

TRANSFORMATIONS IN QUALITY OF RECHARGING
EFFLUENT IN THE SANTA CRUZ RIVER

by

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INTRODUCTION

Since 1955 secondary treated effluent from the City of Tucson Treatment Plant has been released to the Santa Cruz River, the principal drainage tributary of the Tucson Basin. Because the river is ephemeral, it has functioned essentially as an artificial recharge facility for sewage effluent. For example, in Fiscal Year 1973-1974, the total volume of effluent released to the river channel was about 34,460 acre-ft (Dye, 1974). Assuming 90% recharge (Davidson, 1973), the total volume of effluent artificially recharged amounted to about 31,000 ac-ft. Such recharge has affected not only the groundwater levels in the vicinity of the river but also water quality (ibid.). Recharge of nitrate is of particular concern.

An investigation, in progress since 1973, involves studying the interactions between effluent infiltrating into the Santa Cruz River and the deposits within two landfills, which adjoin the river. A monitoring program associated with the investigation involved constructing sampling wells in the vicinity of the landfills. As it turned out, samples from the well system near the upstream landfill (the Ruthrauff Rd landfill) indicated certain transformations in chemical and microbial quality of recharging sewage effluent. This paper reviews results of the sampling program in the Spring of 1974, with particular emphasis on transformations in nitrogen.

MONITORING PROGRAM

SAMPLING LOCATIONS

The Ruthrauff Sanitary Landfill, managed by The Pima County Department of Sanitation, is located about 0.5 miles downstream of the outfall from the City of Tucson Treatment Plant (see Figure 1). The relative locations of five sampling sites in the vicinity of the landfill are shown on Figure 1. Samples of surface water were obtained directly from the Santa Cruz River, about 0.5 miles downstream of the Ruthrauff Road bridge. The landfill well, installed at the base of the landfill in an area not yet covered with refuse, consists of a 16 ft section of 2 inch diameter PVC pipe, with a screened well point. This well taps a perched water table, which appears to have developed on a caliche layer, within the zone of aeration. Apparently this perched layer and the river are hydraulically connected - an inference based on the observation that the water level in the well responds to discharge events in the Santa Cruz River. When the well was installed, the water level in the unit was about 25 ft below a reference point in the river channel.

The site designated "city well" represents a 95 ft well, installed by the City of Tucson next to the Santa Cruz River. The well is about 1.5 inch I.D., constructed from drill stem with an open, unscreened end. The water level in the unit was about 71 ft below the river channel when the well was first installed.

The "downstream control well", also installed by the City of Tucson, is 105 ft deep, and the initial water level was about 72 ft below the Santa Cruz River channel. The "downstream control well" is about 1000 ft west of the "city well".

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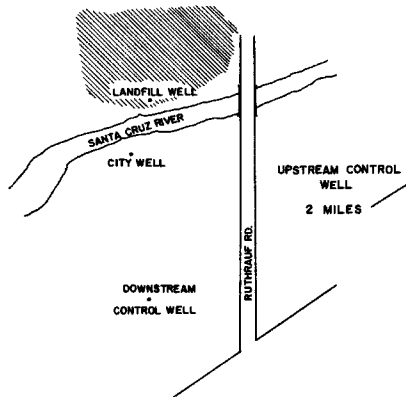


FIG. 1
SAMPLING LOCATIONS, RUTHRAUF LANDFILL SITE

The "upstream control well", another City of Tucson well, was installed about 1.5 miles upstream of the outfall from the City of Tucson Treatment Plant. The rationale for installing the well at this location was that water samples would represent indigenous groundwater quality. This well is 120 ft deep.

SAMPLING PROCEDURES AND ANALYSES

In the Spring of 1974, 24-hour composite samples were obtained from the Santa Cruz River five times a week. The landfill well was sampled three to five times a week. The deeper wells were sampled once a week. Water levels were measured in each well prior to sampling.

Samples intended for analyses of nitrogen series were preserved with mercuric chloride and stored at 4° C.

