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AN INVESTIGATION OF INORGANIC NITROGEN COMPOUNDS IN THE GROUNDWATER IN THE VALLEY OF MEXICO

M. C. RYAN*

RESUMEN

Este es un estudio de los compuestos del nitrógeno en el agua subterránea del Valle de México, motivado principalmente por la clausura de un conjunto de pozos en la parte sur del Valle, ocasionada por las altas concentraciones de amonio. Se intentó determinar si las fuentes de los compuestos del nitrógeno en el agua subterránea eran antropogénicas, particularmente las aguas de desechos (aguas negras). Las aguas de desecho son conducidas a través de toda la Ciudad de México por una red de canales no revestidos, que también son utilizados dentro del Valle para la irrigación. Se optó por el estudio de los nitrógenos en particular, ya que éstos son ampliamente reconocidos en los desechos domésticos y sus procesos geoquímicos están razonablemente bien entendidos. El principal riesgo conocido de los compuestos del nitrógeno en el agua de beber es la metahemoglobinemia, una patología de la infancia temprana. El límite máximo para nitratos recomendado por la Organización Mundial de la Salud, es 10 mg/l como N.

Se tomaron muestras de agua de pozo y agua superficial contaminada y se analizaron parámetros geoquímicos e isótopos ambientales. Los resultados fueron intercomparados en un intento por identificar la presencia del agua superficial en el agua de pozo. Desafortunadamente, las características del agua superficial no resultaron, en general, conclusivamente diferentes de las del agua de pozos, como para determinar si la contaminación antropogénica estaba ocurriendo en forma generalizada.

* *University of Waterloo, Waterloo, Ontario, Canada, N2L 3G1.*

La contaminación antropógena en las áreas de recarga parece estar indicada por las elevadas concentraciones que allí se presentan. La contaminación antropógena en la parte sur del Valle (en la vecindad de los Ramales Tecómitl, Tláhuac y Santa Catarina) fue demostrada por las altas concentraciones de amonio y la presencia de coliformes fecales en el agua subterránea. Aún cuando los pozos en la parte central del valle están sellados en el tramo que atraviesa una capa de arcillas y no parecen estar contaminados, no debemos concluir que la arcilla es impermeable, y que por lo tanto ofrece una protección completa contra las fuentes superficiales de contaminación.

ABSTRACT

A study of nitrogen compounds in the groundwater in the Valley of Mexico was prompted primarily by the closing of a series of wells in the southern part of the valley due to high ammonium concentrations. The study attempted to determine if the source of nitrogen compounds in the groundwater was from anthropogenic sources, namely wastewater (aguas negras). Wastewater is conducted throughout Mexico City in a network of unlined canals and is also used to irrigate agricultural fields within the valley. Nitrogen compounds were studied in particular because they are a widely recognized constituent of domestic waste and their geochemical processes are reasonably well understood. The principal known risk of nitrogen compounds in drinking water is methaemoglobinaemia, a health hazard to young children. A drinking water limit for nitrate of 10 mg/l as elemental N is recommended by the World Health Organization.

Contaminated surface water and well water from various locations in the valley were sampled and analysed for geochemical and environmental isotope parameters. The results were compared in an attempt to identify the presence of the surface water in the well water. Unfortunately the characteristics of the surface water were generally not different enough from the well water to determine if widespread anthropogenic contamination was occurring.

Anthropogenic contamination in recharge areas appears to be indicated by elevated nitrate concentrations in these areas. Anthropogenic contamination in the southern part of the valley (in the vicinity of Ramales Tecomitl, Tlahuac and Santa Catarina) was demonstrated by high ammonium concentrations and the presence of faecal coliforms in the groundwater. Although wells completed below the clay in the central part of the valley do not appear to be contaminated, we should not assume that the clay is impermeable and therefore offers complete protection from surface sources of contamination.

INTRODUCTION

Nitrogen compounds in the groundwater in the Valley of Mexico were studied to evaluate the possibility of contamination of the groundwater by surface wastewater. The study area consisted of the Valley of Mexico which is the area of lowest elevation in the Mexico Basin. The valley consists of a central clay plain roughly delineated by the 2 230 m.a.s.l. contour line (Figure 1). Groundwater is pumped from the alluvial aquifer which directly underlies the clay. Industrial and domestic wastewater is channeled through the city via a system of unlined canals to the main artery known as the Grand Canal. The water is then carried north of the city where a fraction of it is used to irrigate agricultural fields. The closing of water wells in the south-

