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Potential groundwater contamination by organic compounds in the Mexico City metropolitan area

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UNIVERSITY OF CALIFORNIA

Los Angeles

Potential Groundwater Contamination by Organic Compounds in the Mexico City Metropolitan Area

A dissertation submitted in partial satisfaction
of the requirements for the degree
Doctor of Environmental Science and Engineering

by

Marisa Mazari Hiriart

1992

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Cl^-	chloride
f_{oc}	fraction of organic carbon
f_{om}	fraction of organic matter
^3H	tritium
K_d	distribution coefficient
K_{oc}	organic carbon sorption coefficient
LC_{50}	lethal concentration, 50% mortality point
V_T	total volume of the sample
V_V	volume of the voids
W_s	weight of dry soil
W_{mw}	weight of flask + water
W_{mws}	weight of flask + water + sample
ρ_b	bulk density
ρ_s	solid density
θ	porosity
θ_w	volumetric moisture content

Abbreviations

ABS	alkyl aryl sulfonate
APHA	American Public Health Association
API	American Petroleum Institute

BOD	biochemical oxygen demand
CAE	Consejo Asesor en Epidemiología
CAVM	Comisión de Aguas del Valle de México
CFE	Comisión Federal de Electricidad
CNA	Comisión Nacional del Agua
CNS	central nervous system
COD	chemical oxygen demand
CONACYT	Consejo Nacional de Ciencia y Tecnología
CPEUM	Constitución Política de los Estados Unidos Mexicanos
CTET	carbon tetrachloride
DCA	1,1-dichloroethane
1,2- DCA	1,2-dichloroethane
DCE	1,1-dichloroethylene
1,2-DCE	1,2-dichloroethylene
DCM	dichloromethane
DDF	Departamento del Distrito Federal
D.F.	Distrito Federal
DGCOH	Dirección General de Construcción y Operación Hidráulica
DNAPLs	dense nonaqueous phase liquids
DOF	Diario Oficial de la Federación
ECD	electron capture detector

GC	Gran Canal del Desagüe or Gran Canal
GC	gas chromatograph
GC/ECD	gas chromatograph with electron capture detector
HPLC/FL	high performance liquid chromatography with fluorescence detection
INEGI	Instituto Nacional de Estadística Geografía e Informática
LAS	linear alkyl aryl sulfonate
LFA	Ley Federal de Aguas
LGS	Ley General de Salud
LNAPLs	light nonaqueous phase liquids
MBAS	methylene blue active substances
MCMA	Mexico City Metropolitan Area
MDL	method detection limit
NaLS	sodium dodecyl sulfate
NAPLs	nonaqueous phase liquids
NRC	National Research Council
NWRI	National Water Research Institute
OTA	Office of Technology Assessment
PCB	Polychlorinated biphenyls
PCE	perchloroethylene or tetrachloroethylene
PEMEX	Petróleos Mexicanos
R	retardation factor

RR	Río de los Remedios or Rio Remedios
SARH	Secretaría de Agricultura y Recursos Hidráulicos
S.D.	standard deviation
SEDESOL	Secretaría de Desarrollo Social
SEDUE	Secretaría de Desarrollo Urbano y Ecología
SS	Secretaría de Salud
TCA	1,1,1-trichloroethane
TCE	trichloroethylene
TOC	total organic carbon
UCLA	University of California, Los Angeles
UC MEXUS	Consortium UC MEXUS
UNAM	Universidad Nacional Autónoma de México
US	Urban Site
U.S. EPA	United States Environmental Protection Agency
UW	University of Waterloo
VOCs or VOC	volatile organic compounds

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ABSTRACT OF THE DISSERTATION

Potential Groundwater Contamination by Organic Compounds in the Mexico City Metropolitan Area

by

Marisa Mazari Hiriart
Doctor of Environmental Science and Engineering
University of California, Los Angeles, 1992
Professor Douglas M. Mackay, Co-Chair
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Mexico City derives 75% of its water supply from an aquifer system that underlies the metropolitan area. A surficial clay aquitard has been presumed to prevent downward migration of contaminants to the underlying groundwater, but data to prove or refute this have not been available.

In this research, potential routes of contaminants were identified considering hydrogeological characteristics and location of contaminant sources. One route, downward migration of contaminants from the unlined sewer canals, was investigated in a field study. Core samples from the clay aquitard were collected adjacent to two canals and from a nearby urban area. Physical characteristics of the surface soil and clay were determined. Pore water samples were obtained by squeezing the clays in a stainless steel squeezer. Pore water samples were analyzed for two classes of organic contaminants: 1) anionic surfactants and 2) halogenated organic volatile compounds (VOCs). Canal water from a one-day sampling was analyzed for qualitative comparison with pore water.

The field study indicates that anionic surfactants and certain VOCs have penetrated downwards into the clay aquitard. Although the measured concentrations are low and the penetration distances shallow, the results are significant since the observed migration is considerably farther than predicted for a homogeneous clay formation. Similar evidence for inorganic chemicals obtained by colleagues in this collaborative study (C. Pitre and D. Rudolph, University of Waterloo), suggests that the migration is dominated by flow in fractures within the clay. While the contaminant concentrations and migration distances observed at one site do not currently appear to present an immediate threat to the underiying groundwater, the situation is likely to worsen since migration rate of contaminants is likely to increase with time and may become significant. There are many other areas in the metropolitan area where contaminant sources and downward migration rates are likely to be much more significant. It is recommended that monitoring and other field studies be conducted at the sites most vulnerable to contaminant infiltration, several of which are identified in this work.

Chapter 1

Introduction

General

Groundwater is a heavily used resource (NRC, 1984). It constitutes a large proportion of domestic water supplies which accounts for over 50% in the United States, almost 30% in Canada, and about 70% in Europe (Gillham and Rao, 1990). Although in the past groundwater resources have been assumed to be naturally protected from various sources of contamination, the effects of contaminants from industrial, municipal or agricultural origin have been detected in recent years at an alarming rate (Cherry, 1984). Therefore, it is important to understand the way in which contaminants enter, migrate and disperse in groundwater systems, particularly when it is recognized that once contaminated, remediation of groundwater supplies, if at all feasible, is a costly and generally very long term undertaking (Gillham and Rao, 1990).

The use of synthetic organic chemicals has grown at an increasing rate during this century, in particular since the 1940s (NRC, 1984). More than three million organic compounds are known to exist and more than 40 thousand are currently manufactured (Cherry, 1984). Even though production increased, it was not until the late 1970s, when the analytical capability to measure the compounds by gas chromatography became available, that a variety of organic compounds were found in groundwater in many locations throughout different countries (Westrick, 1990). Local contamination problems have been reported in the United States and Canada (e.g. Pye et al., 1983; NRC, 1984; OTA, 1984; Patrick et al., 1987; Pupp, 1985; Cherry, 1987; Mackay et al., 1988; Mackay and Cherry, 1989; Smith et al., 1990; Westrick, 1990; Mackay and Smith, 1992). In some European countries, such as Germany, the United Kingdom, Italy and the Netherlands, this has been an important environmental issue (e.g. Fielding, et al., 1981; Trouwborst 1981; Cavallaro, et al. 1985; Kenrick, 1985; Schwille, 1988; Rivett et al., 1990a, b). Contamination of groundwater by organic compounds has been a topic of great interest in older industrialized countries for almost two decades. It is becoming increasingly important in countries which have experienced a rapid industrialization more recently, which began to use synthetic organic chemicals somewhat later than the older industrialized nations.

Of the various organic contaminants found in groundwater, the widely used industrial solvents and aromatic hydrocarbons from petroleum products are most common (Mackay et al., 1988; Mackay and Cherry, 1989). Much of groundwater contamination is caused by leakage, spillage, or disposal of organic liquids immiscible with water known as nonaqueous phase liquids (NAPLs) into the ground surface (Mackay and Cherry, 1989; Gillham and Rao, 1990). These immiscible fluids fall into two categories: those that have a density greater than that of water (dense nonaqueous phase liquids or DNAPLs) and those that have a density less than that of water (light nonaqueous phase liquids or LNAPLs) (Gillham and Rao, 1990; Huling and Weaver, 1991). The DNAPLs, many of which are chlorinated solvents, are used for a variety of purposes such as dry cleaning, metal works, wood preservation, electronics manufacturing, machining, print shops, automotive production and repair, asphalt operations, and aviation equipment maintenance (Cherry, 1987; Schwille, 1988; U.S. EPA, 1992). Many of the organic chemicals found in groundwater originate from urban or industrial activities, or inadequate waste disposal. Therefore, contaminated groundwater has often been located near industrialized, heavily populated areas, a circumstance that increases the likelihood of human exposure (Patrick et al., 1987).

Organic contaminants are also the most common health-threatening chemicals detected in groundwater (Mackay and Cherry, 1989). Several of these substances produce central nervous system (CNS) depression, and liver and kidney dysfunctions if exposure is sufficiently high (Thomas, 1990). A significant degree of water quality degradation is commonly considered to exist when a potentially toxic organic compound achieves concentrations of several tens of micrograms per liter or more. Many common organic compounds have solubilities in water on the order of tens or hundreds of milligrams per liter. Therefore, only small masses of these organic compounds need to affect the groundwater resource in order to have the potential, by long term dissolution, advection and dispersion, to cause large plumes of contamination. The threat that organic liquids pose to groundwater quality derives from their considerable solubilities relative to drinking water limits and from the mobility in groundwater of contaminants derived from them (Cherry, 1984). The recognition of groundwater contamination has often occurred after groundwater users have been exposed to a potential health risk. Once contamination is recognized, cleaning the aquifer to its original condition is often not feasible with current technology (Cherry, 1987).

The discoveries of serious environmental problems in older industrialized countries should be a forewarning of what could occur or may be occurring already in recent industrialized nations. The Mexico City Metropolitan Area (MCMA) represents a case study where the first hints of organic contamination of groundwater are starting to be observed.

Perspectives of this Study

This research project was conceived to evaluate and apply sampling and analytical methods appropriate for use in the Basin of Mexico. It was part of a team effort with a group from the Waterloo Centre for Groundwater Research, University of Waterloo (UW), Ontario, Canada. C. Pitre, a graduate student from the UW, focused on the hydrogeological conditions and the behavior of inorganic constituents, and was advised by Dr. D.L. Rudolph and Dr. J.A. Cherry. Dr. D.M. Mackay advised on the organic constituents research. The sampling techniques used for the field work were designed and developed at the University of Waterloo by Dr. R.C. Starr and R.A. Ingleton.

The specific goals of this study are the following:

1. To develop, present in public forums and publish an overview of the potential degradation of groundwater quality in Mexico City, with special emphasis on contaminant pathways.

2. To explore the importance of specific pathways in a selected study area in the Basin of Mexico.

3. To develop basic organic analytical capabilities in the Universidad Nacional Autónoma de México, Centro de Ecología, specifically for analysis of halogenated volatile organic compounds (VOCs).

4. To understand vertical transport in the clay strata of the lacustrine area in the MCMA by determining the concentration of anionic surfactants and chlorinated hydrocarbons.

5. To understand the potential routes of organic chemicals that could represent a risk to the groundwater resources in the Basin of Mexico by interpreting hydraulic and geochemical information.

6. To define research priority areas for future work in Mexico regarding water resources, which include surface water and groundwater.