Analyses on samples included: Specific conductance, pH, sodium, potassium, calcium, magnesium, chloride, carbonate, bicarbonate, sulfate and hardness. Nitrate-N, nitrite-N and ammonia-N were determined via a steam distillation method reported by Bremner (1965). As a check, ammonia-N together with organic-N were determined via the Kjeldahl method.

Total and fecal coliform levels in river and well samples were measured periodically via the Millipore membrane filter technique.

HYDROGEOLOGICAL FEATURES

Sediments underlying the monitoring site are more or less typical of alluvium in the Tucson Basin. Specific geologic units and their water bearing properties are thoroughly reviewed by Davidson (1973). Surficial deposits in the zone of aeration may have transmissivity values in excess of 150,000 gpd/ft (ibid.).

Analyses of auger samples taken during construction of the City of Tucson wells reflect the variability of surficial deposits within the zone of aeration (Davis, 1975). For example, samples from the site of the "city well" manifested coarse deposits ("gravelly sand with silt") to about 40 ft below land surface, with underlying deposits to 85 ft being highly stratified and defined as "gravelly-clayey-sand". Silt plus clay averaged about 5% in materials to 40 ft and 30% in deeper materials. In addition, the driller encountered an apparent perched water table at about 60 ft

(ibid.). Caliche beds were encountered during installation of the "downstream control well".

A prominent feature of shallow river bed materials, downstream of the treatment plant, is the presence of an illuviated, black deposit (Sebenik, 1972). Apparently, this deposit consists of reduced forms of iron and sulfate, together with organic materials. Incidentally, such deposits penetrate soils underlying oxidation ponds (Deming, 1963). In time, the black deposit may promote the formation of a shallow, perched water table.

RESULTS AND DISCUSSION

GENERAL RESULTS

Mean values of the various water quality parameters from the five sampling locations during the period January 1, 1974 to May 30, 1974, are shown on Table 1. These values represent the means of the following total number of samples: Santa Cruz River, 67; landfill well, 20; city well, 19; downstream control well, 19; upstream control well, 11.

Mean values of chloride in samples from the river, landfill well and city well were about the same, suggesting a common source - sewage effluent in the river. Chloride concentrations in the downstream well averaged about 20 mg/l less, and in the upstream well almost 100 mg/l more, than in the three locations in and near the river. Trends in chloride concentrations are shown on Figure 2. The lower values in the downstream well may represent dilution with good quality underflow from the Tucson Mountains, immediately to the west. The higher levels of chloride in the upstream well may reflect the passage of a wave of poor quality water, possibly leachate from an upstream sanitary landfill or industrial effluent recharged in an upstream artificial recharge pit.

Substantially higher concentrations of calcium, magnesium, and bicarbonate were observed in landfill well samples than in river water. Lesser increases were observed in samples from the city well. Possibly these increases reflect the dissolution of native (relict) salts during infiltration of sewage effluent (Laney, 1972). In contrast to calcium, magnesium and bicarbonate, the mean concentrations of sulfate were less in well samples than in river samples. Possibly, reducing conditions in the near-surface stream deposits promote the formation of hydrogen sulfide from the sulfate present in effluent.

Excessive levels of total and fecal coliform were present in river samples (e.g. maximum total coliform was 675,000 colonies per 100 ml). Because of filtration through shallow surficial deposits, the corresponding values in well samples, including those from the shallow landfill well, were generally within the limit of recommended public health tolerances.

NITROGEN TRANSFORMATIONS

During the monitoring period, the total nitrogen levels in well samples were markedly lower, on the average, than corresponding levels in river samples. For example, using the values in Table 1, total nitrogen in samples from the landfill well averaged only 21% of the total-N in river samples. Therefore, 79% of the total-N originally present in the effluent infiltrating into the river channel was lost in transit to the landfill well. Similarly, 88% of the total-N of recharging effluent was lost between the river channel and the sampling region of the "city well".

