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**ABSTRACT:** Wastewater from the city of León, Mexico, has been used for irrigation of agricultural land close to the city for the last 40 years. The wastewater contains a significant percentage of industrial effluent from the extensive tanning industry, including high concentrations of salt and hexavalent chromium compounds, and is used untreated. The irrigated area overlies an aquifer which provides an important part of the municipal water supply. Infiltration of the irrigated water has led to the formation of a localised layer of shallow, poor-quality water above the regional aquifer. Investigation has shown changes in the quality of the infiltrating wastewater as it passes through the soil and shallow aquifer layers. These significantly reduce the concentrations of chromium, sodium, sulphate and nitrogen. However, high chloride concentrations remain to pose an immediate threat to groundwater quality in the lower part of the aquifer and chloride concentrations in groundwater from some deep municipal supply boreholes are now rising rapidly.

## 1 INTRODUCTION

The city of Leon in Guanajuato State, is situated in a wide upland valley at an altitude of 1800 m, about 500 km north of Mexico City. It has one of the fastest growing populations in Mexico, which is highly dependent on groundwater resources for public water supply. The climate is semi-arid, so there is also a heavy dependence on irrigation for agricultural crops. Groundwater is drawn from a complex aquifer system in the alluvial valley fill downstream of the city, including areas which have been subjected to wastewater reuse for agricultural irrigation for up to 40 years (Figure 1).

Wastewater generated in the city is highly polluted due to effluent derived from the prominent leather processing and shoe manufacturing industry. Several of the leather manufacturing processes give rise to highly polluting effluents. Sodium chloride, used to preserve hides before tanning, and hexavalent chromium are of particular concern here. The effluents are combined with domestic wastewater via sewers which feed into a series of open canals carrying the wastewater directly into the irrigation area. The subsequent distribution system is complex and subject to change depending on operational requirements. There are two large, dammed, settlement lagoons, but only a fraction of the water passes through the first of these holding lagoons before being applied directly to

crops, mainly by flood irrigation. The second lagoon is further downstream and only intercepts water which has already passed through the study area. Infiltration of excess irrigated wastewater is sustaining a shallow groundwater body beneath the wastewater area, superimposed on rapidly declining regional groundwater levels.

This chemical study forms part of a wider project whose overall objective was to determine the effects of wastewater reuse on groundwater resources including quantity, quality and management issues (Chilton et al., 1997). As part of this aim, a regular programme of quality monitoring of both deep and shallow groundwater was established, surface geophysical techniques were employed to estimate the depth of penetration and lateral extent of poor quality water and both soil profiling and the drilling of cored observation wells were used to investigate the vertical dimension of groundwater quality variation. A more detailed description of the procedures used is provided in BGS et al. (1996). This paper is concerned with describing the observed chemical behaviour of the wastewater and the consequent effects on and implications for groundwater quality.