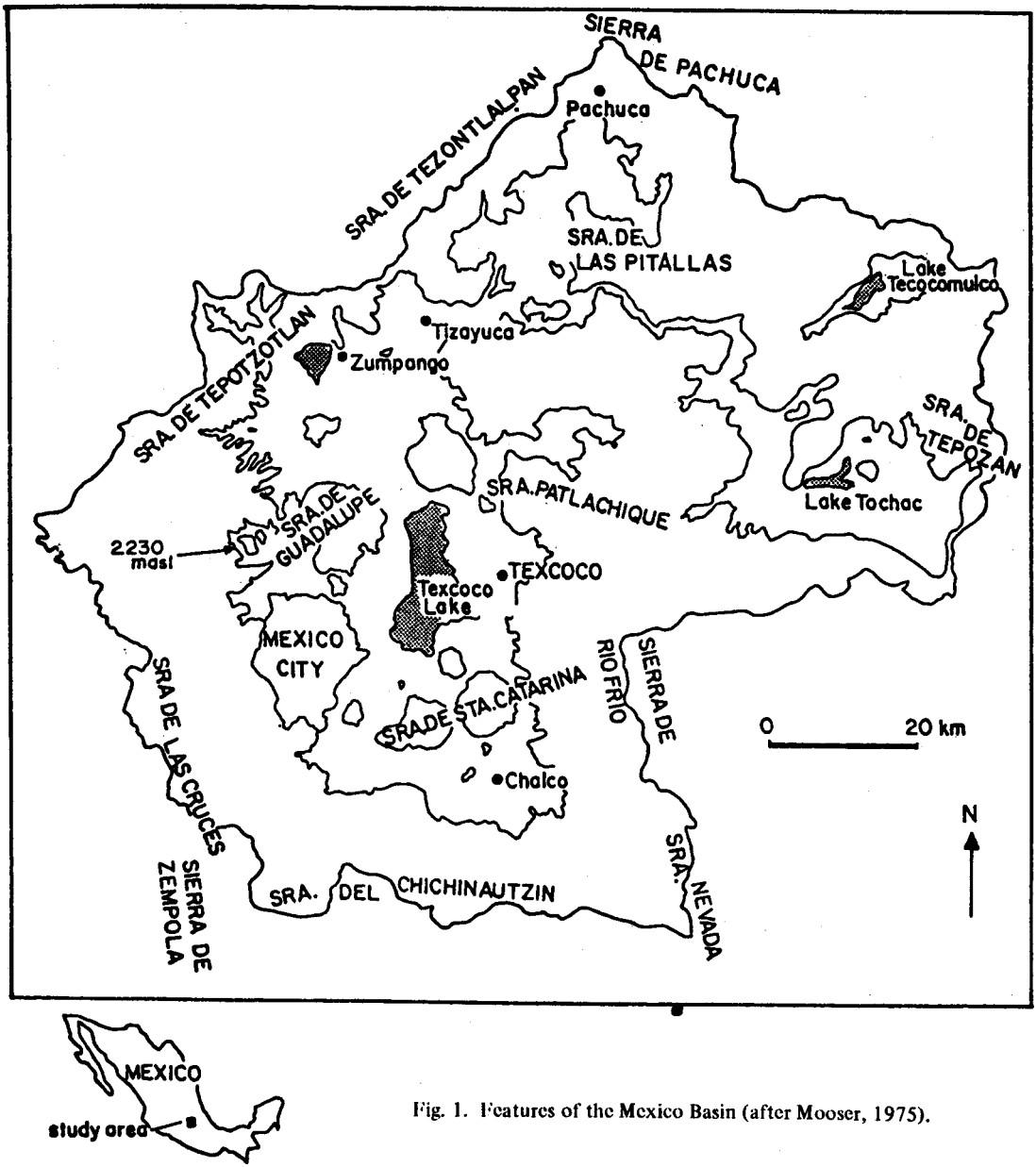

Fig. 1. Features of the Mexico Basin (after Mooser, 1975).

ern part of the valley due to high concentrations of ammonium indicated the potential for contamination of well water by the wastewater. In the past it has been assumed that the clay plain would act as a barrier to the infiltration of contaminated surface water.

The well groups studied were operating water wells located in lines or 'ramales' along right of ways such as railway lines and sewage canals. Figure 2 shows the location of the various ramales studied. The location of water wells along sewage canals presents a likely scenario for direct contamination of well water by wastewater moving as a consequence of induced recharge gradients.

Groundwater contamination from surface wastewater can only occur in areas with downward hydraulic gradients or in recharge areas. Important areas of recharge in the Valley of Mexico are comprised of the lower slopes of the mountains surrounding the clay plain (Figure 1). The rock units include the Tarango formation (deposited on the slopes of the Sierra de las Cruces), the basalts found in the Sierras de Chichinautzin, de Guadalupe and de Santa Catarina and the Tertiary volcanics of the Sierras Nevada and de las Cruces (González, 1983 and Thomson, 1987).

Recharge gradients in the clay plain itself can also be induced by heavy pumping of the groundwater from the underlying aquifer. Piezometric data measured by Rudolph (1989) indicate that downward gradients presently exist in the clay under a wastewater canal near Lake Texcoco. The site was located in an area of heavy pumping of saline groundwater.

As part of the present study, water samples were taken from water wells and surface water for geochemical and isotopic analyses. It was hoped that the wastewater would have a distinct geochemical or isotopic signature that would allow the recognition of any wastewater contribution to well water.

NITROGEN COMPOUNDS IN GROUNDWATER

The most common sources of nitrogen contamination reported in the literature are from agricultural activities or from human and animal wastes. The principal known risk of nitrogen compounds in drinking water is methaemoglobinaemia, a health hazard to young children. A drinking water limit of 10 mg/l of nitrate as elemental N is recommended by the World Health Organization.