The results of this project are organized as follows: Chapter 2 is an overview of the groundwater resources and the potential degradation of the water quality in the Mexico City area. It is written in manuscript form for submission as a feature article to the journal Environmental Science and Technology. Chapter 3 describes field investigations conducted to assess specific organic contaminants migration beneath some of the sewer canals traversing Mexico City. Additional modelling is needed to complete this part of the project and to finish the publication. It is written as a research article for submission to an appropriate journal such as Environmental Toxicology and Chemistry. Chapter 4 is an overview of the current Mexican regulatory framework related to water issues. Chapter 5 includes the general conclusions of this research. It also incorporates recommendations for priorities for future research with regards to water quality in Mexico.

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Chapter 2

Potential Degradation of Groundwater Quality in Mexico City

Development of the Mexico City Metropolitan Area

Mexico City is located in an originally closed hydrologic basin in the south central part of Mexico, opened artificially in the late 1700s. As depicted in Figure 2.1 the Basin of Mexico (also called the Valley of Mexico) occupies 9,560 km^2.

The Basin of Mexico has historically been one of the most densely populated areas of the world. The two main cultures that settled in the basin passed through cycles of expansion followed by decline (Ezcurra, 1990; Serra, 1990). The Teotihuacan culture arose in 100 B.C. in the northeastern part of the basin, eventually reaching a population of 125,000 by 650 A.D. (Serra, 1990). This culture declined due to the overexploitation of the natural resources and the lack of appropriate technology to utilize the soils (Sanders, 1976a; Sanders et al., 1979).

The Aztec city of Tenochtitlan developed in the central part of the lacustrine zone around 1150 A.D.; its population rose to approximately 200,000 by 1500 A.D. At the time of the Spanish Conquest (1519 A.D.), the total population in the basin was approximately 400,000 (Ezcurra, 1990; Serra, 1990). The second decline occurred at this time, due in part to deaths in the war of domination, due to migration of the local indigenous

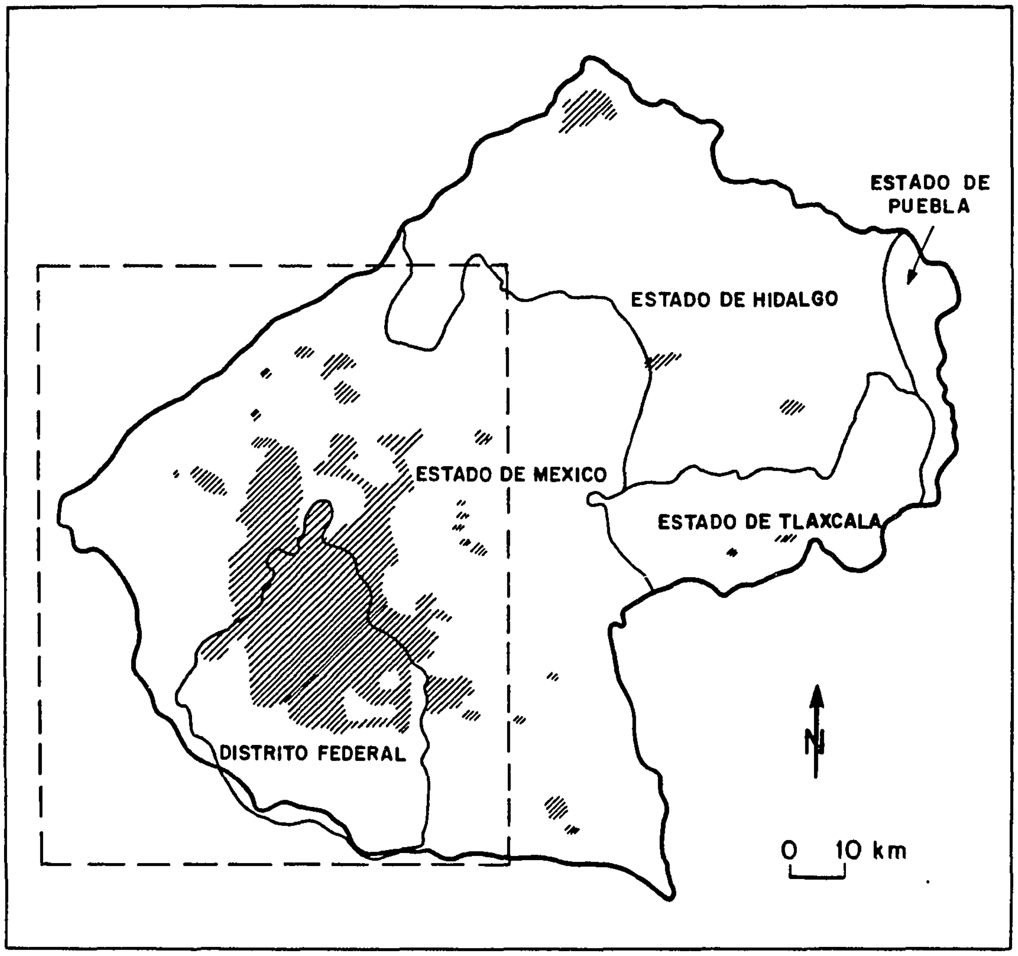

Figure 2.1. The Basin of Mexico and (shaded) the Mexico City Metropolitan Area.

people, but most importantly due to the introduction of new infectious diseases brought from Europe, to which the indigenous population had no immunological resistance (León-Portilla et al., 1972).

Before the rise of the Aztec Empire (1000 A.D.), a lacustrine system covered approximately 1,500 km^2 in the Basin of Mexico and included five major lakes reaching from north to south: Zumpango, Xaltocan, Texcoco, Xochimilco and Chalco. Nine major environmental zones were recognized within the basin before considerable human transformations took place (Parsons, 1971; Sanders, 1976b; Sanders et al., 1979; Ezcurra, 1990). In general terms these zones were 1) the lacustrine system, an important habitat for migratory birds; 2) the saline lakeshore, with halophytes; 3) the deep alluvium soil, covered by sedges and swamp cypresses (*Taxodium mucronatum*); 4) the thin alluvium soil, covered by grasses and agaves (*Agave* sp.); 5) the upland alluvium, vegetated by oaks (*Quercus* sp.) and acacias (*Acacia* sp.); 6) the lower piedmont, with gentle slopes and low oak forest; 7) the middle piedmont, with broadleaf oaks; 8) the upper piedmont, occupying elevations from 2,500 m to 2,700 m and vegetated by oaks, tepozanes (*Buddleja* spp.), alder (*Alnus* sp.), and madrones (*Arbutus xalapensis*); and the sierras, at elevations above 2,700 m and harboring temperate plant communities with pines, fir (*Abies religiosa*), and juniper (*Juniperus deppeana*).

The Basin of Mexico has changed from a natural lacustrine plain into a highly urbanized area built on the lacustrine sediments and expanding into the surrounding mountains. The natural water bodies have almost disappeared. At present, only small and reconstructed sections of Lake Texcoco and Lake Zumpango exist. Remnants of Lake Xochimilco persist as irrigation canals (Parsons, 1971). More than 3,000 km^2 in the southwestern part of the basin are now urbanized. This urbanized area is referred to hereafter as the Mexico City Metropolitan Area (MCMA).

Modern Population and Water Demand

The MCMA is continuing to grow at an accelerated rate. The 1990 census data indicate a population approaching 20 million (INEGI, 1990) and the population is predicted to reach 25 million by the year 2000 (Cabrera, 1990). Figure 2.2 depicts the expectations for population growth in the MCMA.

The current water use in the MCMA is approximately 60 m^3/s (DDF, 1989, Mazari et al., 1992) with an increasing demand (Figure 2.2). The aquifer system that underlies the urban area is extremely important, since approximately 75% of the total water used in the MCMA, i.e. an average of 45 m^3/s, is extracted from local groundwater supplies (CAVM, 1988; Herrera and Cortés, 1989; Murillo, 1990; DDF, 1991; Mazari et al., 1992). An additional 15 m^3/s are pumped from two distant basins: Lerma and Cutzamala (Mazari et al., 1992). Water supply from outside sources is limited

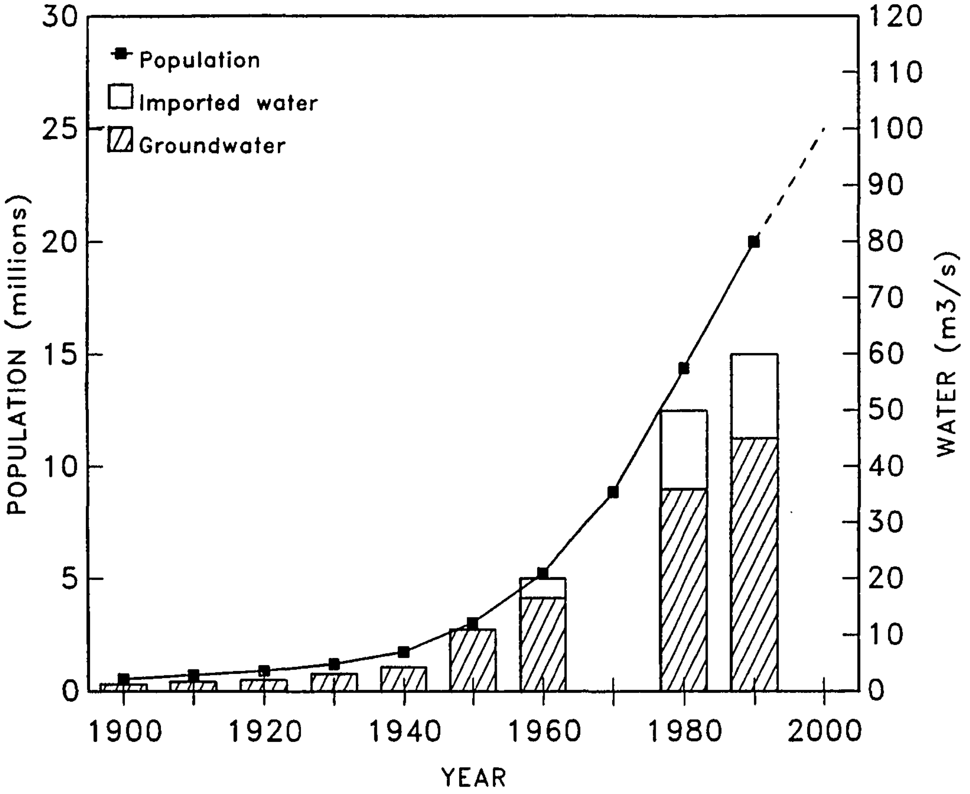

Figure 2.2. Population growth and water demand in the Mexico City Metropolitan Area.

and expensive due to pumping and transportation costs and its exploitation leads to negative impacts on other basins (Aguilar et al., 1992). Water is used in the MCMA for domestic, commercial, industrial and agricultural activities (DDF, 1989).

The Groundwater Resource

From the geotechnical point of view, three zones can be distinguished in the Basin of Mexico: the lacustrine, the transition, and the mountainous zone (DDF, 1998a; Marsal and Mazari, 1969, 1987, 1990). The areal extents of these zones are illustrated in Figure 2.3a. A schematic of the stratigraphy of the lacustrine, transition and mountainous areas is depicted in Figure 2.4.

The mountainous area is the product of volcanic activity, with fractured basalts, volcanic ash, and glacial and fluvial deposits. From the point of view of water supply, the mountainous areas serve primarily to direct precipitation towards the central part of the basin, either in surface runoff or in subsurface flows through the more permeable media in the mountainous areas.