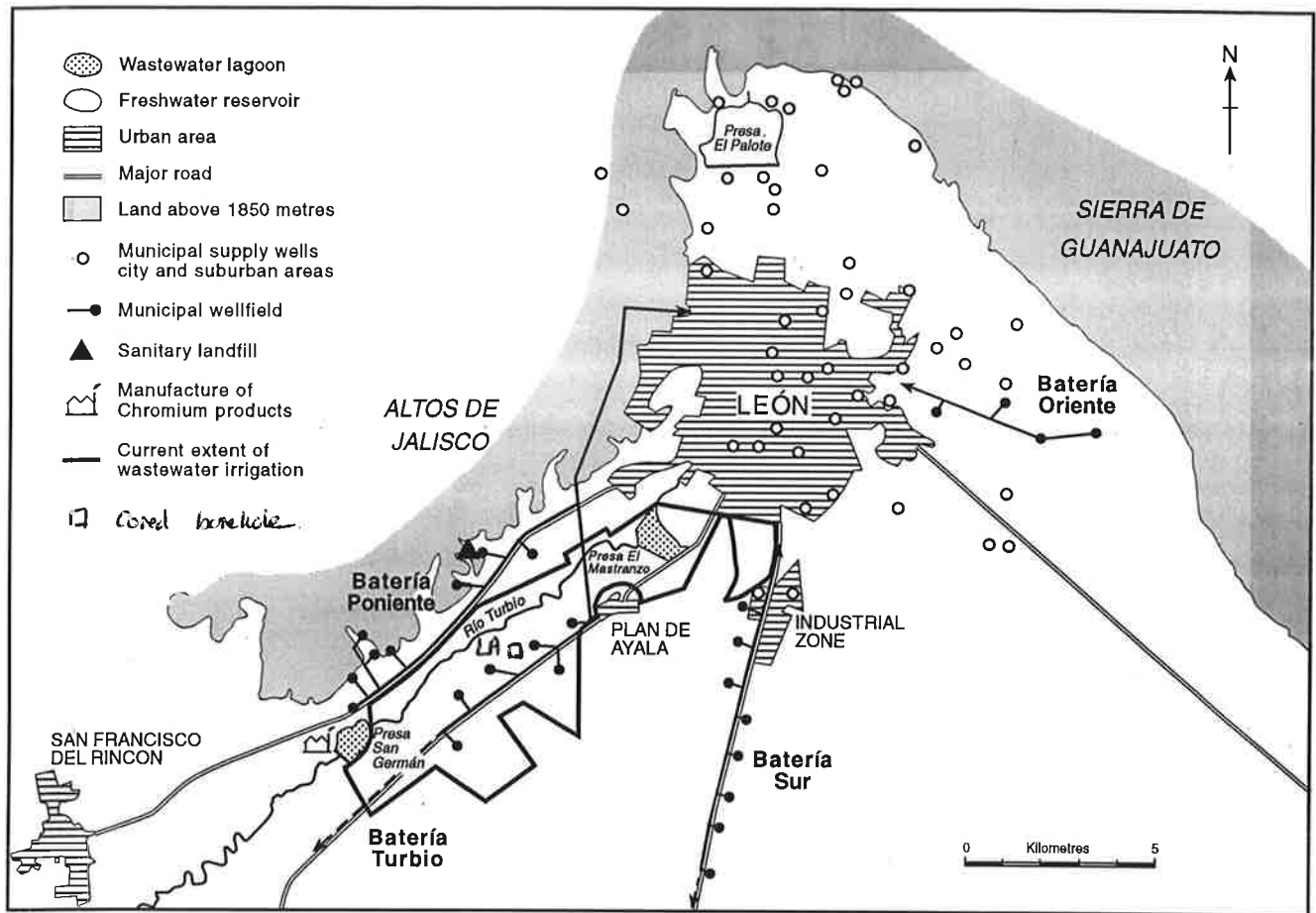


Figure 1. Location map showing wastewater irrigation area and municipal well fields.

## 2 PROCESSES IN THE DISTRIBUTION SYSTEM AND SHALLOW SOILS

Wastewater samples were collected as part of the regular monitoring programme at a series of points in the wastewater distribution system. A summary of the typical analyses is presented in Table 1. The dilution of the tannery effluents by other industrial and domestic waste during progression through the system can be clearly seen. It is also clear, from comparison of the quality of the collector canals and the lagoon outfall, that the lagoons act as highly efficient chromium removal sinks.

Soil core samples were taken from sites with a range of irrigation histories including: former settlement lagoon beds; fields irrigated with water from different wastewater sources; and fields irrigated with wastewater over different timescales. Control samples were obtained from fields which had never been irrigated with wastewater. Sampling of sediments from active storage lagoons was impractical for reasons of safety and hygiene. At each site, simple sub-sampling and field averaging procedures were used to try to improve the representativeness of samples. The final composited samples were analyzed for chromium and other heavy metals using a dilute nitric acid extraction and ICP-OES.

The analytical results provide clear evidence that chromium is accumulating in the soils affected by wastewater irrigation. All sites which have been exposed to varying durations of wastewater irrigation had extractable chromium contents at least one order of magnitude higher than unexposed samples. The degree of accumulation is related to the total period of irrigation although it must be remembered that the accelerating expansion of industry will not give rise to a constant accumulation rate. The variation in other heavy metals, such as Zn, Cu and Pb is not so pronounced, but elevated concentrations are still associated with the use of wastewater.

The soil analyses also confirm the picture of metal accumulation in lagoon sediments, evidenced by the very high concentrations in the sediment from the former (now disused) lagoon at Presa Blanca.

There is unequivocal evidence of decrease of metal concentrations with depth, particularly for chromium. At all sites the major fraction of chromium is contained within the top 0.3 m of the profile. Below 0.6 m concentrations are at, or close to, background concentrations, even at those sites which have the highest concentrations in the uppermost horizons (Figure 2). This pattern agrees well with other studies reported in the literature (McGrath, 1995).

Table 1. Typical values of key water quality parameters at the different stages of the wastewater distribution system.