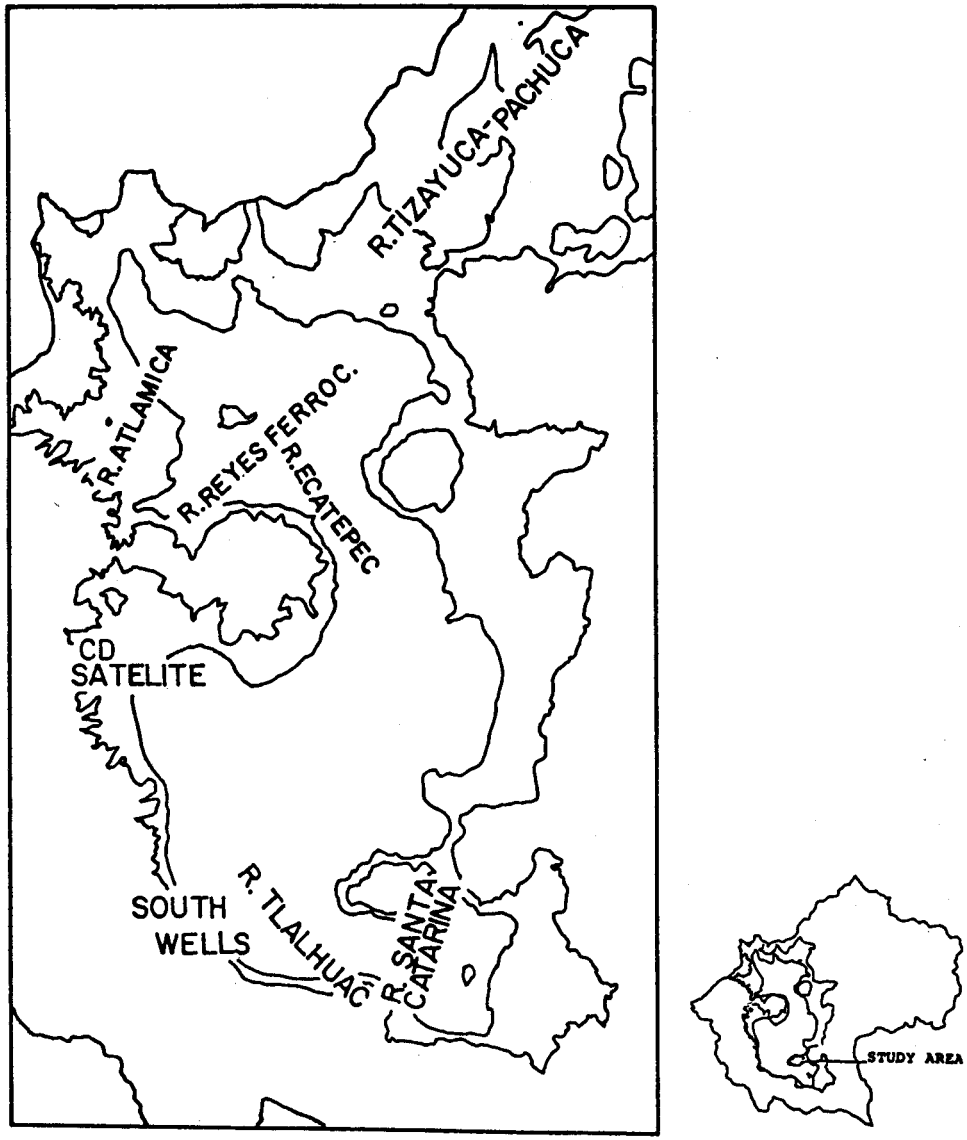

Fig. 2. Well groups available for sampling.

The natural generation of nitrogen compounds in groundwater also occurs and possible sources in the Valley of Mexico include diagenesis and volcanic activities. When decomposed organic material becomes incorporated into sediments as organic or inorganic nitrogen, it can be subsequently mineralized by microorganisms or fixed as ammonium (NH_4^+) by clay minerals, producing diagenetic nitrogen compounds. This process may produce relatively widespread nitrogen compounds throughout the deposit (Strathouse *et al.*, 1980). Volcanic activity usually produces nitrogen compounds in relatively isolated areas, for example, associated with fumarol deposits (White, 1957 a, b).

Four inorganic nitrogen compounds are commonly found in groundwater: nitrogen gas (N_2), nitrate (NO_3^-), nitrite (NO_2^-) and ammonium (NH_4^+). The type of nitrogen compound found in a specific groundwater environment varies according to factors such as the redox potential (or the tendency of the system to reduce or oxidize compounds in the system), the dissolved oxygen content of the water, the presence or lack of microorganisms which participate in transformation of one compound to another and the presence of a food source for these bacteria. Inorganic nitrogen in wastewater is generally in the reduced form of ammonium, which is strongly sorbed to aquifer materials and relatively immobile. A compound is said to be reduced if the oxidation state or valence of the element of interest is more negative than the valence of the same element in other compounds. Nitrogen has a valence of -5 in the ammonium form and valences of +3 and +5 in nitrite and nitrate respectively. Ammonium concentrations between 3.09 and 7.85 mg/l as N were measured in the wastewater.

The two major geochemical processes involving nitrogen that occur in groundwater are the redox reactions (or reactions that change the oxidation state of nitrogen) known as nitrification and denitrification. Nitrification is a process in which nitrogen is oxidized from ammonium to nitrite and then to nitrate. Nitrate is a relatively unstable compound and is usually transformed to nitrate. These transformations generally occur in the presence of dissolved oxygen and are mediated by specific microorganisms. Nitrate is relatively mobile in groundwater (Freeze and Cherry, 1979).

Denitrification is the transformation of nitrate to nitrogen gas (N_2) an innocuous form of nitrogen. It usually occurs in anaerobic environments and is also mediated by specific bacteria. Gillham and Cherry (1978) hypothesized that denitrification