The lacustrine clay deposits are characterized by extremely high compressibility (mean values 0.745 cm^2/kg recompression, 2.285 cm^2/kg virgin) and high porosity (80% to 90%). The strata are arranged in upper and lower clay formations, 30 to 70 m thick, divided by a hard layer (*Capa Dura*) composed predominantly of silt and sand (Marsal and Mazari, 1969). The clayey zone is considered an aquitard since it represents an interval of

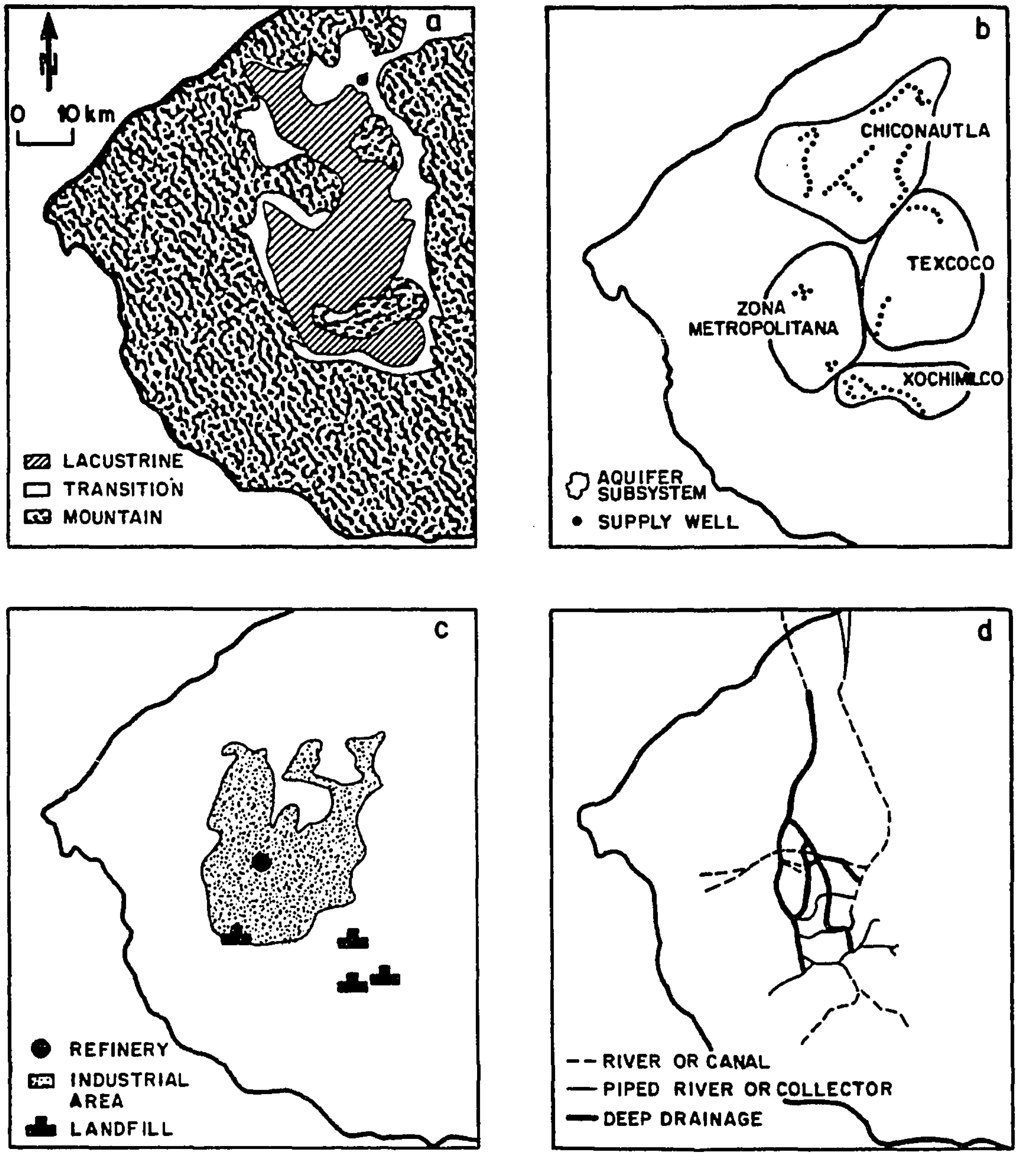

Figure 2.3. The Mexico City Metropolitan Area, a)stratigraphic zoning, b) well system and aquifer subsystem, c) industrial area, refinery and main landfills, d) drainage system.

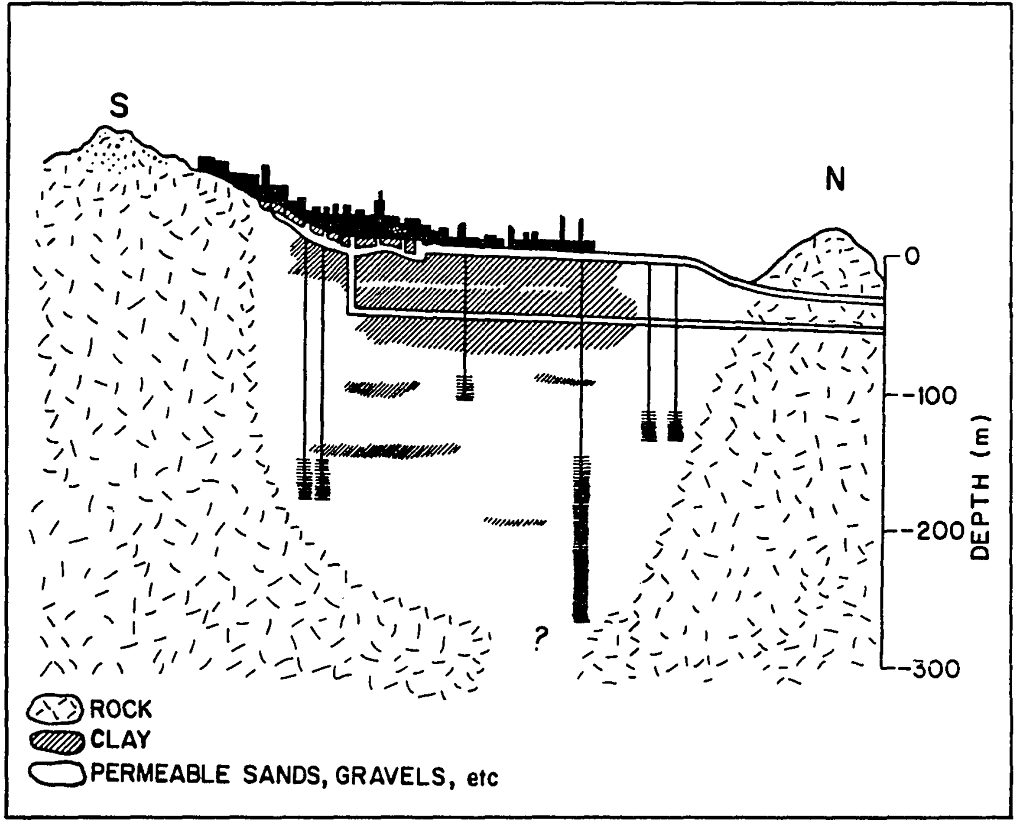

Figure 2.4. Basin of Mexico schematic vertical section.

less permeable strata in the stratigraphic sequence. Although these clayey layers are not sufficiently permeable to allow extraction of significant amounts of water by wells, they are permeable enough to allow some water movement, as discussed later.

The fringe area between the lacustrine and the mountainous areas is known as the transition zone. In these areas, clay deposits alternate with deep soils of alluvial origin, which reflect the ancient lacustrine system movement. In other areas close to the volcanoes, the transition zone is comprised of fractured basalts. The boundary between the lacustrine and the transition zone is generally taken as the edge of the thick upper clay formation. Within the transition zone, there are areas in which the upper clay formation is not present; in other areas, the clays are interbedded with silt and sand strata of alluvial origin and vary in thickness. The surficial media in the transition zone have a relatively high permeability as compared to that of the lacustrine clays. Thus, the majority of the recharge of the aquifers occurs through the transition zone, primarily during the rainy season (Marsal and Mazari, 1969; DDF, 1998a).

The main aquifer in the Basin of Mexico is composed of alluvial and volcanoclastic sediments ranging in thickness from 100 m to 500 m. The aquifer is a heterogeneous unit of silt, sand and gravel, directly overlain by the lacustrine clays (Marsal and Mazari, 1969; Ortega and Farvolden, 1989). The aquifer in the Basin of Mexico can be divided into several subsystems:

Xochimilco-Tláhuac-Chalco, **Zona Metropolitana**, Lago de **Texcoco**, and Teoloyucan-Tizayuca-Los Reyes-**Chiconautla** (DDF, 1987b). The names in bold are used for brevity in Figure 2.3b and subsequent discussion. In general, this subdivision of the aquifer subsystems is consistent with available stratigraphic and piezometric data as discussed by Mazari et al. (1992).

The aquifers were subject to artesian pressure in the past, with overall hydraulic gradients and water flow in an upward direction through the overlying clay aquitards. However, the hydrologic regime was impacted significantly by the utilization of groundwater resources, particularly the exploitation of the Zona Metropolitana subsystem starting in 1847 and expanding significantly in the 1940s. Now the gradients and flow in the upper part of the basin deposits are generally downward, towards heavily pumped zones (Marsal and Mazari, 1969; Ortega and Farvolden, 1989; Durazo and Farvolden, 1989).

Due to the population growth beginning at the end of last century, the number of wells in the Zona Metropolitana increased dramatically. By 1925, groundwater extraction had led to subsidence of Mexico City by approximately 1.25 m (Gayol, 1933). In 1940, to meet the demands of the rapidly increasing population, the first 150 deep production wells were installed. This expanded water extraction induced subsidence in the city during the 1940s and early 1950s at a rate of 35 cm/yr, down to 8 m total, which caused many problems with buildings, roads, piping, etc. (Mazari and Alberro, 1990). Nevertheless, water supply wells located in the central area of the MCMA were used to extract water from the Zona Metropolitana aquifer subsystem until 1954. At that time, due to the continuing subsidence problems, most of these wells were closed and new wells installed to exploit the Xochimilco aquifer system to the south and the Chiconautla aquifer system to the north, as shown in Figure 2.3b. In the late 1950s, subsidence in the central area of the MCMA dropped dramatically to 7.5 cm/yr. From the 1960s to the 1990s the subsidence in the city diminished further to 4.5 cm/yr (Mazari and Alberro, 1990).

The current extraction rates within the aquifer subsystems are as follow: Xochimilco 27 m^3/s, Zona Metropolitana 8.3 m^3/s, Texcoco 5.2 m^3/s, Chiconautla 4.5 m^3/s (Mazari et al., 1992). Within the Chalco-Xochimilco area, there is now subsidence of 30 cm/yr, leading to the same types of problems already experienced in the central part of the MCMA.

The majority of the new wells are located in or near the transition zones in areas where the aquifers are semiconfined. The wells have typical depths between 100 m to 200 m, although some are as shallow as 70 m or as deep as 300 m, as illustrated schematically in Figure 2.4. At present there are approximately 1,000 registered wells, of which about 40% are used occasionally during the dry season. No information is available on the number or characteristics of unregistered wells in the MCMA. It is possible that some industries have clandestine wells, but since 1954 there has been strict control on well drilling and it is likely that few unregistered wells were installed since that time. However, it is possible that there are wells in the basin which were installed before 1954 which are not currently registered and which were probably not sealed when their use was abandoned. Such has proven to be the case in many formerly agricultural areas of the U.S. into which metropolitan areas have expanded.