Water type	Total Cr (mg/l)	Total N (mg/l)	Chemical oxygen demand (mg/l)	Conductivity ( $\mu\text{S/cm}$ )	pH
Tannery discharge	200	400	-	20000	8.0
Industrial collector	40	240	5000	9000	9.0
Domestic collector	20	100	1000	3500	8.4
River Turbio	4-29	50	250	1800	8.3
Lagoon exits	0.1-0.4	40-80	170-350	2000-2300	8.3
Irrigation canal	0.06	40	200	1200	7.9
Shallow polluted groundwater	0.002-0.005	2-14 (as $\text{NO}_3$ )	10-60	2700	6.7
Regional background quality	0.002-0.005	0-2 (as $\text{NO}_3$ )	0-4	480	7.2

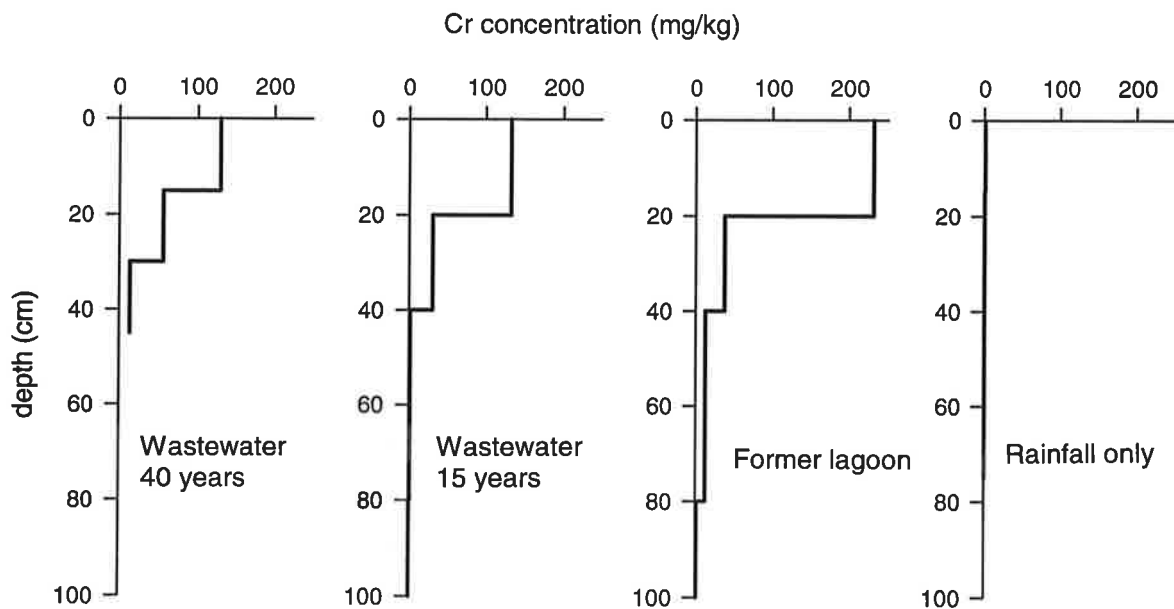


Figure 2. Chromium profiles in soils with different irrigation histories.

The data in Table 1 also show considerable improvements in the concentrations of nitrogen and organic carbon within the lagoons. The nitrogen loading may be reduced by degradation of organic nitrogen directly to ammonia, which is then volatilized, or by denitrification of inorganic nitrate to nitrogen gas in the anaerobic bottom sediments of the lagoons and canals. Soil under continuous alfalfa cover and receiving large quantities of organic matter in wastewater is also likely to remain anaerobic for much of the irrigation cycle. Ammonia may be leached from the soil, but is not very mobile. Organic matter in the wastewater is more likely to be oxidised to carbon dioxide or bicarbonate in the shallow groundwater which tends to remain slightly aerobic.