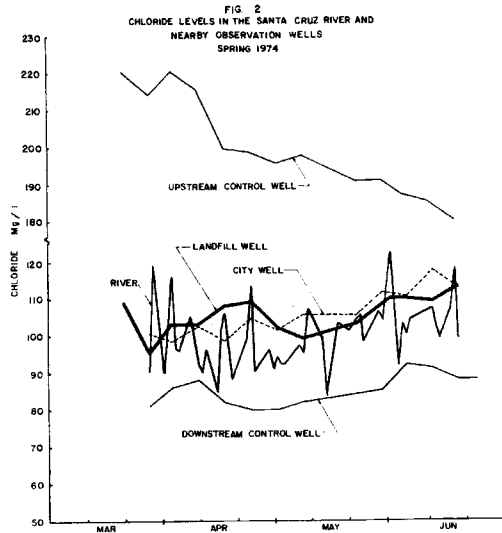
Trends in total-N in the river, landfill well and city well samples are shown on Figure 3. The disparateness of total-N values between river samples and well samples is evident on this figure. Peaks in total-N of river samples possibly reflect the release of sludge or supernatant from the treatment plant into the river. Of interest on the figure is the gradual decrease in total-N in the river samples as the season progressed, whereas, the corresponding values for the well samples oscillated about their means. Assuming the total-N of raw sewage entering the treatment plant remains constant, the decrease in total-N in treated effluent represents a seasonal loss in transit within the facility.

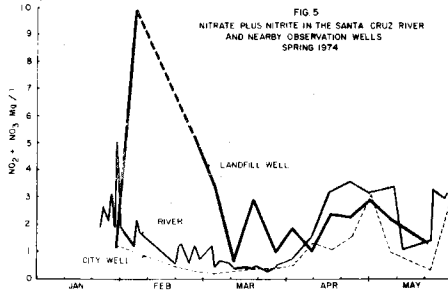
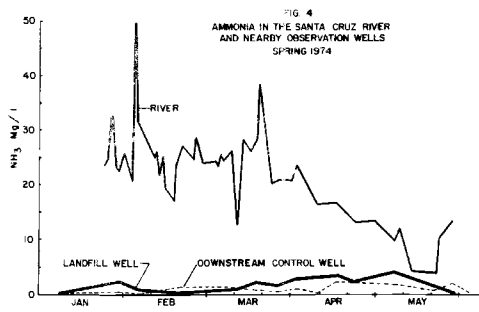
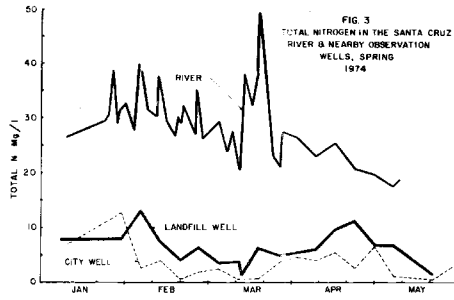
Trends in $\text{NH}_3\text{-N}$ in samples from the river, landfill well and city well are shown on Figure 4. Again, the $\text{NH}_3\text{-N}$ levels in the river tended to greatly exceed the corresponding values in the wells, at least until about the middle of March. Thereafter, $\text{NH}_3\text{-N}$ decreased in the river samples. This

TABLE 1.
MEAN WATER QUALITY VALUES,
LANDFILL PROJECT, 1974

	Santa Cruz River	Landfill Well	City Well	Downstream Control Well	Upstream Control Well
EC (mmho/cm)	1.09	1.17	1.53	0.94	1.56
pH	7.71	7.23	7.43	7.08	7.06
NH ₃ -N*	22.91	2.05	1.05	0.67	2.26
NO ₂ /NO ₃ -N	1.43	2.57	0.86	0.49	0.94
KJN	30.69	4.34	2.87	2.63	3.92
Total-N	32.12	6.91	3.73	3.12	4.86
Na	129.27	129.36	130.54	102.31	190.25
K	15.65	12.50	12.25	12.60	
Ca	55.15	94.25	70.80	69.75	116.87
Mg	8.32	13.41	9.33	13.25	24.12
Cl	102.22	104.20	103.40	84.00	200.40
HCO ₃	266.93	427.17	297.17	263.33	307.83
SO ₄	154.00	100.00	87.00	135.00	249.00

*All constituents below NH₃-N are in mg/l.





decrease suggests that ammonia volatilization may have occurred during transit of effluent within the plant site, and/or that nitrification increased during the season. Both reactions are temperature dependent.