At present the natural recharge of the aquifer is much lower than extraction in the basin (Murillo, 1990; Ramírez, 1990; Mazari et al., 1992). Groundwater extraction from the basin is 45 m^3/s, of which 25 m^3/s is replenished by natural recharge, and 20 m^3/s constitutes overexploitation. Therefore, about 45% of current extraction is overexploitation (Mazari et al., 1992). Since the hydraulic gradients are now downward through the clays in much of the MCMA, there is a potential for downward migration of water from surface sources through the clays towards the groundwater reservoirs. When the source of the water is contaminated, e.g. in sewer canals, disposal pits, etc., then there is a clear potential for the contaminants to be transported towards the underlying aquifers. However, even when the water is initially uncontaminated, e.g. rainfall, irrigation or leaking water supply lines, it may pick up contaminants which have been released onto or into the subsurface from other sources. Furthermore, certain organic liquid contaminants (e.g. petroleum products and other organic solvents) are now known to be able to penetrate into some types of subsurface materials on their own, without requiring transport by infiltrating water (Mackay and Cherry, 1989).

Thus, two questions of importance for the MCMA are 1) whether the surficial deposits could allow significant downward transport of water and/or organic liquids, and 2) whether there are or have been significant releases of contaminants to the subsurface. These issues are discussed separately below.

Aquifer Vulnerability

Certainly a potentially very important route for transport of contaminants into the aquifers is through the surficial materials in the transition zones. It is, after all, through these zones that a majority of the recharge of the aquifers occurs. Clearly any contaminants released to the subsurface in the transition zones could potentially migrate themselves or be carried down by recharge waters towards the aquifers. We will return later to consider what is known about contaminant sources in the transition areas. The importance of these sources and this potential route of aquifer contamination is considerable since most of the supply wells now draw from zones within or near the transition zone.

The lacustrine clay unit or aquitard which overlies much of the aquifer in the Basin of Mexico has been considered a barrier which greatly restricts the downward migration of water and surface contaminants towards the aquifer system. Thus the main aquifer generally has been considered hydrogeologically closed to contamination which originates in the lacustrine area (CAVM, 1988; Herrera and Cortés, 1989; Durazo and Farvolden, 1989). The reliance on the lacustrine clays to act as an efficient barrier to contaminants is based in large part on the assumption that they act hydrogeologically as relatively homogeneous, impervious units. However, there are at least two ways by which the integrity of the clays in the MCMA may have been breached: human activities and natural fracturing.

Engineered Breaches of the Clays

Over the years there have been a wide variety of activities in the basin that have caused the penetration of all or a portion of the lacustrine clays, e.g. drilling, excavations, pile driving, etc. The most obvious complete penetration of the clays occurs when a well is installed into the underlying aquifer. Another issue of potential importance is the downward migration of water and contaminants along the outside of wells which were installed without the now common procedures (grouting, sealing, etc.) to prevent this problem. If significant at all in the MCMA, this problem is likely to be limited to the older wells since drilling controls have been strict in the last forty years. A more important aspect of the older wells may be that they have been retired from use but their interiors not sealed. Thus, if an old water supply well has been cut off or covered during construction of new surface facilities and its top left open near surface, the well may in effect act as a drain drawing water and contaminants from the surface directly into the aquifer. Abandoned wells have been identified as potentially significant short circuits for contaminant migration through aquitards in some areas of the U.S., particularly where urbanization has occurred in previously agricultural areas such as the Santa Clara ("Silicon") Valley in California (U.S. EPA, 1984, 1986).

Other engineering activities are likely to have affected the hydraulic integrity of the lacustrine clays in the MCMA. To our knowledge, no overview of this topic is available, but the potential importance is illustrated by two examples. A deep drainage system and a subway system were installed in the MCMA, both of which required extensive excavations into the clays. From the point of view of aquifer vulnerability to contamination, several questions arise: 1) do the excavations completely penetrate the clays at any point? (this is known to be true for portions of the deep drainage system), 2) is it possible for water and contaminants to move along the exterior of the buried structures?, and 3) what happens to water and contaminants that collect in the interior of the subway tunnels or is it possible that there are leaks in the deep drainage system? Although many issues such as these were likely to have been taken into account during the design of the subway and deep drainage, they warrant reexamination considering the aging of the installations and damage that may occur due to the earthquake activity in the basin.

Natural Fracturing of the Clays

Recent studies suggest that cracks and fractures exist in the clays in various parts of the basin, for example in the Lago de Texcoco, along Rio Churubusco and in the Valley of Chalco (Alberro and Hernández, 1990; Rudolph et al., 1991). Surface cracking is known to result from the subsidence process (Hiriart and Marsal, 1969; Reséndiz and Zonana, 1969). In addition, fractures in the upper clay formation may, under some circumstances, develop as a result of ponding from the first heavy rains following the dry season (Alberro and Hernández, 1990). A review of the various mechanisms for the fracturing of the clays is presented by Alberro and Hernández (1990).

According to Alberro (1991) and based on soil mechanics (Terzaghi, 1948), fractures would be expected to close due to compression and the plastic characteristics of the clay, provided they are not filled with other materials. In virgin clays unaffected by pumping, unfilled fractures would be predicted to close at approximately 12 m. In cases of heavy pumping, such as occur in some parts of the basin, unfilled fractures would be predicted to close at a depth of approximately 25 m.

In the Lago de Texcoco, Rudolph et al. (1991) observed fractures in continuous core samples taken to depths of approximately 10 m and on the ground surface in shallow test pits. Many of these fractures were filled with silt and sand of apparent aeolian origin. Based on matching of measured geochemical profiles with computer simulations, Rudolph et al. (1991) concluded that transport of chemicals through the upper clay formation in the Lago de Texcoco area occurs more rapidly than would be expected for the unfractured clay. Thus, they concluded that chemical migration in the clay aquitard is dominated by water movement through the fractures.

These findings are consistent with an increasing body of evidence on the importance of fractures to solute transport through clay deposits in the United States and Canada (Williams and Farvolden, 1967; Grisak and Cherry, 1975; Keller et al., 1986; Pankow et al., 1986; D'Astous et al., 1989). It is now clear that in many areas clayey deposits which were viewed as long term protection of underlying aquifers may not be providing complete protection (Cherry, 1989). Whether contaminant transport through such media may lead to significant alteration of the quality of the underlying groundwater resource depends on various factors. These are, the extent and interconnection of fracturing, the hydraulic gradients through the clays, the size and properties of the aquifer, the locations of extraction wells, and, of course, the locations, types and amounts of contaminants released by human activity.

Contaminant Sources

The MCMA is the major urban and industrial center of Mexico. The MCMA contains 25% of the population of the whole country and about 50% of the industrial activity. From studies in similarly complex metropolitan areas throughout the world, it is known that there are many types and sources of contaminants of potential importance to subsurface water quality (e.g. Freeze and Cherry, 1979; Pye et al., 1983; OTA, 1984; NRC, 1984; Pupp, 1985; Cherry, 1987; Mackay and Smith, 1992). In the following, we evaluate for the MCMA the existing evidence for or the probable importance of each major type and source of contaminants.

Microbiological Contaminants

In general, the contaminants of most immediate concern and with the most obvious impact are microbiological in nature, including pathogenic bacteria and viruses. In Mexico infectious and parasitic diseases continue to be among the most common causes of death in the country, especially for infants (CAE, 1990). Some of this problem is related to the poor quality of drinking water, due in part to cross contamination between drinking and wastewater pipelines. Nevertheless, there is also the potential for microorganisms to be transported from sources to the groundwater supplies.

The most common sources of bacteria and viruses which are pathogenic to humans are solid and liquid domestic wastes. In Mexico City, such wastes are in some cases disposed of locally, often in cesspools, septic tanks or even open-pit latrines where water is more scarce; it has been estimated that 26% of the population in the MCMA has no drainage service (DDF, 1987a). Wastewater from the other 74% of the population is conveyed through the wastewater system which is described in more detail later. As is evident by comparing Figure 2.1 and Figure 2.3a considerable areas in the transition zone are populated. Thus, there is the potential for microbiological contaminants to migrate from the surface downwards through relatively permeable media towards the aquifer.

Microbiological contaminants are also present in wastes from medical facilities (Lee et al., 1991). At present, there is little information on the methods for disposal of such wastes in the MCMA, but it is likely that medical wastes are in general collected and disposed in the same way as municipal wastes. Only radioactive materials are disposed in a controlled manner in Mexico. As discussed later, there is evidence of groundwater contamination from landfill leachate in the MCMA; although microbial pathogens have not been the major focus of investigations to date, some attention to their migration may be warranted.

Transport and survival of microorganisms in groundwater is an area of considerable current research interest (e.g. Gerba et al., 1975; Yates et al., 1987). In controlled tests, groundwater transport of bacteria and viruses have been shown to occur over several meter distances through sandy media, although their numbers are greatly reduced during migration, in part by filtration (Harvey et al., 1989; Harvey and Garabedian, 1991). McKay et al. (1992) conducted controlled tests in fractured clay and found that bacteriophage were transported rapidly through such media, as compared to a salt tracer, apparently because they were excluded by their size from attenuation by diffusion from the fracture into the clay matrix. The potential importance of this issue recently prompted a research program in the U.S. to investigate the groundwater transport of microorganisms, particularly viruses, to pumping wells; the broad goal is to determine whether regulations on groundwater disinfection are necessary (RWRI, 1992). It would appear that similar close attention to this issue is warranted in Mexico.

Chemical Contaminants

The other class of contaminants of concern to water quality in urban areas include the inorganic and organic chemicals that are used widely in commercial and industrial activities and are also contained in a variety of household products. These chemicals may be released to the subsurface at any point during their life cycle from creation to final disposal. Since the MCMA is the country's most important commercial and industrial center, it can be expected to have many if not all of the same problems with chemical use and disposal that have been identified in other cities in industrialized nations. Figure 2.3c shows the main industrial area in the MCMA.

Inorganic Contaminants. Commercial and industrial activities in the MCMA use a variety of inorganic compounds as raw materials. Thus, many types of inorganic wastes are likely to be released to the environment accidentally or through inadequate waste disposal. Although the potential for significant contamination of groundwater exists when subsurface chemical and hydrogeological conditions permit, in general, the migration of inorganic contaminants is viewed as being limited relatively efficiently by natural processes (NRC, 1984). Nevertheless, inorganic contaminants cannot be neglected as groundwater contaminants of potential significance in the MCMA. For example, a chromate plant which disposed of a large amount of residues on its property has caused serious local contamination problems in the northern part of the MCMA (Gutiérrez, 1990). More work on this and other such problems is necessary to decide whether the inorganic contamination presents a significant threat to underlying groundwater.

Petroleum Hydrocarbons. In the MCMA, a likely source of significant subsurface contamination is the petroleum refinery (Refineria 18 de Marzo) which was operated by PEMEX (Petróleos Mexicanos) in the Azcapotzalco area from 1948 until 1991 (indicated in Figure 2.3c). The potential for release of significant quantities of petroleum products from such facilities is best exemplified in Mexico by the explosion in Guadalajara in early 1992 which apparently resulted from gasoline released into sewers by a PEMEX facility there. Such releases of gasoline and other petroleum products also create the potential for contamination of soils and groundwater (API, 1972). This is a common problem at U.S. refineries, particularly the older ones, where releases of petroleum products have occurred because of leaking tanks, pipes and other equipment, as well as spills during other operations. Thus, although the PEMEX refinery in Mexico City was closed in 1991, it is currently used for storage. There may well have been significant releases during its past operation. In addition remaining surface, underground storage tanks, and pipelines could contain residual organic compounds that may eventually be released. Clearly, to assess whether a significant problem exists it is necessary to conduct site specific soil and groundwater surveys such as have been conducted at many sites in the U.S. Furthermore, in addition to considering the refinery itself, such surveys should include the pipelines which were used to transport petroleum products in liquid and gaseous form to and from the refinery.