### 3 CHEMICAL PROCESSES IN THE AQUIFER

Regional groundwater quality is generally very good, consistent with meteoric water in a volcanic aquifer. The waters are of mixed calcium/sodium type (see Figure 3) with low concentrations of chloride and sulphate and the unpolluted waters have significant concentrations of dissolved oxygen, even at depth. This low level of background mineralization makes the impact of infiltrating wastewater readily distinguishable. Within the area of wastewater reuse all of the relatively shallow private irrigation wells which were sampled have a distinctive and characteristic major ion chemistry. Samples from within the wastewater area are found in the upper

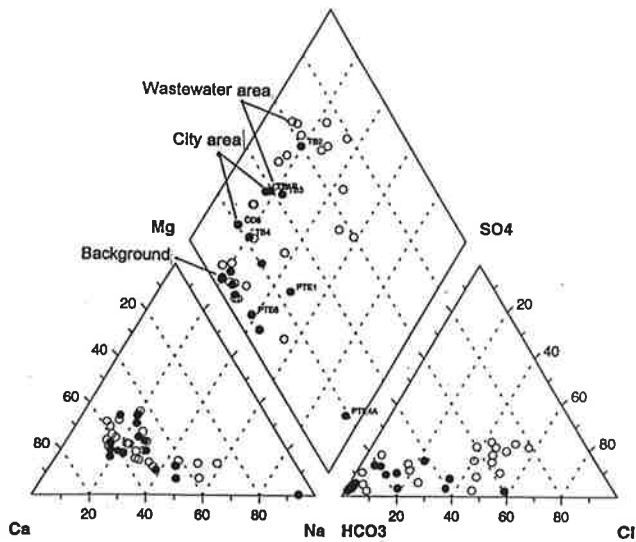


Figure 3. Piper trilinear diagram showing the impact of wastewater infiltration on groundwater

portion of the trilinear plot in Fig. 3, reflecting their higher proportion of chloride. Samples from the deep municipal supply boreholes located within the wastewater area are also found in this part of the diagram.

The infiltrating wastewater undergoes a sequence of chemical changes in the shallow layers of the aquifer. These are illustrated by a depth profile of porewater from borehole LA drilled in the wastewater area (Figure 4). There are heavy evaporation losses during the irrigation process so that porewaters in the unsaturated zone have about double the concentrations of major ions of the original wastewater. Oxidation of organic matter to bicarbonate leads to cation

dissolution from the aquifer matrix. This process combined with cation exchange results in the replacement of the majority of the sodium in the original water by calcium. The sodium concentration falls rapidly from 600-800 mg/l at the surface to below 100 mg/l by 25 m, with a corresponding rise in calcium to 400 mg/l. Cation exchange sites are thought to occur on clay particles of the aquifer matrix and to contain significant amounts of calcium and magnesium. Sulphate concentrations also decline over the interval 20-35 m. This is likely to be related to the increase in calcium concentration allowing the precipitation of gypsum.

Assuming that chloride ions are conservative, the decline in concentration indicates dilution of the infiltration by better quality residual water, throughflow from beneath the city or recharge from the valley sides. Below 35 m no further changes in the relative ratios of the major ions are seen. Nitrate concentrations remain relatively modest, in the range 2-14 mg/l (as N).

The other two boreholes showed a similar pattern, although less clearly, but no simple relationship between history of irrigation and depth of penetration of poor quality water could be observed. This was due to the highly variable nature of the deposits forming the aquifer and the local impact on hydraulic conditions of high discharge pumping.

Shallow wells in the wastewater retain higher concentrations of heavy metals other than chromium compared to background levels, although these are well below potable limits. Trace of uranium are also seen. These are thought to be derived from mobilisation of disseminated uranium in the aquifer matrix by infiltrating bicarbonate.