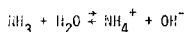
Figure 5 illustrates the trends in $\text{NO}_2\text{-N} + \text{NO}_3\text{-N}$ levels at the three sites. Note the change in ordinate scale between this figure and Figures 3 and 4. For the initial period, $\text{NO}_2\text{-N} + \text{NO}_3\text{-N}$ concentrations were higher in the landfill samples than in either the river or city well. The peak value in the landfill well may correspond to the high total-N values in the river. The trend reversed after about March 15, with nitrate levels increasing in the river. As indicated above, nitrification was probably enhanced by the increasing springtime temperatures. The mean $\text{NO}_2\text{-N} + \text{NO}_3\text{-N}$ values in the city well was only 2.63 mg/l, considerably below the recommended limit of 10 mg/l for drinking water.

FACTORS AFFECTING NITROGEN TRANSFORMATIONS

Results of the monitoring program in the vicinity of the Ruthrauff landfill suggest that during the observation period, recharge of effluent from the river did not contribute a substantial amount of nitrogen to groundwater in the area. In fact, if nitrogen values in the upstream control well, with a mean total-N value of 4.06 mg/l, are representative of indigenous groundwater quality, total-N actually may have been reduced as a consequence of recharge. Naturally it is not possible to extrapolate these results to other downstream sites - similar monitoring programs will be required, particularly in the vicinity of farming areas.

Possible mechanisms responsible for the marked loss in total-N during recharge of effluent from the river include nitrogen volatilization, together with nitrate assimilation, sorption and fixation of ammonia on clays and organic matter.

Ammonia volatilization is governed by the reaction (Stratton, 1968):



A pH increase causes a shift to the left and ammonia gas is evolved. According to Stratton (ibid.) under favorable temperatures and pH conditions substantial gaseous evolution of ammonia may occur in stream channels. However, Wilson (1974) found little difference in total-N levels in river samples taken at Ruthrauff Road and at a sampling site 4 miles downstream, suggesting that ammonia volatilization was not active in the reach.

Denitrification involves the reduction of nitrate to gaseous nitrogen compounds, via the activity of heterotrophic microorganisms, in an environment with low dissolved oxygen (D.O.) and an available source of energy. Nitrification and denitrification may occur simultaneously in a system (Keeney, 1973). For example, nitrification of added $\text{NH}_3\text{-N}$ has been observed in the surface layers of rice paddy soils, with denitrification of $\text{NO}_3\text{-N}$ subsequently occurring in the anaerobic subsurface layers (ibid.).

Denitrification may have been a significant mechanism for the loss in total-N observed during the monitoring study. In particular, the presence of a water table within surface deposits is ideal for promoting denitrification. As indicated earlier, this water table apparently develops upon a layer clogged by the eluviation of reduced iron and sulfate, and organic substances. However, a prerequisite for denitrification is that ammonia be nitrified to $\text{NO}_3\text{-N}$, and this step requires adequate aeration. Such aeration may be promoted in surface deposits by the diurnal fluctuations in effluent discharge rate. The presence of an oxidized surface layer and anaerobic underlying region is thus analogous to the conditions in rice paddies. For denitrification to proceed in the water table an energy source is also needed for the heterotrophic organisms. Studies by Sebenik (1975) suggest that sufficient organic carbon is present in shallow layers to serve as such an energy source.

In addition to denitrification, nitrate may also be reduced by microorganisms when used as a nutrient source, i.e., during "nitrate assimilation" (Alexander, 1961). Many researchers feel that assimilation may be negligible compared to denitrification in most soils (Keeney, 1973). Insufficient data are available, however, to quantify the importance of the mechanism in this study.