Other common sources of petroleum hydrocarbon contamination in the U.S. are leaks from piping and tanks at the myriad gas stations that exist throughout metropolitan areas. It is likely the PEMEX stations in the MCMA have the same sorts of problems, perhaps exacerbated by the subsidence problems and deformation of the soil which would tend to strain piping, the tanks and connections between them as well as any concrete structures within which the tanks may be installed. After the explosion in Guadalajara in

1992, a program was initiated to identify and correct leaks at gas stations in the MCMA. It is likely that such a survey will indicate the need for additional surveys to determine the extent and importance of petroleum hydrocarbon contamination of soils and groundwater.

Although the potential for petroleum hydrocarbon contamination of the subsurface in the MCMA is very high, it does not necessarily follow that the threat to the groundwater resource is significant. Recent research suggests that many of the more mobile petroleum compounds may degrade during migration in the subsurface, especially if sufficient oxygen is available. This finding appears to explain the fact that while petroleum contamination of soils and groundwater in the U.S. is a serious and continuing problem near contaminant sources, the petroleum hydrocarbons are relatively rarely found in significant concentrations in public supply wells (Hadley and Armstrong, 1991; Mackay and Smith, 1992). Of course, there are cases in the U.S. where conditions are such that the petroleum hydrocarbons persist to form long plumes of contamination that do impact supply wells. More information specific to the MCMA would be necessary to determine whether the petroleum hydrocarbons pose a significant current or future risk to the groundwater resources.

Halogenated Organic Solvents. Among may other types of industries which exist in the MCMA are the electronics and metal fabricators.

In the U.S., these types of industries have in the past utilized large quantities of synthetic halogenated organic solvents for various cleaning purposes. Other important users of significant quantities of halogenated solvents are dry cleaning establishments. In the U.S., many commercial, industrial and military users of halogenated solvents have discovered that significant releases of the solvents have occurred by spills and/or leaks. These solvents are termed dense non-aqueous phase liquids (DNAPLs) because the organic liquid is denser than water. Furthermore, in some cases large volumes of DNAPLs have migrated down into the underlying aquifers, dissolving slowly into the passing groundwater. At many sites, this process has led to the contamination of billions of gallons of groundwater (Mackay and Cherry, 1989; U.S. EPA, 1992).

To the best of our knowledge, there has been no evaluation of the importance of DNAPL contaminants as a threat to the groundwater resources in the MCMA. Consideration of a few facts will illustrate that this issue should be taken as a high priority for investigation. In the MCMA there are on the order of 100 manufacturers of electronic products, most of them concentrated in the northern section (Islas, 1992). This is one type of industry which is quite likely to use halogenated solvents. Some of these electronics manufacturers appear to be located in the transition area, with little or no surficial clays to protect the underlying aquifer. It would seem likely that there are also dry cleaners throughout portions of the transition zone. High priority should be given to the investigation of these industries, since experience in the U.S. and elsewhere has shown that very significant contamination of groundwater is often discovered due to even seemingly small releases of solvents (Mackay and Cherry, 1989; U.S. EPA, 1992).

Solid Domestic and Hazardous Wastes. The disposal of solid wastes from municipal and industrial origins is also a problem in the basin. The city generates approximately 12,000 tons of solid waste per day, almost half (48%) of which is of industrial origin, while 52% is domestic waste (DDF, 1990). Five out of six landfills in the MCMA were designed for municipal waste, and are not lined nor outfitted specifically for containment of hazardous waste. Nevertheless, they all have received mixed domestic and industrial wastes. They were originally located in areas outside of the urban zone, but the city has since expanded to surround them. The main landfills in the MCMA are indicated in Figure 2.3c. Some industries store portions of their solid wastes on their own property, though information on this is not readily available. Other clandestine dump sites also exist in the urban area, but most are believed to receive mainly domestic waste. In some cases, canyons or old mines in the mountainous areas contain non-compacted fill or garbage (DDF, 1998a).

Two of the main landfills, which were closed in 1983 and 1986, have been under investigation by the Departamento del Distrito Federal (DDF), a local agency of the Distrito Federal (D.F., or Federal District) for several years. As found at similar facilities worldwide (e.g. Bramlett et al., 1987), the landfills are releasing leachate to the subsurface containing a complex mixture of contaminants (DDF, unpublished data). Although there are no official published reports, leachate migration is known to have led to contamination of production wells on the order of 2 km from one of the sites. At one site the contamination is moving through permeable fractured basalts, while at the other the migration is apparently occurring through an area of fractured clay. At least one of the landfills remaining in operation is located in the transition zone, with minimal natural barriers to subsurface migration. Although the importance of the existing or potential contamination from landfills in the MCMA has yet to be addressed in documents available to the public, this issue clearly warrants attention.

Liquid Hazardous Wastes. More than 90% of the liquid industrial wastes generated in Mexico City, which total approximately 1.5 million tons annually, are disposed directly into the sewage system without previous treatment (DDF, 1992). There is a lack of understanding of the characteristics of these wastes, but since there is a great variety of industries in the MCMA it is likely that liquid wastes contain hazardous chemicals. This fact highlights the importance of the wastewater system as a possible, areally extensive source for release of water and a variety of contaminants to the subsurface.

Wastewater Disposal

The wastewater system of the MCMA is a combined scheme, carrying stormwater and wastewater through the drainage system illustrated in Figures 2.3d and 2.4. The system includes three main unlined sewer canals (Gran Canal del Desagüe, Río de los Remedios, and Canal Nacional), sewers, reservoirs, lagoons, pumping stations, and the Deep Drainage Subsystem (DDF, 1975, 1982, 1988b).

The majority of wastewater generated by the MCMA is disposed to the drainage system with no previous treatment. However, there are on the order of 10 wastewater treatment plants in the MCMA, mostly activated sludge systems (Athié, 1987). The combined capacity of the treatment plants is about 5 m^3/s, but they presently treat approximately 3.5 m^3/s. The treated water, which accounts for only 6% of the water used in the basin (Murillo, 1990), is utilized for irrigation of green areas within the city and for agricultural canal recharge in the Xochimilco area (DDF, 1987b).

The sewer pipes are not likely to be in perfect condition, either due to improper installation or more likely due to deterioration or disruption by building activities, subsidence, and earthquakes. However, no information on the extent of leakage is available. It is likely that early networks were constructed more carefully than some of the recent ones. Also, the early networks were shallower than the modern parts of the drainage system. Therefore even if the materials used have improved it is likely that the older systems represent less of a contaminant risk as compared to much of the new drainage sections. Furthermore, since some of the newer portions of the system have been installed as the city has grown into the transition and mountainous areas, leakage from these portions of the system could be relatively significant since there is essentially unimpeded access to the aquifer.

Some of the sewer pipes empty or are pumped into a system of open, unlined canals. The Gran Canal del Desagüe, constructed at the beginning of the century operated by pumping water from the lower part of the drainage system to the origin of the Gran Canal and the flowing out the MCMA by gravity. The subsequent demographic growth and the subsidence of the city led to the need for pumping stations along the canal. The Río de los Remedios, originally a natural river that crossed the northern part of the MCMA, has for several decades been used to carry domestic and industrial wastewater. There is no man-made lining beneath either of these canals, except at junctions and other sites subject to erosion.

Since the canals are unlined in large part, the potential exists for migration of water and contaminants from the canals down towards the aquifers. This is of special concern in the northern part of the basin where the canals traverse the transition zone (Figures 2.3a and 2.3d). To date, no monitoring has been conducted to determine if significant migration of contaminants has occurred from the canals in the transition zone, an activity that would appear to be of relatively high priority considering the proximity of supply wells in that area. The potential for subsurface contamination by the canals also exists in the lacustrine area since there are significant downward hydraulic gradients which are likely to increase over time (Pitre, 1992). In fact, recent research at the confluence of the Gran Canal del Desagüe and the Río de los Remedios appears to confirm that infiltration of contaminated water has begun (Pitre, 1992). Tritium and several organic contaminants (halogenated solvents and surfactants) have been detected at low concentrations at depths consistent with migration dominated by fracture flow; indeed fractures have been observed in cores at this site down to 15 m depth (Pitre, 1992). Since the downward hydraulic gradients are expected to increase with time (Pitre, 1992), the progress of this infiltration would be expected to accelerate. These findings underscore the need to replace these two main open sewer canals with closed, piped systems, which has been planned to occur between 1992 and 1995.

During the 1970s the Deep Drainage Subsystem was built to allow disposal of flood waters during the rainy season (Figure 2.3d). Today both run-off and wastewater are disposed during the rainy season. The system is composed of three large (3 m to 5 m diameter) tunnels constructed at depths ranging from 30 m to 50 m, and operating by gravity (DDF, 1975, 1988b). In the central area of the MCMA, this system is constructed primarily in the lacustrine clays although parts required excavation into the aquifer. As the system leaves the basin to the north, the tunnels cross the transition zone. The Deep Drainage System is thought to be leakproof, but the fact that it occasionally requires repairs during the dry season suggests that short-term leaks are not ruled out. To our knowledge there is no monitoring conducted to determine if the Deep Drainage System may have released significant amounts of contaminants to the aquifer or transition zone.

The untreated wastewaters flow towards the north eventually into two reservoirs, called Requena and Endhó. Some of the wastewater is used for irrigation in the State of Hidalgo. Wastewaters finally flow towards the Gulf of Mexico through the Tula-Moctezuma-Pánuco River System. A hydroelectric plant, Zimapán, is under construction by the Federal Energy Commission (CFE) which will generate power using the wastewater in the Tula-Moctezuma River system.

Water Quality Monitoring

Systematic water quality monitoring started in the MCMA in the 1930s, increasing since 1955. The bacteriological, physical and chemical monitoring conducted in the last 35 years shows an unfavorable evolution of water quality which has been attributed to overexploitation of groundwater, and extraction of water from geologic formations that contain higher concentrations of some ions (e.g. iron and manganese). In some wells higher bacterial counts have been observed, attributed to lack of seals to protect against infiltration of surface runoff along the casing (DDF, 1982). Variations in pressure are observed in the water supply lines which may be due to leakage in pipelines caused by age or subsidence; this lack of system integrity indicates a potential for degradation of water quality. Finally, water quality deterioration can also occur in the small cisterns and storage tanks used in many houses, hotels, etc.

Most water management activities in the MCMA are conducted by the DDF. For example, DDF controls groundwater extraction, distribution and waste disposal in the D.F. Some groundwater extraction in the Estado de México is conducted by the Ministry of Agriculture and Hydraulic Resources (SARH) which operates in conjunction with DDF.

Water quality monitoring is carried out by DDF. This agency has a modern laboratory set up for typical bacteriological and inorganic analyses. It is also equipped with modern instruments for the analysis of a variety of organic compounds.

The bacteriological determinations are generally based on indicators such as total and fecal coliforms, although in some cases specific pathogens are determined. The physicochemical parameters that are commonly reported for groundwater are major ions (e.g. calcium, magnesium, sodium, potassium, bicarbonates, chloride, sulfates), total dissolved solids, total hardness, and pH, iron, manganese, nitrite and nitrate (DDF, 1982, 1985). Some heavy metals (e.g. chromium, cadmium, lead and zinc) are also reported. DDF began monitoring for several classes of synthetic organics in drinking water some years ago. However, neither the data nor their implications are discussed in reports available to the public.

