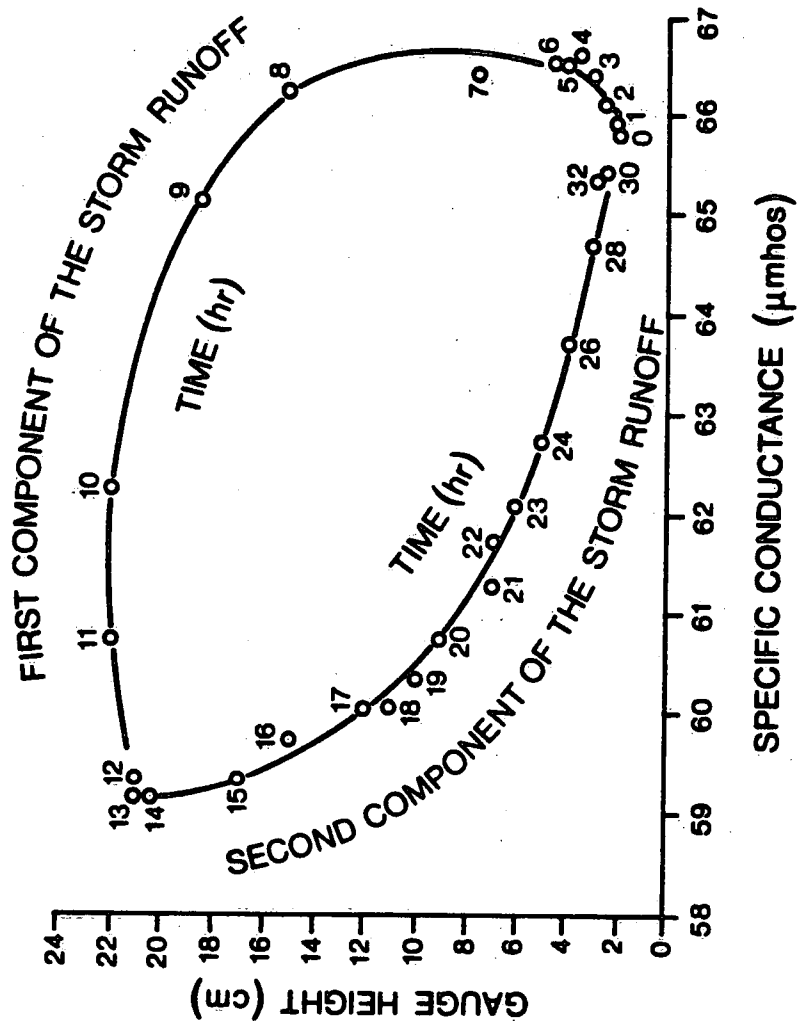
where

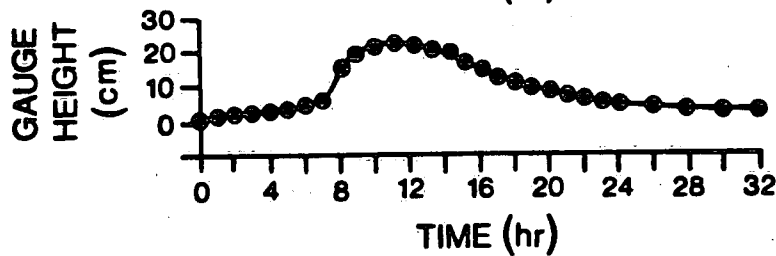
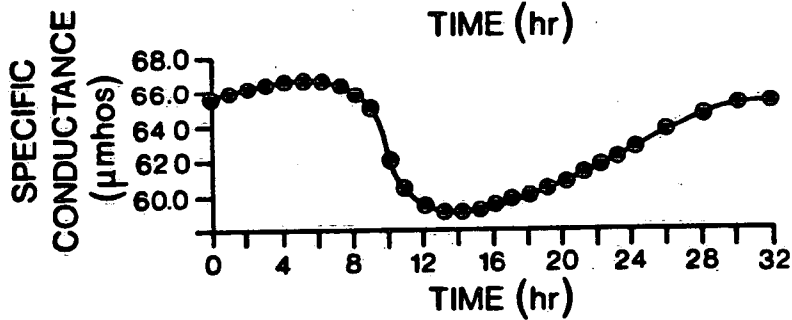
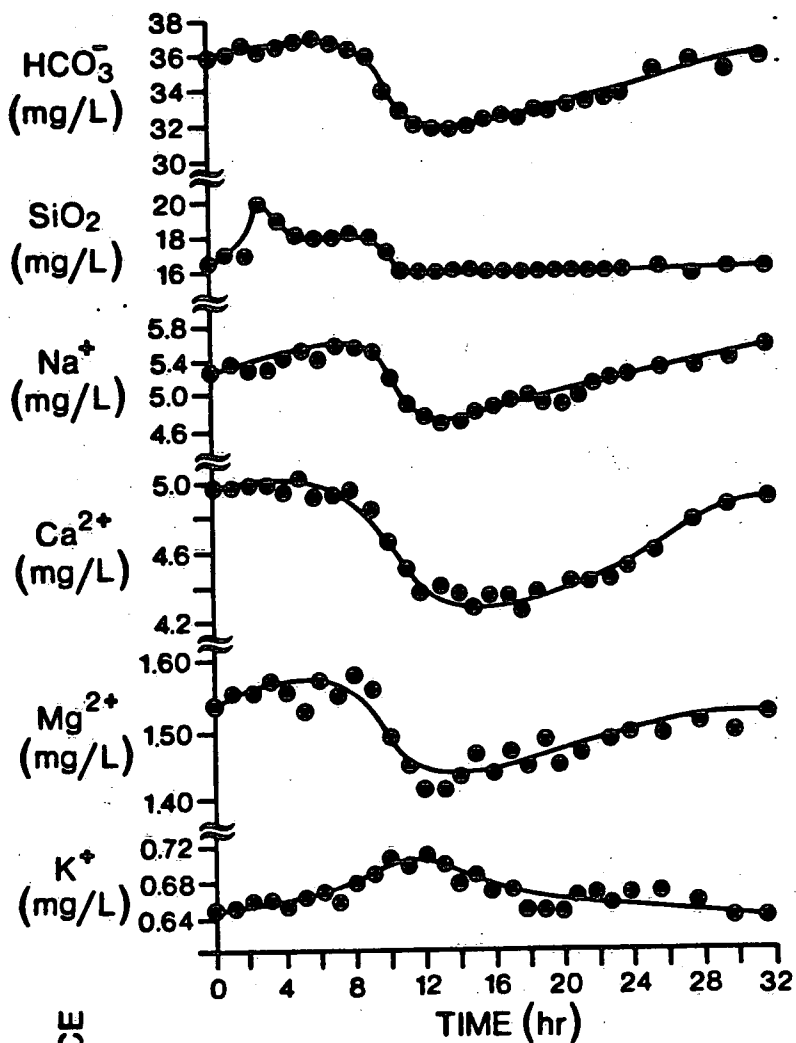
- α = conversion factor to take account of period record
