THE USE OF CHEMICAL HYDROGRAPHS IN GROUNDWATER QUALITY STUDIES

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INTRODUCTION

A graph showing changes with respect to time of some property of water in a stream, or underground, is generally termed a hydrograph. Hem (1959) illustrated the significance of both long and short-term fluctuations in the quality of groundwaters. The purpose of this paper is to illustrate how chemical hydrographs were used in a study of nitrate in groundwater of the Fresno-Clovis Metropolitan Area (F.C.M.A.) of central California.

High nitrates in drinking water are significant in relation to an infant disease, methemoglobinemia. Concentrations exceeding the 1962 U.S. Public Health Service limit of 45 parts per million (ppm) were noted in the F.C.M.A. by the California Department of Water Resources (1965). The primary sources of nitrate were identified as sewage percolation ponds and septic tank disposal systems. Schmidt (1971) noted several other sources, such as winery wastewaters, meat-packing plant wastes, and agricultural fertilizers. Hydrogeologic factors were shown to be intricately related to the distribution of nitrate in groundwater of the F.C.M.A.

The Fresno-Clovis Metropolitan Area comprises about 145 square miles which lie between the Kings and San Joaquin Rivers in the east-central portion of the San Joaquin Valley. Population of the metropolitan area in 1969 was 310,000. Urban water use is derived entirely from wells, whereas the surrounding agricultural area relies on surface water and groundwater. Climate is Mediterranean in type and annual precipitation averages eleven inches at Fresno. Groundwater recharge comes from streamflow infiltration and canal seepage.

Alluvial-fan deposits comprise the unconfined aquifer of the Fresno area. Sand, gravel, cobbles, silt, and clay strata dip gently to t he southwest and occur to depths of several thousand feet near Fresno. Depth to water averages about seventy feet and well depths range from less than 100 to more than 500 feet. The average specific capacity is about 130 gallons per minute per foot and the average transmissibility exceeds 220,000 gallons per day per foot. Cobble zones are related to deposits of the ancestral San Joaquin River and comprise the most favorable water-bearing materials. An impermeable hardpan locally limits the percolation of surface water in some parts of the area.

Chemical hydrographs were prepared for all wells in the F.C.M.A. with more than four separate chemical analyses. The following paragraphs summarize some of the more pertinent uses of chemical hydrographs in relation to the distribution of nitrate in the groundwater of the F.C.M.A.

DETERMINATION OF ERRONEOUS OR ATYPICAL ANALYSES

There are a number of sources of errors in chemical analyses.

One method of checking analyses involves comparing the summation of cations to the summation of anions (American Public Health Association, Inc., 1965). A close balance should be obtained for most groundwater. This method of checking the correctness of analyses has inherent limitations, because of the occurrence of calculated values for some constituents.

Other factors besides errors can lead to atypical analyses for certain constituents. Several methods of analysis are in common use for the determination of most ionic species, and results for the same water sample may not be equivalent. Concentration of nitrate can change with time since pumping began. The period of time between sample collection and determination can be crucial for some constituents, such as nitrate. Contamination of the sample bottles and variation in the method of sampling can cause variations in analytical results.

Plotting of chemical hydrographs commonly indicates these erroneous or atypical values. Erroneous or atypical values can lead to invalid conclusions regarding changes occurring in water quality. Judgment as to the determination of erroneous or atypical concentrations for a specific well must necessarily be based on a knowledge of the hydrologic framework and seasonal variation of constituent concentrations. Once these erroneous or atypical values are deleted from consideration, meaningful trends are usually apparent, and generally illustrate that changes in chemical quality are gradual in groundwater.

DOCUMENTATION OF MAJOR CHANGES
IN GROUNDWATER QUALITY

Natural concentrations of the ionic species in groundwater are very low in the F.C.M.A. As a result, man-induced changes in quality are reflected by locally high concentrations. The development of septic tank disposal systems, sewage percolation ponds, industrial waste disposal ponds, and nitrogen fertilization in agricultural areas have resulted in substantial increases in the nitrate content of groundwater.

Chemical hydrographs usually display increases in nitrate content since about 1950 (Figure 1). Well PS 27 was in a sewered area and the primary source of nitrate was groundwater inflow from the vicinity of the Fresno Sewage Treatment Plant. The nitrate content exceeded 45 parts per million in 1963 and the well was abandoned in 1966. The increasing nitrate was primarily due to a decline in water level near the well. Groundwater inflow of sewage effluent was hastened by the lower head near the well.