Studies in the U.S. have illustrated that monitoring of supply wells is a poor way to detect the onset of groundwater contamination, in part because supply wells tend to draw from deeper portions of aquifers and often from very wide vertical intervals (Mackay and Smith, 1992). Thus, when contamination is noted in supply wells, it may generally be presumed to have affected relatively large volumes of the aquifer. In the U.S. and elsewhere, smaller diameter and shorter screened monitoring wells are used to pinpoint contaminant sources and provide information on contaminant distribution and water flow. With this more detailed understanding, it has often been possible to halt the expansion of the contaminant plume before supply wells are affected.

In the MCMA, no wells have been installed specifically to monitor the quality of the groundwater throughout the basin. It would seem a high priority to install such monitoring wells, particularly in areas of high aquifer vulnerability, such as the transition zone or areas likely to be deeply fractured, or near probable sources of significant contamination (e.g. electronics industries, the refinery, dry cleaners, gas stations, and other facilities at which metals are degreased such as metro yards, the airport, etc.).

Summary and Implications

Groundwater in the MCMA is a critical resource which is known to be overexploited and likely to be vulnerable to or already impacted by contamination arising from a wide variety of sources. Given the known exploitation, past studies have focussed on the quantity of water available for use. There is very little information on present or potential contamination of the soils and groundwater in the Basin of Mexico. Apparently there have been some efforts over the last few years to assess the quality of the groundwater resources, but neither the results of these efforts nor their implications have been made public.

There exists no comprehensive examination and comparison of the potential routes by which contaminants may reach the groundwater resource in the MCMA. This paper was intended to serve as a first step towards that goal. Without a much more extensive overview, however, it will be difficult for reasonable priorities to be set for actions within the MCMA to protect the groundwater aquifers. Some clear priorities, however, can be determined by drawing from experience in the U.S. and other countries. Given that the MCMA is similar in major respects with metropolitan areas throughout the world, it is very likely that soil and groundwater contamination similar to that observed elsewhere has occurred and continues in the MCMA.

Areas of aquifer vulnerability and contaminant sources should be mapped throughout the basin. Where the two overlap, monitoring activities should be undertaken to determine if significant contamination has already occurred. One such overlap identified in this work is the collection of electronics manufacturing industries located in or near the transition zone in the northern part of the MCMA. Other potentially important contaminant sources, which have been under investigation by DDF, are the landfills located on permeable soils. A third, and areally extensive, potential source is the sewage system. Since the sewage system conveys considerable amounts of domestic and industrial wastes, the possibility that the sewers and unlined canals release significant amounts of contaminants into the subsurface should be evaluated by monitoring activities at points along the system where the potential for downward migration is high.

Within the last decade, there has been a tightening of legislation (DOF, 1988a) and regulations for drinking water (DOF, 1988b), for drinking water supply sources (DOF, 1989), for disposal of industrial wastewater (DOF, 1988c,d,e,f) and liquid hazardous waste (DOF, 1988g,h), and for the design, construction, and operation of landfills (DOF, 1988i,j,k,l). This was certainly needed and will undoubtedly prove beneficial over the long term. However, the regulatory infrastructure is unlikely to be able to implement these regulations effectively or completely for some time, especially those regulations addressing drinking water and hazardous waste. Furthermore, the new regulations cannot reverse the contamination that has already occurred. Thus, as noted above, a number of activities are necessary to locate the hot spots of existing contamination so that actions can be taken as soon as possible to prevent further migration of contaminants and degradation of the groundwater supply. Considering the prevalence of organic compounds as groundwater contaminants in the U.S. and elsewhere, it would appear necessary for Mexico to increase its attention to this class of chemicals in its monitoring activities and regulations.

Historically, the Basin of Mexico has been one of the most densely populated areas in the world. The area has survived several population declines over the last two thousand years, each brought on in part by health or environmental crises ranging from exhaustion of cropland to epidemics of new diseases brought by Europeans. In recent years, the MCMA has been assaulted by new problems, such as contamination of air and water, which have accompanied the industrialization. At least with regard to groundwater, Mexico can avoid the costly trial and error approach taken in other parts of the world. By utilizing the essential findings of years of published groundwater research, priorities can be set for the most efficient approach to the problems specific to the MCMA.

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Chapter 3

Infiltration of Organic Contaminants from Sewer Canals in Mexico City

Introduction

The Basin of Mexico, in which Mexico City is located, has changed from a natural lacustrine plain into a highly urbanized area built on lacustrine sediments and expanding into the surrounding mountains. Three main hydrogeological zones can be distinguished in the basin: the lacustrine area composed of relatively impermeable clays, the transition zone composed of more permeable materials and the mountainous area (DDF, 1988a).

The current water use in the Mexico City Metropolitan Area (MCMA) is approximately 60 m^3/s (DDF, 1989; Mazari et al., 1992) and demand is increasing. The aquifer system which underlies the urban area is extremely important, since approximately 75% of the total water used in the MCMA is extracted from local groundwater supplies (CAVM, 1988; Herrera and Cortés, 1989; Murillo, 1990; DDF, 1991; Mazari et al., 1992). Additional water is brought from outside sources, which is limited and expensive due to pumping and transportation costs. The underlying aquifer represents the most important source of groundwater supply for a population approaching 20 million (INEGI, 1990).

Mexico City, as any metropolitan area, is expected to have many if not all of the same problems with chemical use and disposal that have been identified in other industrialized cities, i.e. leaking pipes, hazardous wastes stored areas, landfills, a complex network of drinking water and sewage pipelines, etc. In addition, over 90% of the liquid industrial wastes generated in Mexico City, which total approximately 1.5 million tons annually, are disposed directly to the wastewater collection system without treatment (DDF, 1992). This system consists of lined tunnels and unlined canals traversing Mexico City.

Due to overexploitation of the aquifer subsystems the hydraulic gradients are now downward in much of Mexico City, which increases the potential for migration of water and contaminants from surface sources through the clays towards the groundwater reservoirs.

Considering the Basin of Mexico from the geotechnical standpoint, the transition zone, where significant recharge is known to occur, is potentially the most important area for development of groundwater contamination. However, this study did not have access to the required sites, sampling techniques or funding to allow investigation of the transition zone. Consequently, the focus of this work was on a selected study area within the lacustrine area as shown in Figure 3.1, at which there appeared to be a significant potential for organic contamination transport into the subsurface. A significant potential for contamination was assumed to exist since 1) there were major sources of municipal and industrial contamination nearby, and 2) there were downward hydraulic gradients through the clays, creating the

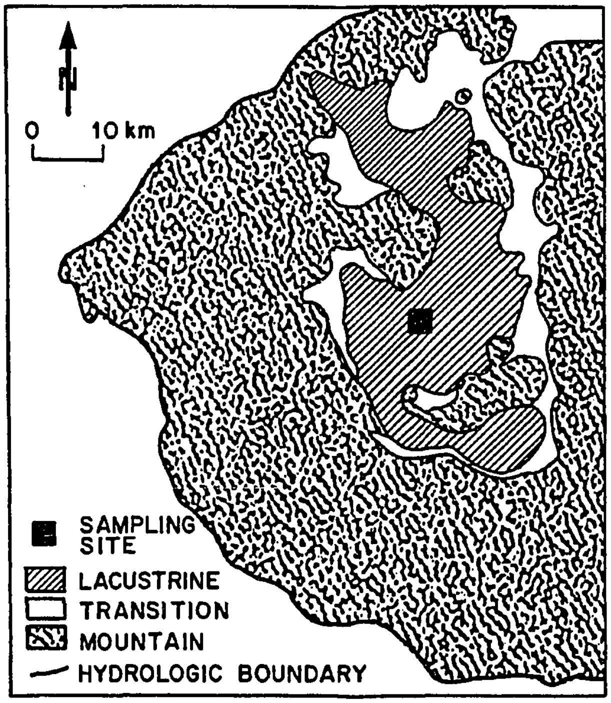

Figure 3.1. Geologic zones and study site in the western portion of the Basin of Mexico.

driving force for contaminant movement towards underlying aquifers. We further assumed that the unlined sewer canals, which receive all types of untreated municipal and industrial wastes, may serve as a significant source of contaminants to the subsurface.

Goals of this Study

The purpose of this project was to evaluate methods to study the impact of organic compounds infiltrating from two of the main sewer canals through the clays of the Basin of Mexico. The chemicals selected, anionic surfactants and halogenated volatile organic compounds (VOCs), are of anthropogenic origin, representative of major classes of contaminants, relatively mobile, and easy to detect.

The major goals of this study were to determine whether anionic surfactants or VOCs could be used as reliable indicators of organic contaminant migration into the lacustrine clays of the Basin of Mexico, and to determine whether the surficial deposits could allow significant downward transport of water and/or any of these compounds. If so, the secondary goals were to determine if there is evidence of migration of any of these compounds, and to assess whether the migration of the contaminants is retarded compared to that of water.

Background

Transport in Clay Aquitards

Clayey deposits which have been viewed as providing long term protection of underlying aquifers may not be completely effective (Cherry, 1989). Whether contaminant transport through such media may lead to significant alteration of the quality of the underlying groundwater resource depends on the extent and interconnection of fracturing, the hydraulic gradients through the clays, the size and properties of the aquifer, the locations of extraction wells, and the locations, types and amounts of contaminants.

In the Basin of Mexico, the lacustrine clays have been studied extensively with regards to the physical properties and soil mechanics, with fractures observed in some areas (e.g. Hiriart and Marsal, 1969; Marsal and Mazari, 1969, 1987, 1990; Reséndiz and Zonana, 1969; DDF, 1988a; Mazari and Alberro, 1990; Alberro and Hernández, 1990). Studies focusing on the hydrogeological aspects of these lacustrine formations have started recently (DDF, 1987; CAVM, 1988; Ortega and Farvolden, 1989; Durazo and Farvolden, 1989; Herrera and Cortés, 1989; Rudolph et al., 1991; Pitre, 1992). From studies in the United States and Canada there is an increasing body of evidence on the importance of fractures to solute transport through clay deposits (Williams and Farvolden, 1967; Grisak and Cherry, 1975; Keller et al., 1986; Pankow et al., 1986; D'Astous et al., 1989).

Pitre and coworkers (Pitre and Rudolph, 1991; Pitre, 1992) evaluated historical and recent records from the Texcoco area in the Basin of Mexico and determined that the hydraulic gradients through the clays in the study area have changed over the last 30 years from vertically upward to vertically downward. They estimate that the downward gradient, and therefore the potential for contaminant migration into the clay, became significant in the mid-1970s.

Hydraulic conductivity for the clays of the Basin of Mexico ranges from 10^{-8} cm/s to 10^{-10} cm/s (Marsal and Mazari, 1969). A stratum composed of silt and sand (called *Capa Dura*) was observed in the sampling sites at about 27 m depth. This stratum has a hydraulic conductivity on the order of 10^{-4} cm/s (Pitre, 1992).

Several types of fractures have been identified in the clay aquitard in the study area, the majority were vertical or subvertical. Pitre (1992) reports a fracture density at one of the study sites (Gran Canal) ranging from 20/m to about 100/m and at another site (Urban Site) ranging from zero to about 20/m. The fractures are not homogeneously distributed and not all fractures appear to be hydraulically active.

Thus, given the presence of hydraulically active fractures and the existence of downward hydraulic gradients, there exists a potential for downward migration of water and chemicals through the clay strata. Pitre (1992) studied the distribution of a number of inorganic species in the clays.

The Tritium (^3H) and chloride (Cl^-) results, among others, confirm that infiltration is occurring at the sampling site, as discussed in more detail later.