- C_i = instantaneous concentration associated with individual samples (mg l^{-1})
- D_i = instantaneous discharge at time of sampling ($\text{m}^3 \text{s}^{-1}$)
- \bar{D}_r = mean discharge for period of record ($\text{m}^3 \text{s}^{-1}$)
- \bar{D}_{pi} = mean discharge for interval between samples ($\text{m}^3 \text{s}^{-1}$)
- n = number of samples



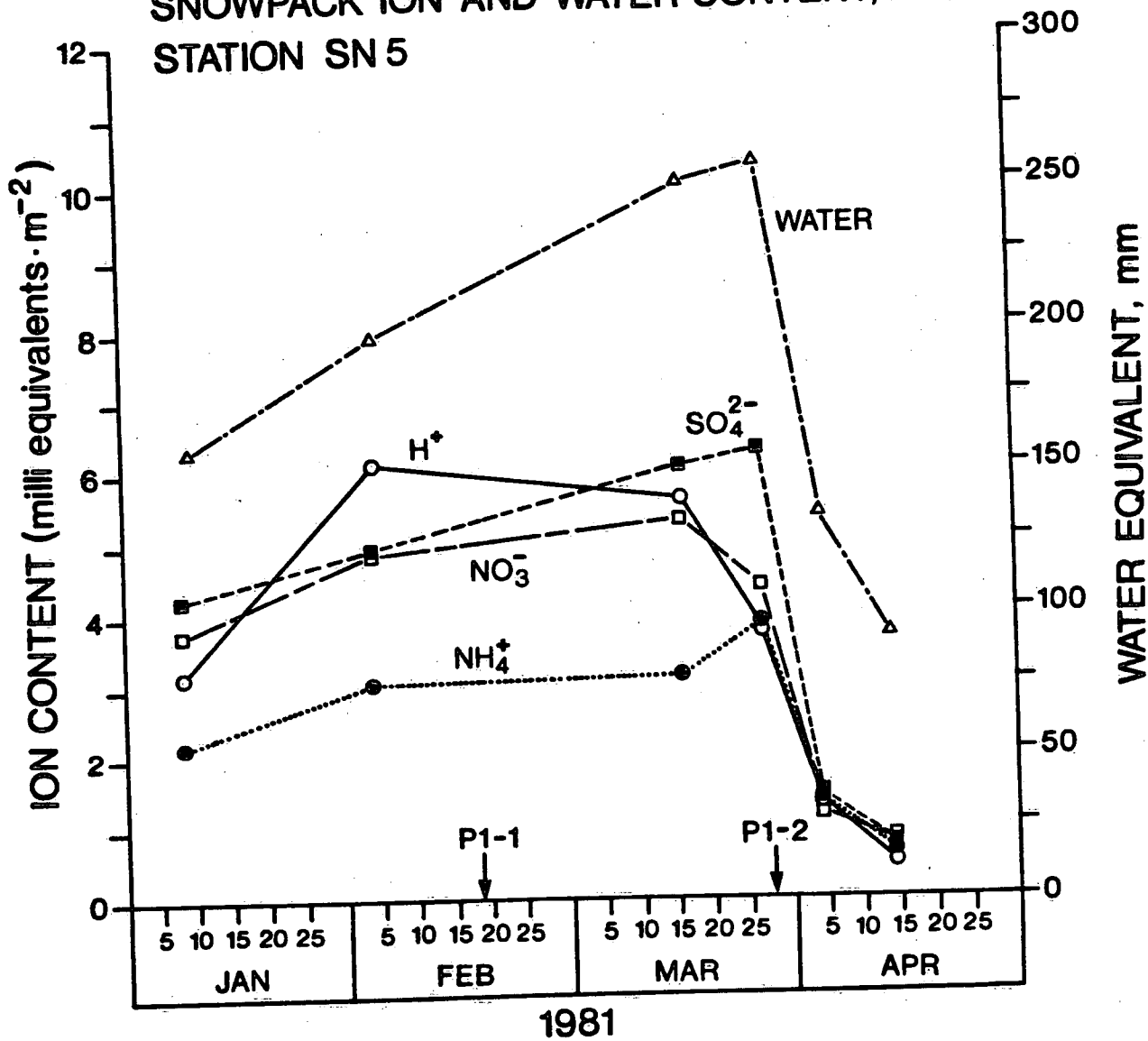








SNOWPACK ION AND WATER CONTENT, 1981 STATION SN 5



SNOWPACK ION AND WATER CONTENT-1982