Ammonia passing into the anaerobic region underlying the stream channel may be sorbed on the cation-exchange complex of clays and organic matter and/or fixed within the crystal lattices of clay mineral and on organic matter. Adsorption of ammonia may not be too significant a mechanism for the observed decrease in total-N at the monitoring site because of the continued presence of an anaerobic zone: Patrick and Mahapatra (1968) found that the ammonia ion is displaced from the exchange complex by ferrous and manganese ions in water-logged soils as reducing conditions increase.

Clay minerals in the Tucson Basin are primarily of 2:1 structure, such as illite and montmorillonite with some of 1:1 structure such as kaolinite. Fixation of $\text{NH}_3\text{-N}$ is greater on the 2:1 types than on the 1:1 types. However, according to Nonnik (1965) fixation on illitic clays is markedly affected by K saturation, and montmorillonitic clays do not fix $\text{NH}_3\text{-N}$ under wet conditions. Fixation is increased by an increase in organic matter in soils (ibid.). Consequently, if organic matter increases in river sediments during infiltration of effluent, fixation of $\text{NH}_3\text{-N}$ might also be expected to increase. At this time, data are not available on the relative importance of $\text{NH}_3\text{-N}$ fixation on clays or organic matter at the monitoring site.

Trends observed in the Spring of 1974 were not continued into the fall of 1974. In particular, the loss in total-N was markedly diminished. Scouring of riverbed deposits by discharge events in the summer of 1974 possibly destroyed the black, anaerobic layer eliminating the shallow water table observed in the Spring. Conceivably, as the layer redevelops conditions favoring denitrification will be reestablished.

SUMMARY AND CONCLUSIONS

As part of a groundwater monitoring program in the vicinity of the Ruthrauff Rd landfill and the Santa Cruz River of southern Arizona, observations were made on the transformation in quality of effluent recharging from the river. Samples were obtained in the Santa Cruz River about 0.5 miles downstream of the City of Tucson Treatment Plant; from a shallow well terminating within a perched water table in the 70 ft thick zone of aeration; and from a deeper well tapping the surface of the main water table. A downstream control well, also reaching to the water table, was sampled to provide data on groundwater quality west of the river. Similarly, a well upstream of the Treatment Plant outfall was sampled to indicate "indigenous" groundwater quality.

It appeared that "indigenous" groundwater quality was poorer in general than groundwater downstream of the treatment plant or to the west. For example, chloride in the upstream well was almost twice that in samples from downstream wells. A wave of poorer quality water may have been moving through the upstream site at the time of observation. In comparison to the other wells, quality was substantially better in the downstream control well. Possibly low salinity groundwater moving in from the Tucson Mountains promoted dilution with indigenous groundwater and westerly-migrating, recharged effluent.

In both the shallow well and deeper well near the river, an increase in calcium, magnesium and bicarbonate over river effluent possibly manifested the dissolution of relict salts. Sulfate levels decreased in samples from these wells, compared to river samples. It is hypothesized that sulfate was reduced in an anaerobic zone within river bed deposits.

Although high concentrations of both fecal and total coliform were observed in river effluent, corresponding levels in well samples were within allowable limits.

The most interesting and significant observation of the study was the substantial difference in total-N between river samples and the shallow and deeper test wells. For example, an apparent loss of 79% in total-N was observed in the shallow well and 88% in the deeper well. Possible mechanisms for these losses include, ammonia volatilization, denitrification, assimilatory reduction, adsorption of NH_4 on the exchange complex of clays and organic matter, and fixation on clays and/or organic matter. Of these mechanisms it is speculated that denitrification was the most significant in causing the observed losses in total-N. Conceivably, diurnal changes in effluent discharge rates would permit the development of an oxidized surface layer such that nitrification could proceed. Subsequently, denitrification would occur within a shallow water table which developed above an illuviated layer of reduced iron, sulfate and organic material.

The study illustrated the value of monitoring in the zone of aeration vis a vis determining the possible sources of nitrate in groundwater. Thus, for the period of monitoring in the vicinity of the Ruthrauff landfill, it appears that recharge of sewage effluent in the river did not contribute

nitrate to native groundwater supplies. Similar studies downstream, however, may produce entirely different results.

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