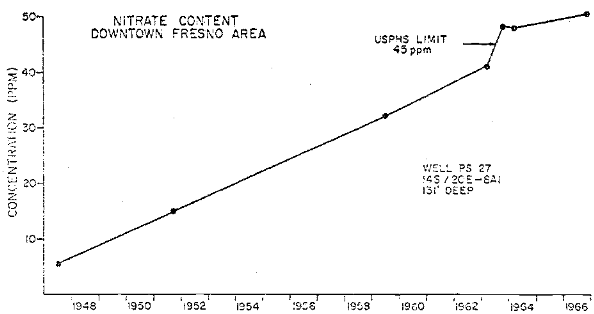

Figure 1

Long term increases in nitrate content can also be attributed to the lowering of the water level near shallow wells in septic tank areas. Nitrate in these areas is stratified in the aquifer of the F.C.M.A., with shallow groundwater having higher concentrations. As water levels have declined in these areas at an average rate of about three feet per year, wells have tended to draw on shallower portions of the aquifer. This factor alone tends to increase the nitrate concentration in a well over a period of years or decades. Hydrographs for wells penetrating deeper portions of the aquifer generally show little long-term variation in nitrate concentration. These wells are seemingly sampling background concentrations of nitrate.

ILLUSTRATION OF SEASONAL VARIATIONS IN QUALITY

Comparisons of chemical quality from one year to the next have sometimes been made without regard to the seasonal variation. Engineering-Science, Inc. (1970) noted that in the Fresno area, samples for nitrate should be collected at approximately the same time each year in order to make valid comparisons. Chemical hydrographs can indicate both the range of concentration exhibited on a seasonal basis and significant trends.

Nitrate hydrographs for wells in septic tank areas of the F.C.M.A. indicate declining concentrations as the summer progresses, with lowest contents in the fall. This trend occurs where the impermeable hardpan is absent and is related to canal recharge during the irrigation season. Abundant unlined canals traverse most of the area. Exceptions to this trend are found in areas where the impermeable hardpan is present. In this case recharge from canal seepage is minimal, and nitrate contents increase during the summer to a peak in the fall. This trend is apparently related to the temperature effect on nitrification, i.e., more nitrification during the warmer months; and to downward flow of shallow water during summer pumping. Vertical flow into the deeper producing zones of many wells results in higher nitrate as the summer progresses.

ILLUSTRATION OF EFFECTS OF HYDROLOGIC FACTORS ON QUALITY

Long term trends shown by chemical hydrographs for wells can illustrate significant changes in the hydrologic regimen. Chloride and nitrate hydrographs are presented for a well in a septic-tank area (Figure 2). Increases in concentration prior to 1966 were due to the development of unsewered suburban areas. Canal recharge was a significant factor in the greatly decreased concentrations of nitrate and chloride in 1967. Annual streamflow for the Kings River, which supplies water to canals of the area, was the largest recorded to that time. Dilution by low nitrate and chloride surface water also occurred in substantial amounts in 1969, which was also a year of very high streamflow.

Several investigators have focused on nitrate changes alone and hypothesized concepts such as denitrification to explain these

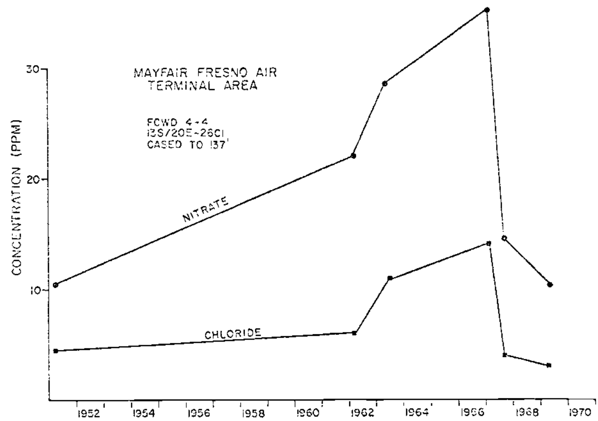

Figure 2

changes. However, plots of other constituents, particularly chloride, can indicate if a change is peculiar to nitrate alone. In the case illustrated by Figure 2, chloride trend is similar to that of nitrate. Thus hydrogeologic factors have likely produced the significant changes in trend. Chloride is perhaps an ideal tracer in this area due to its mobility and low abundance in natural groundwater. A discussion of long-term trends displayed by chemical hydrographs must include reference to the historical streamflow records of the area.

ILLUSTRATION OF EFFECTS OF CHANGES IN WELL CONSTRUCTION

Changes in well depth can produce substantial changes in trend for nitrate content (Figure 3). The nitrate hydrograph

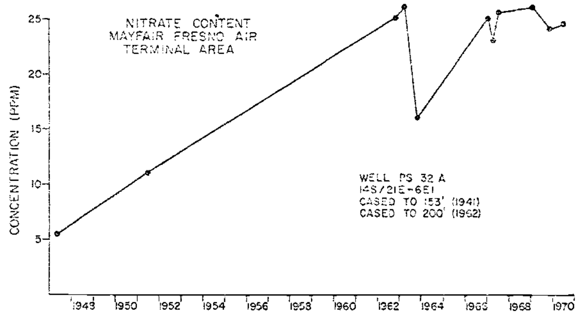

Figure 3

indicates a linear increase to about 1962, with relatively constant concentrations thereafter. Prior to 1962 well PS 32A was open-bottomed and cased to 153 feet. However, in 1962 the well was deepened and cased to 200 feet. This well sampled shallower water in the aquifer prior to 1962 and the increasing trend was related to septic tank development. Once the well was cased to a greater depth, nitrate concentration did not significantly change with time. Deeper portions of the aquifer tend to have less fluctuation in nitrate content due to the damping of near-surface effects.