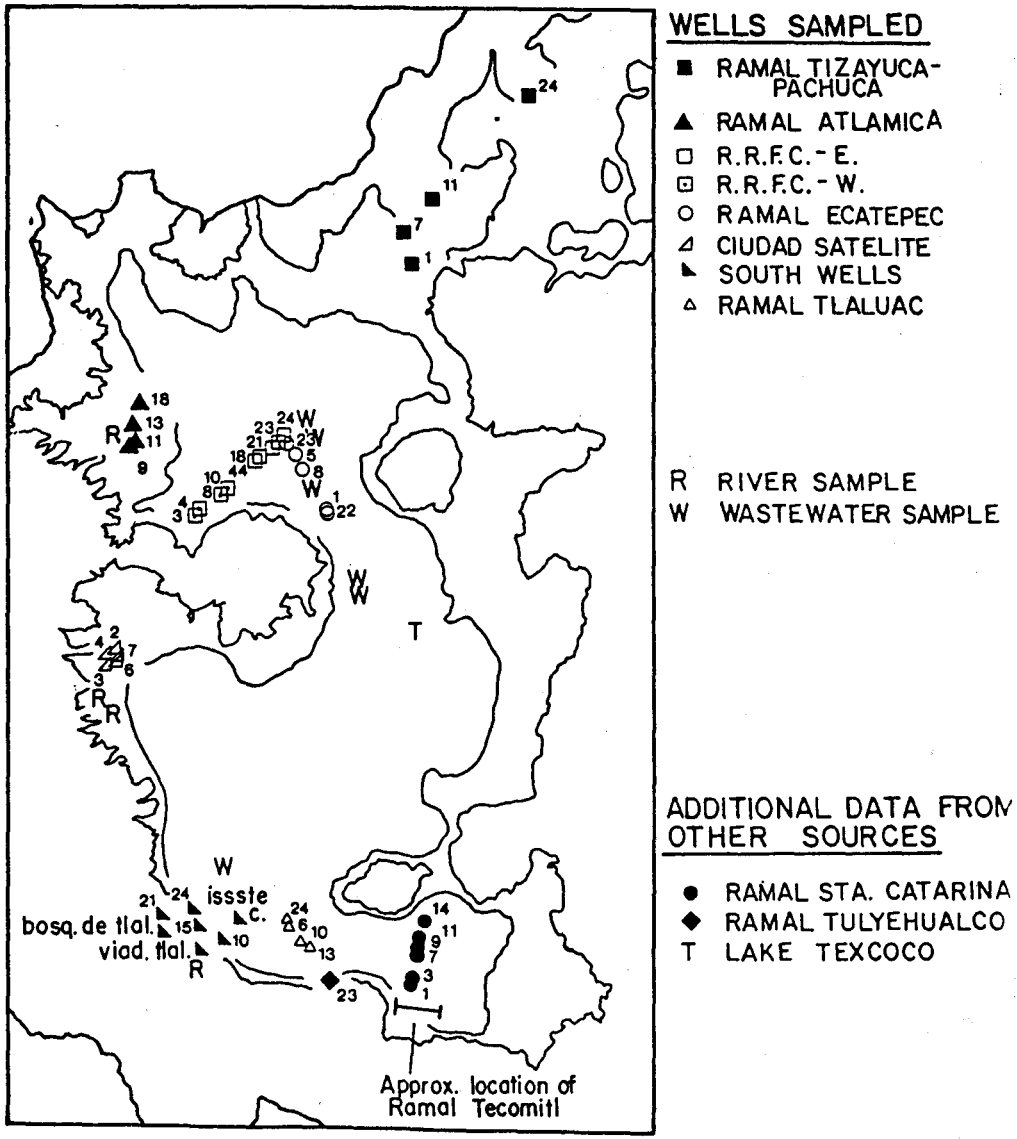

Fig. 3. Location of sampling points.

was occurring below the depth of groundwater oxygenation in aquifers in a small agricultural watershed in Ontario. High nitrate concentrations were found in the shallow groundwater where dissolved oxygen concentrations were commonly between 5 and 50 mg/l. At depths of 2 to 4 meters below the groundwater table low nitrate concentrations occurred and dissolved oxygen concentrations were generally less than 2 mg/l. Trudell *et al.* (1986) used an *in situ* sampler to observe and measure the rate of denitrification. The loss of nitrate was preceeded by a decline in dissolved oxygen (to less than 0.1 gm/m^3) and coincided with an increase in bicarbonate concentrations indicating that CO_2 concentrations had increased due to denitrification. Starr and Gillham (1988) observed that a source of labile organic carbon was necessary for denitrification to occur.

GROUNDWATER AND SURFACE WATER SAMPLING

Figure 3 shows the locations of the surface water and well water samples taken in the study. Well water samples were analysed for geochemical parameters, oxygen-18, deuterium and tritium. Surface waters were sampled for geochemical parameters, oxygen-18 and deuterium. Field measurements included temperature, conductivity, Eh and dissolved oxygen. Sampling methods and errors associated with the analyses are discussed in Ryan, 1987. Additional data for Ramales Sta. Catarina, Tulyehualco and Lake Texcoco were obtained from related studies at the Institute of Geophysics, UNAM.

Tritium

Before above ground nuclear testing was carried out in the 1950's and 1960's, background tritium concentrations in atmospheric precipitation in the northern hemisphere were much lower than present. During the period of atmospheric nuclear testing, tritium concentrations rose by several orders of magnitude (Freeze and Cherry, 1979). Detectable tritium concentrations (greater than 0.8 T.U.), indicating a component of 'modern' water (recharged after 1950) was found only in wells along the periphery of the clay plain as seen in Figure 4. This confirms that these are significant areas of recharge, and are susceptible to contamination by surface waters.