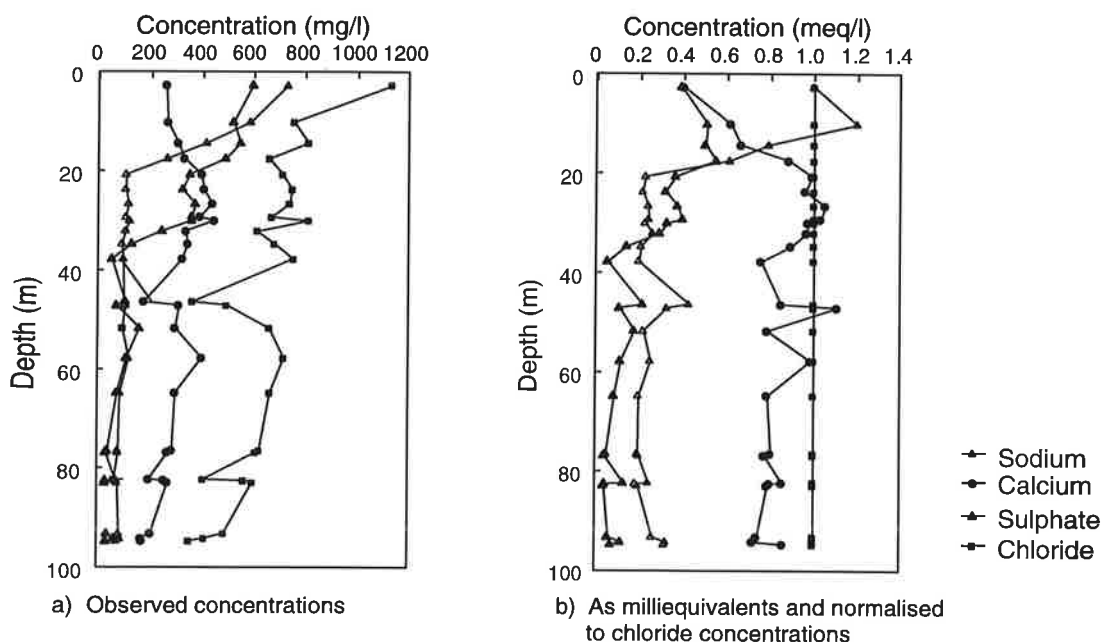


Figure 4. Profiles of porewater chemistry for borehole LA.

#### 4 TIMESCALE OF WATER QUALITY CHANGES

Shallow wells close to one of the most recently developed areas of wastewater reuse have shown a dramatic increase in all major ions since 1986. The areal extent of shallow aquifer contamination is demonstrated by comparison of the regional chloride concentrations in 1984 and 1994. Elevated concentrations of chloride in groundwater have spread south-eastwards down the river valley away from the city (Figure 5).

More seriously, municipal boreholes situated within the wastewater area are now showing a rapid deterioration in quality. These draw water from the lower part of the aquifer sequence and are screened

from 200 to 400 m. The rate of increase of chloride concentration is currently approximately 40 mg/l/a and chloride is likely to exceed the national standard for drinking water (250 mg/l) in the worst affected borehole (TB2) very soon (Figure 6).

#### 5 IMPLICATIONS

The results indicate that to date salt has been the most mobile of the pollutants originating in the applied wastewater. The pollutant loadings of metals, organic carbon and pathogens appear unlikely to penetrate through the thick aquifer system to deep abstraction boreholes. For the municipal water undertaking the