Occurrence and Fate of Surfactants

In the United States and Western Europe, branched-chain surfactants, such as alkyl benzene sulfonates (ABS), were introduced in the late 1940s as replacements for soaps in laundry and other cleaning formulations. Because of the concern of foaming and low degradability of branched-chain surfactants, cleaning formulations in industrialized nations were changed in the mid 1960s to utilize the more rapidly biodegradable linear alkyl sulfonates (LAS) and sodium dodecyl sulfates (NaLS). In recent years, other cationic and nonionic surfactants have been used in addition (Larson, 1990; Thurman et al., 1986; Field et al., 1992a).

However, in some parts of the world, ABS production and use has continued. In Mexico, for example, the majority of the cleaning agents are based on branched-chain ABS (Lichi, 1991), in part because much of the existing technology for surfactant production is outdated. A small portion of the surfactants used in Mexico are LAS.

Although over 50,000 chemicals are used in chemical applications, only a small number have been evaluated as tracers of urban sewage contamination. Among these, surfactants and their byproducts are probably the largest class of technical products in domestic use considered as potential candidates for this purpose (Fernández et al., 1991).

In urban environments like the MCMA, where relatively persistent surfactants are still used and where the groundwater resource is of major concern, monitoring for downward migration of these compounds can be used to identify potential routes of transport for other contaminants. Some surfactants could become potential contaminants in surface and groundwater, their presence might also be expected to influence the behavior of other pollutants. One unique property of surfactants is their solubilization power for relatively water-insoluble compounds (Kile and Chiou, 1989).

The importance of anionic detergents as groundwater contaminants has been recognized for the past 25 years (Thurman et al., 1986). The environmental persistence of the complex mixture of isomers known as ABS is considerable, with estimates of residence in groundwater reported between 20 and 30 years (Swisher, 1970; Barber, 1988; Barber et al., 1988). ABS is biologically refractory, and in fact may actually inhibit microbial degradation (Barber, 1988; Barber et al., 1988). Conversely, LAS degrades rapidly in groundwater under aerobic conditions, with half-lives estimated from 2 to 22 days (Federle and Pastwa, 1988; Larson, 1990; Field et al., 1992a). Under anaerobic conditions, LAS degradation is limited (Field et al., 1992b,c).

Over the last decade, there has been a renewed interest in the transport and transformation of surfactants in various types of environments. This work has utilized new, specific and very accurate analytical methods (Thurman et al., 1986; Brunner et al., 1988; Federle and Pastwa, 1988; Marcomini et al., 1988; Marchand et al., 1989; Larson, 1990; Takada and Ishiwatari, 1990; Field et al., 1992a,b). The MBAS test has more commonly been used as an indicator for anionic surfactants in soils and groundwater studies (Reneau and Pettry, 1975; Thurman et al., 1986; Federle and Pastwa, 1988; Field et al., 1992a,b). Field et al. (1992a) found that ABS concentrations measured by HPLC/FL (high performance liquid chromatography with fluorescence detection) contributed up to 90% of MBAS concentrations in groundwater from samples of at least one well at Otis Air Base, Massachusetts. In this case, apparently, there were few positive interferences with the MBAS technique, i.e. the MBAS result was as useful as the more specific analysis for tracking the ABS migration.

Fink et al. (1970) studied the sorption of ABS by thirty different soils with a wide range of physical and chemical properties. They found that soils vary tremendously in their capacity to adsorb the ABS, ranging from practically zero to sorptive efficiencies approaching that of activated carbon. Acher and Yaron (1977) found that clay soils sorbed various surfactants more strongly than sandy soils. They also mentioned that in different types of clays sorption increased with the length of the alkyl chain and was enhanced by the presence of some ions such as phosphate.

Thurman et al. (1986) measured MBAS concentrations in the range of 0.2 to 2.0 mg/l in a plume of contaminated groundwater which originated from a sewage lagoon at the Otis Air Base in Massachusetts. Little or no biological degradation of the ABS seemed to occur in the aquifer.

Occurrence and Fate of Volatile Organic Compounds

Of the various organic contaminants found in groundwater systems the halogenated organic chemicals which include synthetic chlorinated solvents, and the aromatic hydrocarbons from petroleum products represent some of the most significant contaminants (Feenestra and Cherry, 1988; Mackay and Smith, 1992). Due to their high potential for volatilization dissolved organic compounds are commonly termed volatile organic compounds (VOCs). For the purpose of this study we will focus on chlorinated solvents and will refer to them as VOCs.

In the United States the most frequently identified organic contaminants in groundwater are: carbon tetrachloride (CTET), chlorobenzene, 1,2-dichloroethane (1,2-DCA), 1,2-dichloroethylene (1,2-DCE), tetrachloroethylene also known as perchloroethylene (PCE), 1,1,1-trichloroethane (1,1,1-TCA), trichloroethylene (TCE), benzene, toluene and xylenes (Westrick, 1990). Additionally in places close to hazardous waste sites methylene chloride or dichloromethane (DCM) and 1,1-dichloroethane (1,1-DCA) have been reported (Feenestra and Cherry, 1988). The compounds that occur at relatively high concentrations in the groundwater systems are PCE, 1,2-DCE, TCE, 1,1,1-TCA, and benzene (Westrick, 1990). This research focused on four chlorinated solvents, 1,1-DCE, 1,1,1-TCA, TCE and PCE, three of which are among the most commonly detected in the U.S.

When present as organic liquids, NAPLs behave differently than dissolved solutes in the subsurface. The combination of low solubility, high density and low viscosity enables these compounds when released into the surface to penetrate into the subsurface and move downwards through the vadose (unsaturated) zone and/or groundwater (saturated) zone as a separate non-aqueous phase (U.S. EPA, 1992).

The NAPL potential for migration from the point of release could be influenced by the volume of NAPL released, the area affected by infiltration, the duration of release, the properties of single compounds or multicomponent mixtures of compounds, the properties of the media, and the subsurface flow condition (Feenestra and Cherry, 1988; Mercer and Cohen, 1990; Mackay and Smith, 1992).

The impact of river pollution in groundwater is an area of major concern in Europe, since a significant fraction of groundwater is recharged through infiltration of river water (Schwarzenbach et al., 1983). Studies on this topic have focused on the behavior of organic micropollutants during infiltration of river water and represent a similar scenario to that of the sewage canals in Mexico City; with water quality characteristics and geology quite different for each place. These studies have shown that VOCs move rapidly with infiltrating water from rivers to groundwaters. Therefore if a river is permanently charged with such chemicals, large groundwater areas may be contaminated, unless the compounds are eliminated during infiltration.

Many of these compounds are quite resistant to chemical and/or biological transformation under conditions typical for the subsurface therefore elimination is not likely to occur (Schwarzenbach et al., 1983, 1985). However, for some VOCs, chemical reactions (e.g. hydrolysis, dehydrohalogenation, etc.) and/or biological transformations may be important (Schwarzenbach et al., 1985; Vogel et al., 1987). The biological processes responsible for major elimination of some volatile organochlorine compounds (e.g. alkylated and chlorinated benzenes) occurs predominantly in the first few meters of infiltration (Schwarzenbach et al., 1983). According to Vogel et al. (1987), the fate of halogenated aliphatic compounds in the environment is dependent on their particular chemical properties and potential chemical and biological transformations. Nevertheless, in the presence of hydrogen sulfide, brominated and chlorinated alkanes may undergo nucleophilic substitution leading to a variety of aliphatic sulfur-containing products which seem to be persistent in the subsurface, and are also of concern from the toxicological point of view (Schwarzenbach et al., 1985). It is known that under anaerobic conditions, PCE degrades to TCE, which degrades to DCE (Vogel et al., 1987).

The clay aquitard in the Basin of Mexico can be considered a porous medium, and there is increasing evidence that it behaves as a fractured porous medium (Rudolph et al., 1991; Pitre, 1992), which would have a significant influence on the transport and fate of NAPLs.

Important transport processes in the porous media are molecular diffusion and advection. Molecular diffusion, is the process caused by a concentration gradient in the soil matrix between fractures. Advection, is the process by which solutes are transported by the bulk motion of flowing water in fractures or openings left by roots (Cherry, 1984; Mackay et al., 1985). It also has to be considered that the capacity of the clayey strata to sorb contaminants may be much greater per unit volume than that of the aquifer. Therefore the relatively slow rate of release from the clay by diffusion and the contaminant mass contained in dissolved and sorbed form in the clay could cause a long-term bleed of contaminants into the aquifer (Mackay and Cherry, 1989).

The importance of VOCs lies in their relatively low solubility and the low drinking water standards for most of these chemicals. Also VOCs can persist in the subsurface and cause groundwater contamination problems for many decades or even centuries. Furthermore when DNAPLs are present in the subsurface groundwater contamination can not be eliminated without removal of the source (Feenestra and Cherry, 1988).

Sorption and Retardation of Organic Contaminants

Sorption of hydrophobic organic compounds by geologic media is thought to be dominated by the solid organic carbon content (f_{oc}) of the media, provided that f_{oc} is on the order of 0.1% or greater (Schwarzenbach and Westall, 1981; Karickhoff, 1984). When f_{oc} dominates sorption, the sorption distribution coefficient (K_d, cm^3/g) may be estimated from the following equation:

$$K_d = f_{oc}\, K_{oc}$$

where K_{oc} is the organic carbon sorption coefficient (cm^3/g) and f_{oc} is a unitless fraction (Lyman, 1982).

According to Lyman (1982), the ratio of organic matter to organic carbon varies from soil to soil, but a value of 1.724 is often assumed when conversion is necessary. Thus the f_{oc} may be estimated by dividing the measured fraction of organic matter (f_{om}) by 1.724. This conversion was used in this work to estimate f_{oc} of the samples. The K_{oc} values for the VOCs of interest were taken from Lyman (1982) and Montgomery and Welkom (1990). The K_{oc} value for surfactants was taken from Bromnawell et al. (1991).

If sorption is linear, reversible and instantaneous, the average velocity of a sorbing solute moving by advection or diffusion through a porous medium will be less that the velocity of a non-sorbing solute by a constant factor, termed the retardation factor R (Freeze and Cherry, 1979). R can be estimated as follows:

$$R = 1 + \frac{\rho_b}{\theta} K_d$$

where ρ_b is the bulk density of the aquifer solids, θ is the porosity of the aquifer (unitless), and the units of K_d are cm^3/g.

Field Site

Several areas were identified along the two main sewer canals that traverse Mexico City, where there were major sources of municipal and industrial contamination, and downward hydraulic gradients through the clay. One was selected for this study, because it was most favorable from the point of view of various practical constraints: low banks along the sewer canals to allow easy access and reduce difficulties in coring, accessibility for installing equipment and sampling, etc.