Oxygen-18 and Deuterium

Figure 5 shows the oxygen and hydrogen isotope data plotted on à ^{18}O versus

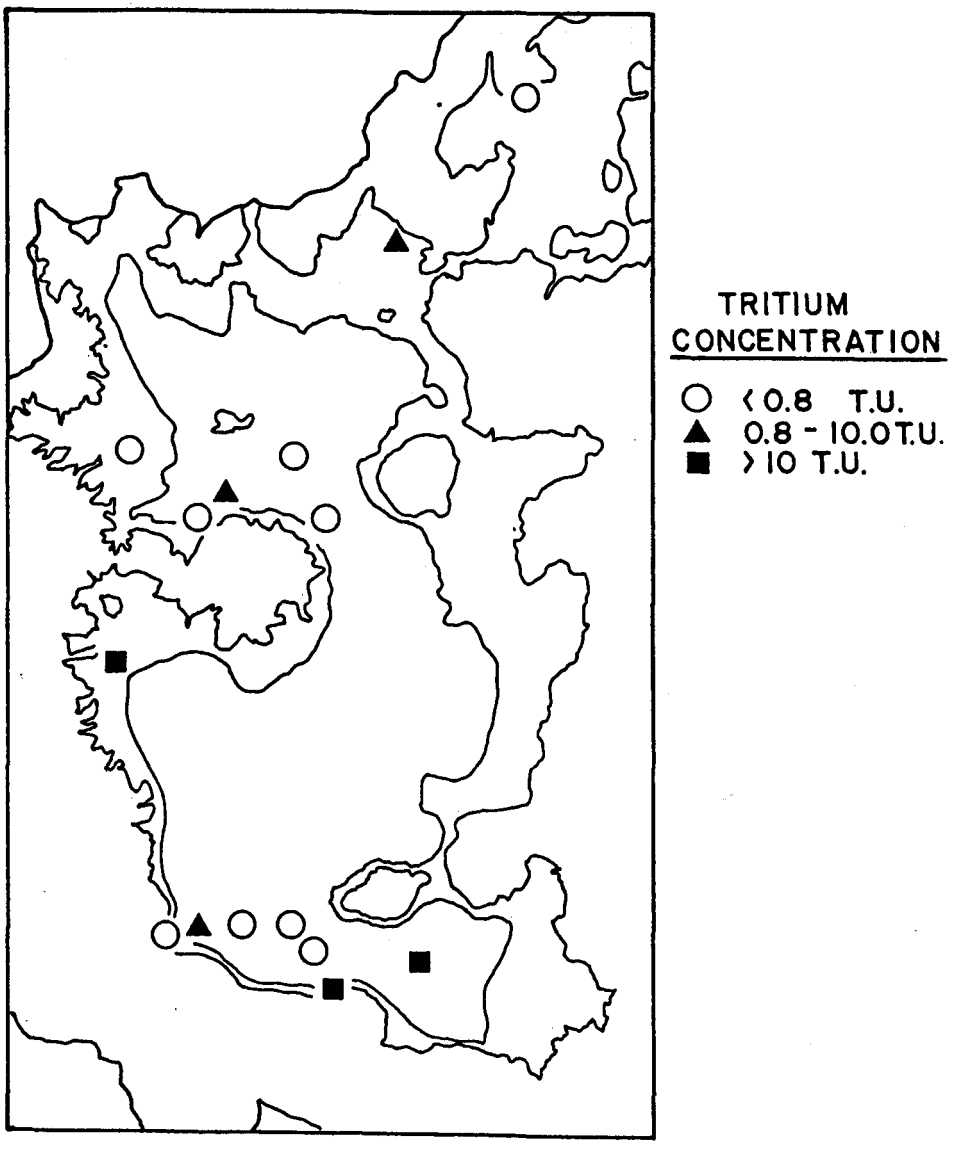

Fig. 4. Tritium concentration in water supply wells (T.U.)