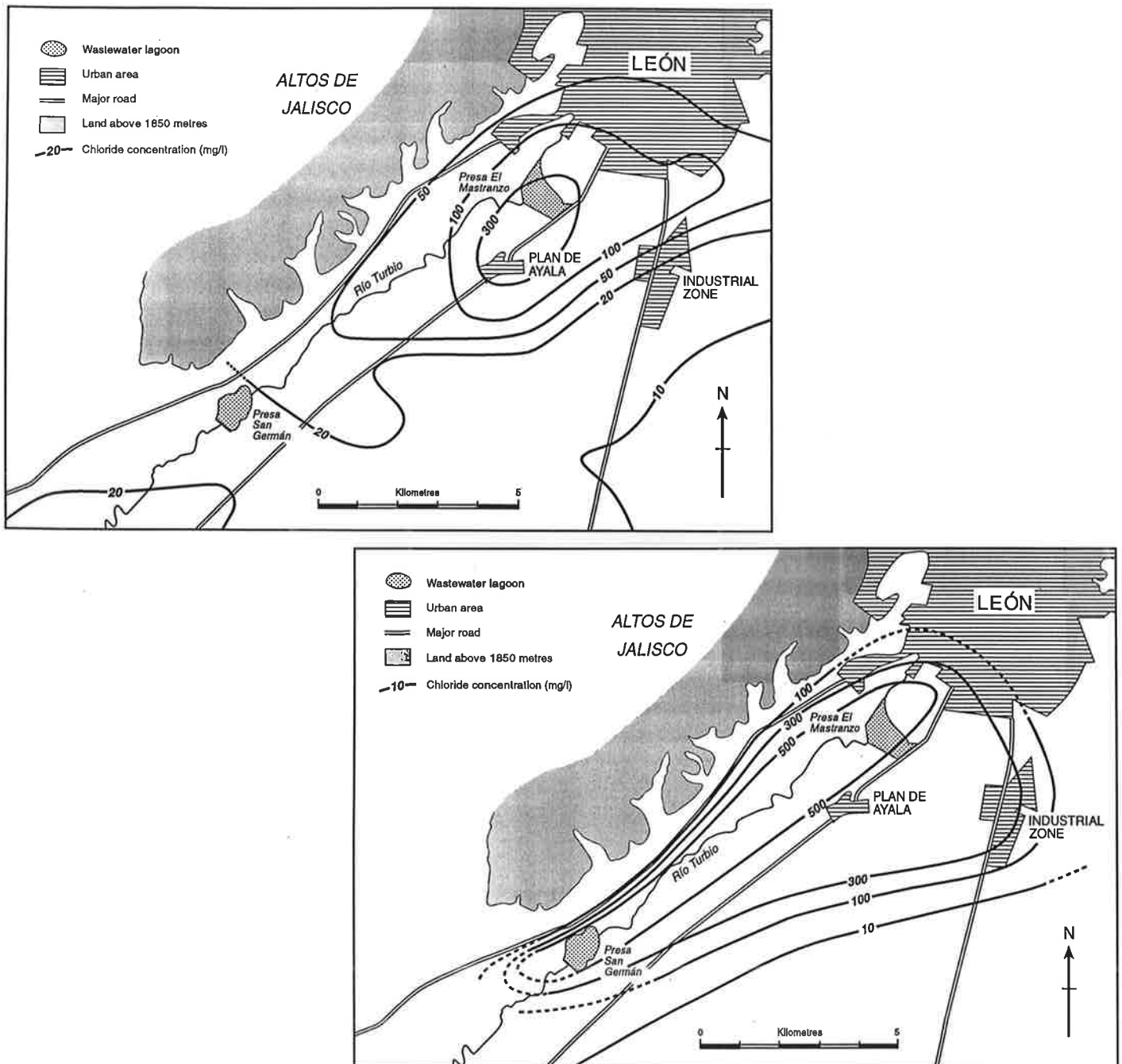


Figure 5. Change in groundwater chloride concentration contours between a) 1986 and b) 1994.

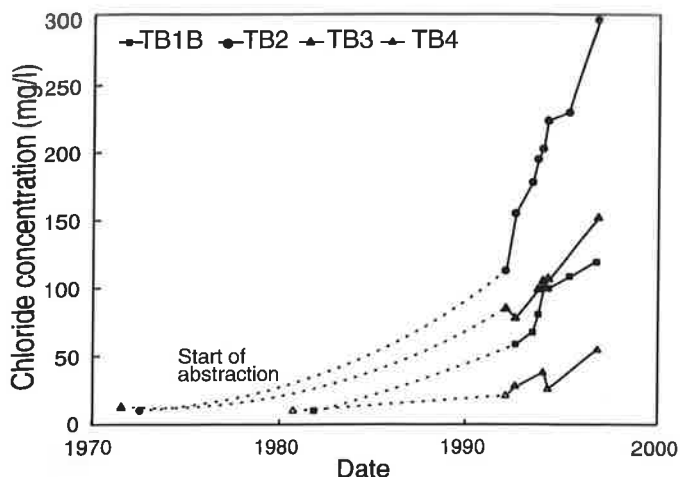


Figure 6. Progressively increasing chloride concentrations in groundwaters from municipal supply boreholes of the Bateria Turbio in the wastewater area.

most pressing issue in relation to the security of potable supplies is therefore the future trend in salinity in the wellfields closest to the wastewater area. These currently supply some 16% of the city's water. A modelled projection of water quality over the next 30 years under the present regime shows that quality in the upper part of the aquifer will continue to deteriorate and the salinity will rise to values approaching those of the infiltrating water.

Consideration of a number of options available to tackle this problem suggests that the most important is to implement separate collection and disposal of industrial effluents, the major source of salinity. Other measures such as increased abstraction from the shallow aquifer and improved irrigation efficiency will also lead to long term amelioration of deep water quality.

#### ACKNOWLEDGEMENTS

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#### REFERENCES

- British Geological Survey, Comision Nacional del Agua, Sistema de Agua Potable y Alcantarillado del Municipio del León & Universidad Autónoma de Chihuahua 1996. Effects of wastewater reuse on urban groundwater resources of Leon, Mexico. *British Geological Survey Technical Report WD/95/64*.
- Chilton, P.J., Stuart, M.E., Osclero, O., Marks, R.J., Gonzalez, A. and Milne C.J. 1997. Groundwater recharge and pollutant transport beneath wastewater irrigation: the case of León, Mexico. *Geol. Soc. Spec. Pub: Groundwater pollution, aquifer recharge and vulnerability*. In press
- McGrath, S. P. 1995. Chromium and nickel. In B. J. Alloway (ed), *Heavy metals in soils*. Blackie.