DETERMINATION OF NITRATE SOURCE

Several potential sources of nitrate occur in some parts of the F.C.M.A. Nitrate and chloride hydrographs were prepared for many wells in septic tank areas (Figure 2). Chloride short-term trends were similar to those for nitrate in virtually all cases. Both chloride and nitrate are contributed by septic-tank effluent and the two ions are both mobile in groundwater of the Fresno area.

Hydrographs were also plotted for wells in the vicinity of sewage treatment plants. The chemical hydrographs in this case indicated an abundance of opposite nitrate and chloride short-term trends. Thus when chloride concentration increased for a specific well, nitrate concentration often decreased. The exact reason for this pattern is unknown, but it may be related to the interference effect of high chloride concentrations on the phenoldisulfonic method for nitrate determination (Malhotra and Zononi, 1970).

Nitrate and chloride hydrographs were plotted for wells in areas where both septic tanks and sewage effluent ponds were potential sources of nitrate. These hydrographs were used in conjunction with trilinear diagrams, distribution of major chemical constituents, and hydrologic data to effectively delineate sources of nitrate in water pumped by specific wells. Conflicting evidence in some cases suggested more than one nitrate source for a specific well, whereas in other areas one source was clearly predominent.

INTERPRETATION OF NITROGEN TRANSFORMATIONS NEAR SEWAGE TREATMENT PLANTS

A typical hydrograph for nitrate in groundwater near the Fresno Sewage Treatment Plant (Figure 4) shows a seasonal variation ranging from 20 to almost 45 parts per million. The highest nitrate contents in groundwater occur during the winery season of

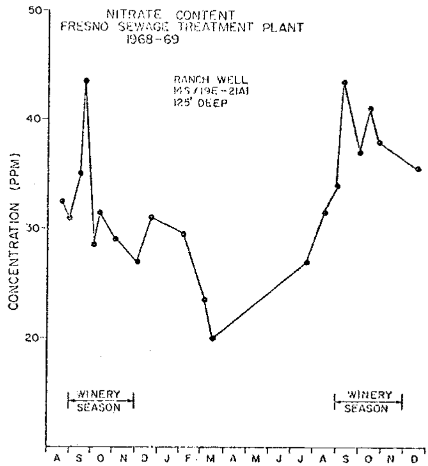

Figure 4

September 1 to December 1. High-nitrogen winery wastewaters during this period produce ammonia and nitrate-nitrogen contents of pond waters about four times greater than during the remainder of the year. However, wastewaters at this time have the highest biochemical oxygen demand for the entire year. As these waters rapidly utilize the available oxygen in the percolation ponds, little nitrification occurs. The nitrogen is retained in the soil in the organic and ammonia forms under these circumstances. Therefore, leached water is low in nitrate and concentrations in the groundwater decrease during this period.

Water lower in biochemical oxygen demand enters the percolation ponds following the winery season. More ponds are periodically dried out as wastewater diminishes in flow, and aerobic conditions develop beneath many ponds. However, nitrification does not proceed rapidly during the winter months, and nitrate contents in groundwater continue to decline. Nitrification proceeds rapidly with the warming temperature of spring and summer. Nitrate is formed and readily leached to the groundwater; thus nitrate contents increase during the summer to a peak in the fall. The peak nitrate contents in the groundwater for a specific year may be derived from nitrogen supplied during the previous winery season. Denitrification occurring under anaerobic conditions could also explain portions of the seasonal variation.

SUMMARY

One of the most troublesome problems in water quality studies concerns erroneous or atypical analyses. A measure of the accuracy of the sample can be determined by plotting chemical hydrographs for individual wells. If hydrographs are prepared and kept up to date, then analyses taken at any particular time can be rechecked when results deviate significantly from previous analyses.

Major changes in groundwater quality over a period of years and decades were documented by chemical hydrographs. Seasonal fluctuations in nitrate were consistent for many parts of the Fresno-Clovis Metropolitan Area and were related to hydrogeologic factors and parameters directly affecting nitrification. Chloride hydrographs were extremely valuable in a study of nitrate in groundwater. However, interpretation of the significance of chemical hydrographs can be difficult. Well deepening commonly results in lower nitrate contents of water pumped by wells. Similarly, changes in water level and pumping patterns, as well as recharge, produce changes in concentration of constituents over a period of years.

Nitrate and chloride hydrographs were used to help determine the source of nitrate in several areas where several possible sources were present. Nitrogen transformations in the vicinity of the Fresno Sewage Treatment Plant were clarified by interpretation of nitrate hydrographs for nearby wells. Seasonal fluctuations in nitrate were related to the nitrogen content of percolation pond water, the waste strength of these wastewaters, temperature effects, and pond operation.

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