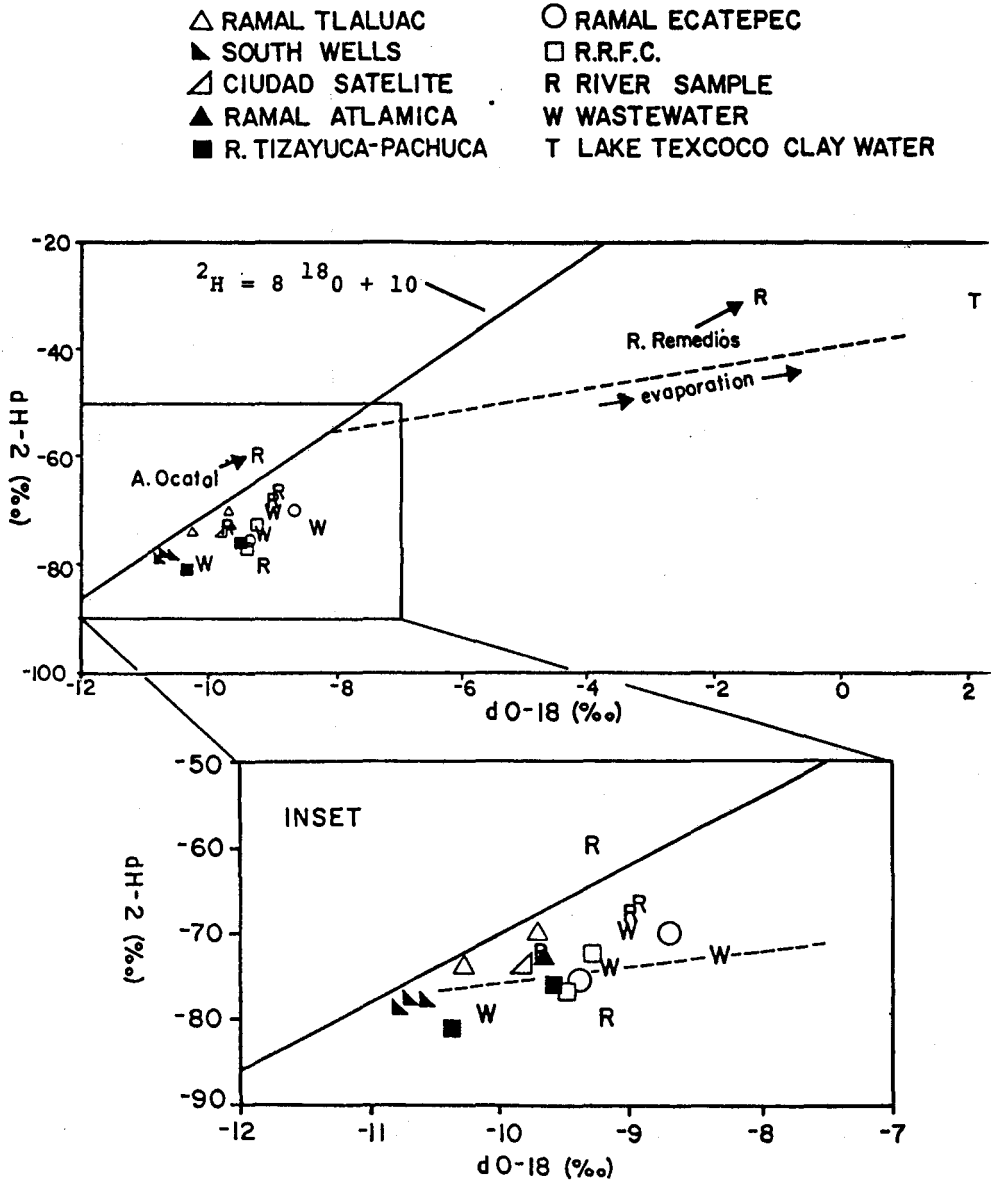

Fig. 5. Oxygen-18 versus deuterium

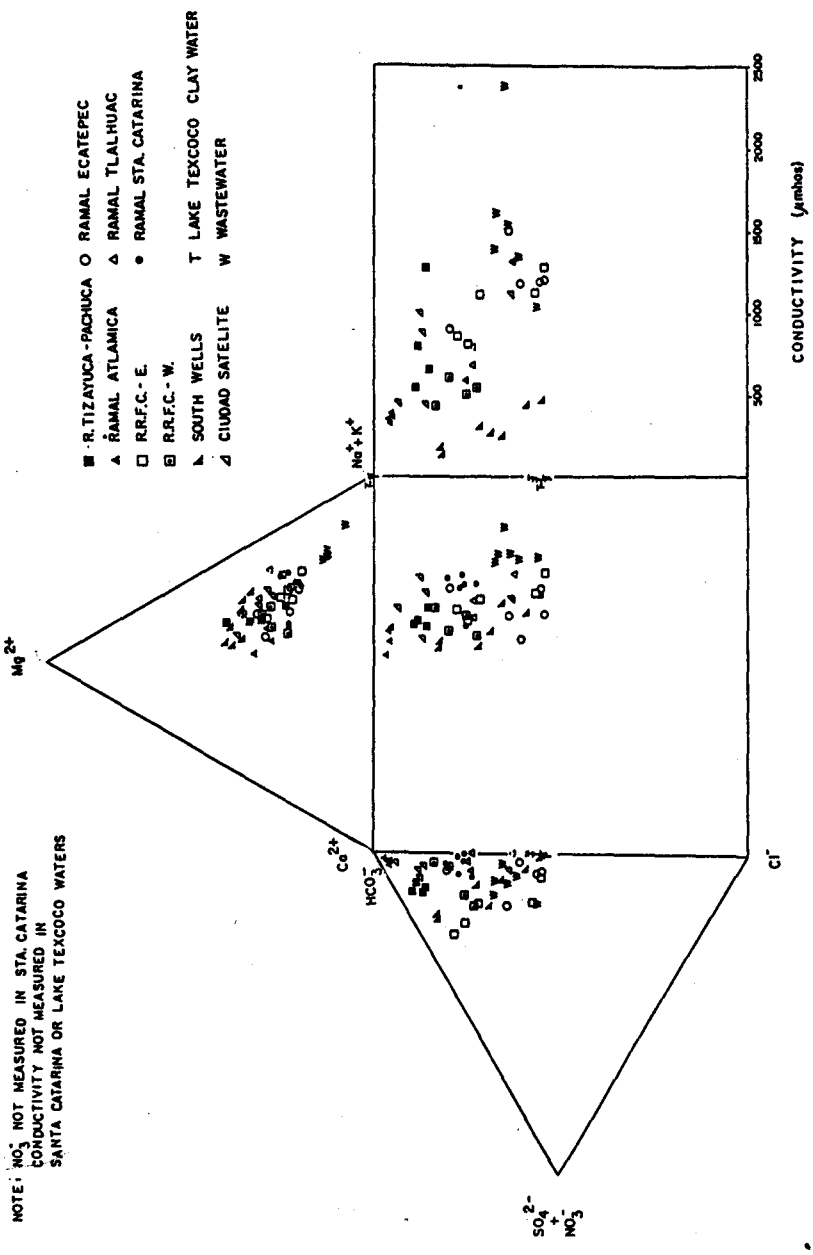

Fig. 6. Hydrochemical classification of groundwater using a modified form of the Durov diagram (in meq/1).

^{2}H graph along with the global meteoric water line (GMWL). Meteoric waters, or waters that have not undergone significant non-meteoric processes, usually plot close to the GMWL. On Figure 5 it can be seen that some water types are shifted further away from the GMWL than others. The most likely process that will change the oxygen-18 and deuterium values in the groundwater in the Valley of Mexico is evaporation. Water that has undergone evaporation is shifted to the right of the MWL along a line whose slope varies according to the humidity under which evaporation occurred (I.A.E.A., 1981).

Well water from principal recharge areas (such as the South Wells and Ramal Tlahuac) lie closest to the line, indicating that these waters have not been subjected to evaporation. The Río de los Remedios and Lake Texcoco samples represent the most highly evaporated waters. Wastewater and the remaining river waters are shifted further from the GMWL than most well waters, suggesting they have undergone the most evaporation. The remaining well waters appear to be intermediate between the recharge waters and surface waters in degree of evaporation.

Although the wastewater is somewhat distinct from the well water, it does not have a clear isotopic signature.

The evaporation shift seen in the isotope data may have been caused by several processes. Sediment interstitial water which was deposited with the aquifer sediments may have been subjected to evaporation during deposition. Alternatively, a component of evaporated water may have been drawn into the aquifer from the surface or from the overlying clay deposit (which is known to have highly evaporated water in some areas, such as the Lake Texcoco sample on Figure 5). Thus, although the wastewater generally shows a larger evaporation shift than the well waters, one cannot determine whether there is a component of wastewater in the well water.

Major ion geochemistry

The major ion geochemistry is shown in Figure 6 in the form of a modified Durov diagram (Howard, 1985). To construct a Durov diagram, the cation and anion positions are extended from the two trilinear plots to a new position on the central square. Conductivity values are also projected on a scale extending to the right of the central square. The diagram is used to classify geochemical groups of groundwaters. Water that results from the mixing of two waters will fall on a line between

the two parent waters on any section of the diagram.

The data show two end members, one represented by low conductivity, Ca, Mg-HCO_3 rich waters found in the South Wells and the other by Mg-HCO_3-Cl-rich waters with increasing conductivities (such as Lake Texcoco, wastewater and Ramal Santa Catarina).

As in the isotope investigations, the wastewater does appear geochemically distinct from the well water, although an unambiguous geochemical signature was not found. Part of the geochemical similarity between the wastewater and well water is surely due to a large contribution of well water in the wastewater (*i.e.* well water is distributed to domestic and industrial users and the same water is later discharged as wastewater). The geochemical trend from Ca, Mg-HCO_3-rich water to Mg-HCO_3-Cl-rich waters may be due to natural groundwater evolution along a flow path. It might also be due to mixing of the aquifer water with infiltrated surface water or with interstitial clay water drawn into the aquifer by pumping.

Nitrate

Figure 7 shows the nitrate concentrations found in well water. The highest concentrations were found along the periphery of the clay plain, generally in recharge areas. This is a strong indication that anthropogenic contamination of these wells is occurring.

It does not appear that widespread nitrate contamination exists in the Central Clay plain. Nitrate may not be present in the other areas of the valley because it never existed in significant quantities or because widespread denitrification has occurred. Further investigations are necessary to determine which of these two cases apply.

The pattern of elevated nitrate concentrations in recharge areas, however, is a strong indication that anthropogenic contamination may be occurring in these areas.

Ammonium

Low levels of ammonium were found in Ramales Atlamica, Reyes, Ferrocarril, Ecatepec and Satélite (Figure 8). Higher levels were detected in Ramal Tlahuac. The

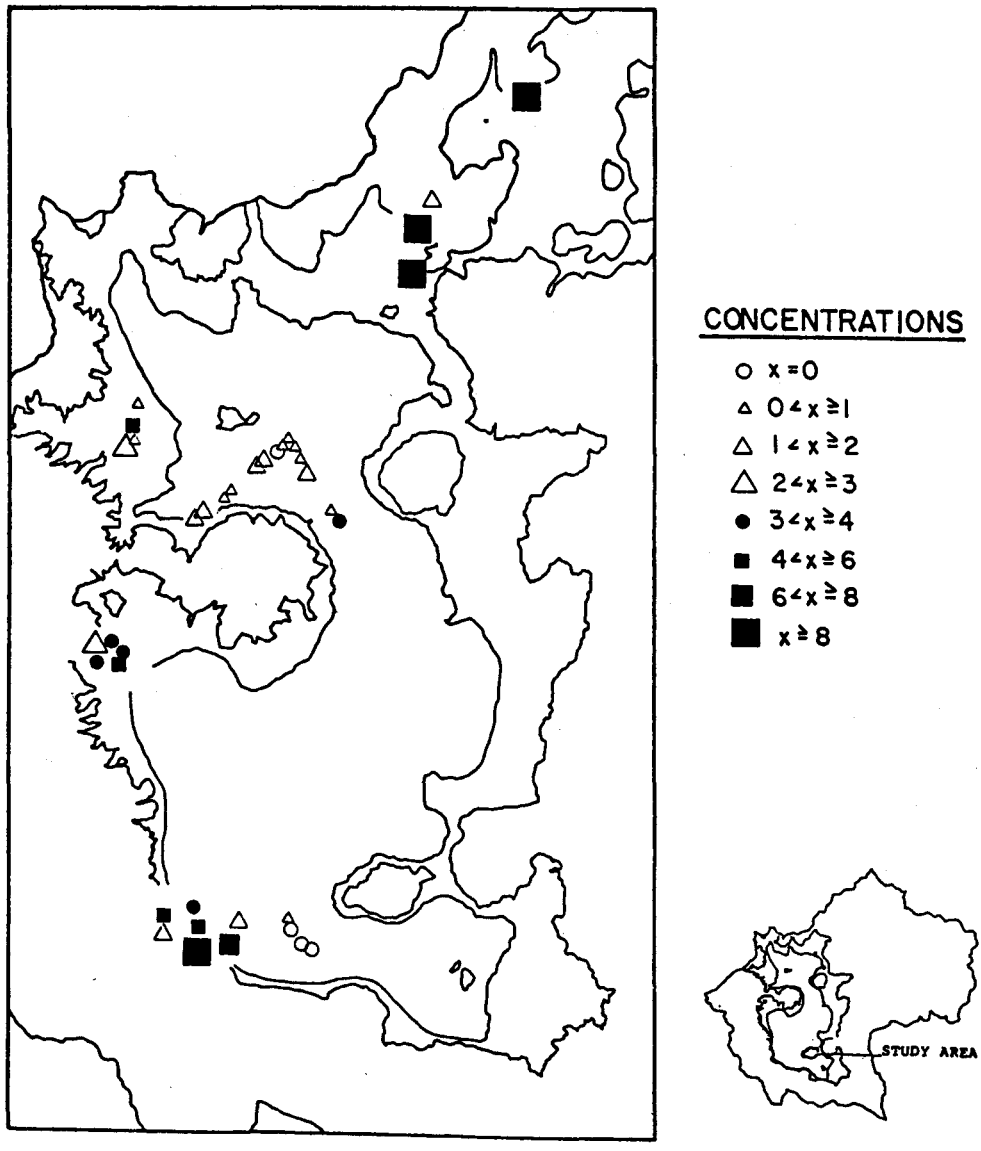

Fig. 7. Nitrate concentrations in water supply wells (mg/1 as N).

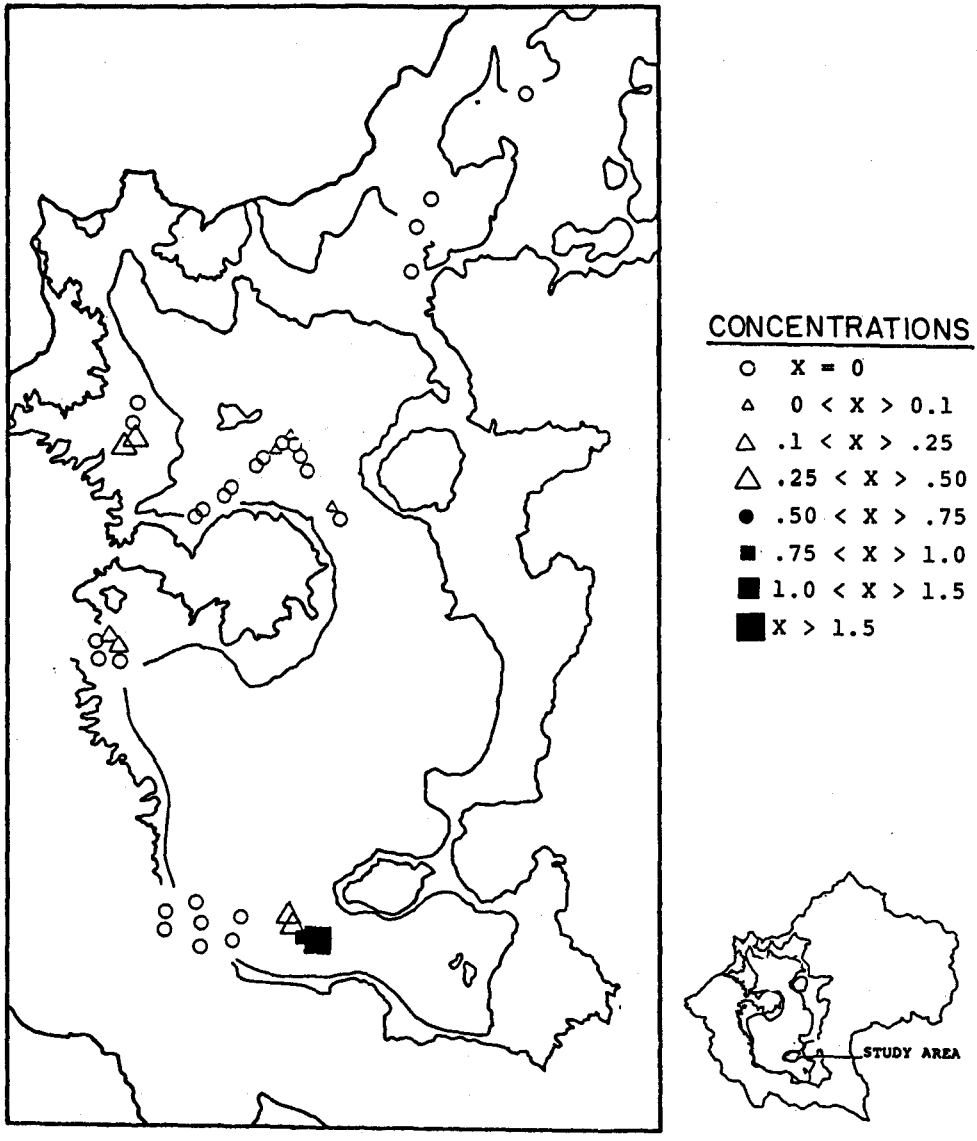

Fig. 8. Ammonium concentrations in water supply wells (mg/l as N).

field analyses (Eh and dissolved oxygen) indicated that reducing conditions prevailed in the Ramal Tlahuac area.

Additional data provided by C. Cruikshank (Institute of Engineering, UNAM) show significant ammonium concentrations (up to 13.5 mg/l as N) were found in Ramal Tecomitl. Three of the Tecomitl wells also tested positive for faecal coliforms which are associated with human and animal wastes. This ramal is in the same vicinity as Ramales Tlahuac and Sta. Catarina. A clear zone of contamination is demonstrated in the southern part of the valley where these ramales are located.

CONCLUSIONS

Wastewater was shown to be geochemically and isotopically related to, but not distinct, from the groundwater pumped from the Valley of Mexico. The occurrence of widespread anthropogenic contamination of well water by wastewater was not clearly demonstrated by the comparison of the geochemical and isotopic characteristics of the two waters.

High nitrate concentrations were found predominantly in recharge areas, suggesting anthropogenic contamination of groundwater in these areas. High ammonium concentrations and the presence of faecal coliforms in the southern part of the valley show anthropogenic contamination is certainly occurring in this area.

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