Three sites were selected in the confluence of the central and north-east zones of the Urban Drainage System for the Distrito Federal (D.F.)(DDF, 1982) as shown in Figure 3.2. The entire drainage system is described in Chapter 2. Two of the sites were located immediately adjacent to two sewage canals that cross the MCMA: 1) Gran Canal del Desagüe (km 9.5), on the border between the D.F. and Estado de México, 2) Río de los Remedios west of the junction with Gran Canal del Desagüe, in Ecatepec, Estado de México; north of Delegación Gustavo A. Madero, D.F., 3) The third site, called the Urban Site, was located approximately 200 m north of

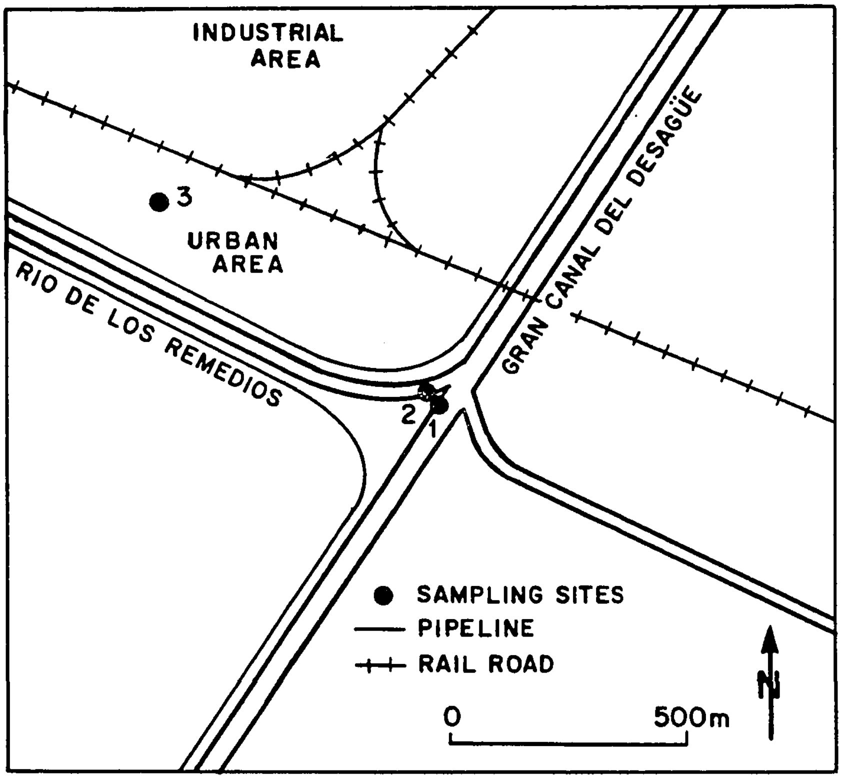

Figure 3.2. Selected study site at the junction of Gran Canal and Rio Remedios.

Rio de los Remedios, and 1,000 m west of the Gran Canal del Desagüe. The sites are hereafter referred to as the Gran Canal (GC), Rio Remedios (RR) and Urban Site (US).

These locations offered the opportunity to sample in an area where a mixture of domestic, commercial and industrial liquid wastes are disposed to the sewage canals without treatment. The Gran Canal receives mainly domestic and commercial liquid wastes since it originates close to a commercial area in downtown and crosses a populated housing area. The western portion of the Rio Remedios receives similar wastes in addition to a wide range of industrial wastes since it crosses one of the main industrial areas in the northern portion of the MCMA, located north of the D.F. and south of Estado de México. A great diversity of industries is located in this area.

Several gas and oil pipelines cross the study area, located at both sides of the western part of Rio Remedios, a few meters away from the canal (Figure 3.2). These originate at a Petróleos Mexicanos Refinery (PEMEX, Refineria 18 de Marzo) which was operating in the Azcapotzalco area from 1948 until 1991. An outfall of wastewater from the refinery to the Gran Canal is located at approximately 2 km north of the study area.

There are seasonal variations in the direction of the flow of the Gran Canal: during the dry season (November-April) it flows from south to north, and during the rainy season (May-October) it flows from north to south. This change is due to the operation of the Deep Drainage System (described in Chapter 2), which occurs only during the rainy season (DDF, 1988b).

Field Methods

Sample Acquisition

Field work was conducted by team effort during June 1991. The team consisted of R. Ingleton (a technician from the University of Waterloo), C. Pitre (an M.S. student from the University of Waterloo), D. Silva (a technician from the Institute of Geophysics, UNAM) and the author.

The techniques used in this project were exclusively portable, hand-operated methods, developed at the University of Waterloo (Rudolph et al., 1991; Starr and Ingleton, 1992). These techniques were designed for sampling and installing equipment in unconsolidated materials without the use of a drill rig.

Continuous core samples were taken as schematically illustrated in Figure 3.3. Cores were taken using a portable 2" (5.08 cm) core rod, which was previously used successfully in the Basin of Mexico clays. The coring assembly consisted of an inner piston that was held immobile via a cable secured at ground surface. The thin-walled aluminum core tube was driven past the piston into the sediment by a hand operated gas-powered jack-hammer. Once the core tube was driven to its limit of 1.5 m (5'), it was extracted by a light chain hoist mounted at surface. The piston helped to

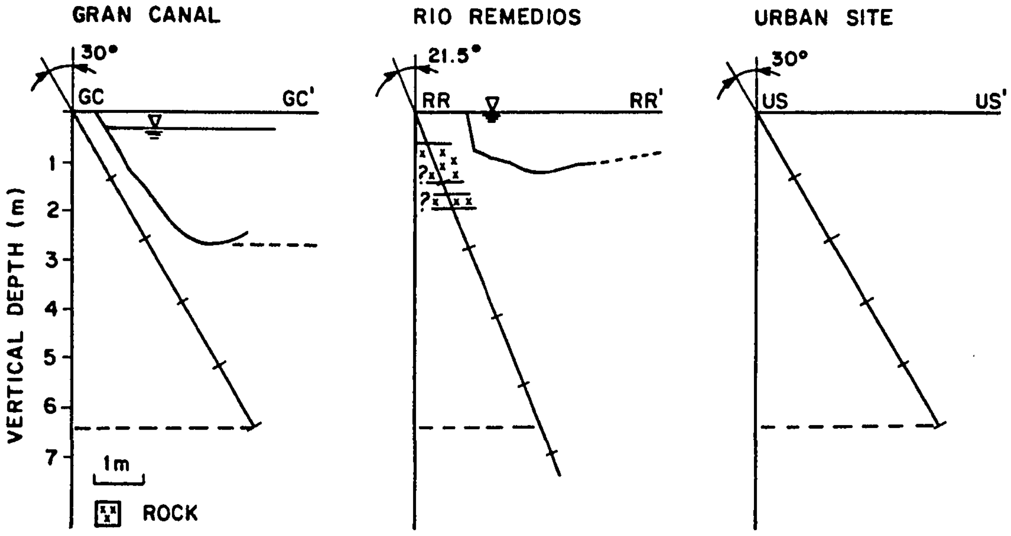

Figure 3.3. Sampling sites cross section.

retain the contents inside the aluminum tube by vacuum. For progressively deeper samples, the core barrel was driven down the same borehole and the process repeated for the next 1.5 m.

Scaffolding and boards were arranged to allow the coring to occur at and angle of 30° from the vertical. At the Gran Canal site, the coring was conducted perpendicular to the axis of the canal, as illustrated in Figure 3.3. At the Rio Remedios site, surface constraints were such that the coring had to occur at an angle of 47° from perpendicular to the axis of the canal. Figure 3.3 indicates that, when projected onto the vertical section perpendicular to the canal, the core could appear to be taken at an angle of 21.5° from the vertical. At the Urban Site, the coring was conducted roughly parallel with the axis of the Gran Canal. Five cores were taken in sequence for a total core length of 7.5 m. Because of the coring angle, the vertical maximum depth below ground surface reached by the cores was 6.5 m.

Two parallel cores were taken at each site, approximately 30 cm apart. The 1.5 m aluminum tubes containing cores were capped immediately after acquisition with plastic caps, labelled and kept on ice until transported to the laboratory. Samples were stored thereafter in a cold room at 4°C.

Sample Processing

The 1.5 m long cores were divided into sections of different length according to the analysis to be performed. As shown in Figure 3.4, one of

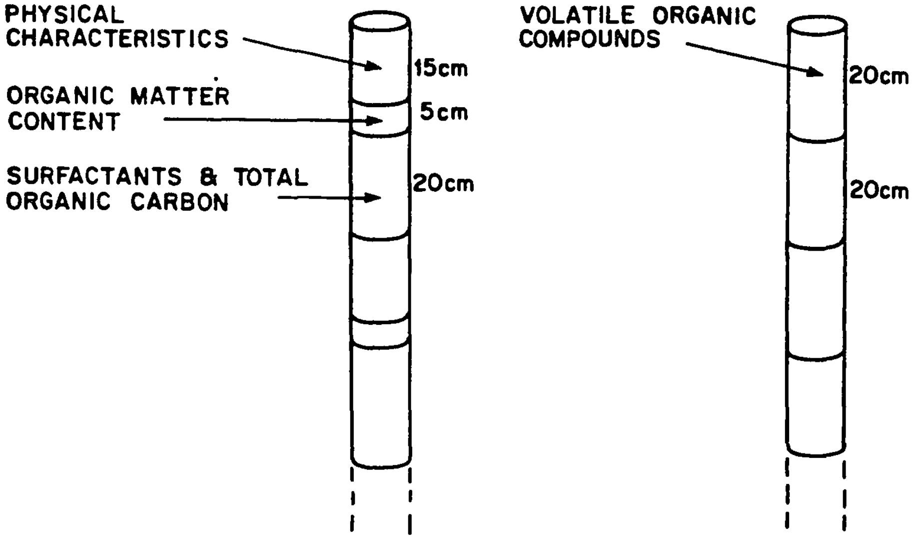

Figure 3.4. Subdivision of core pairs for analyses.

the pair of cores was divided into subsections for analysis of physical characteristics (15 cm), organic matter (5 cm), and surfactants and total organic carbon (TOC) concentrations (20 cm). The other core was divided into 20 cm sections for volatile organic compounds (VOCs) determinations. Before subdivision, approximately 5 cm from each end of the cores were discarded, in order to avoid potential contamination or degradation of the sample.

For core subsamples designated for analysis of surfactants and TOC or for analysis of VOCs, the samples were processed to separate some of the pore water from the solids. The pore water was then analyzed as described later. The technique of Patterson et al. (1978) was used to extract the pore water samples. This technique essentially involves using a stainless steel device to squeeze the cores and produce the water, as illustrated in Figure 3.5.

Some adaptations to the stainless steel squeezer allow the sample to be squeezed while remaining in the 20 cm section of the aluminum tube in which it was taken. This reduces the potential for sample contamination and for loss of volatile constituents from the sample. Stainless steel squeezers also minimized sorption of the organic chemicals to the squeezer material. At the bottom of the core section, as shown in Figure 3.5, a filter paper setup was used to prevent the clayey solids to escape (two Whatman No. 2 filters sandwiched between two stainless steel screens).

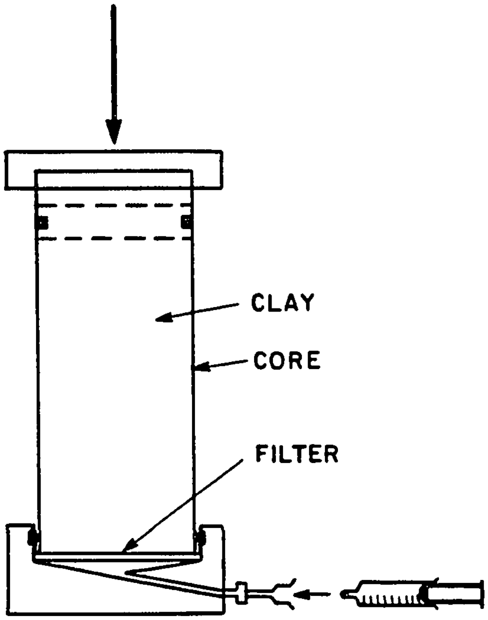

Figure 3.5. Schematic of stainless steel squeezer.

Samples of pore water were obtained by placing 20 cm sections of sediment cores in the mechanical squeezer, which was in turn placed in a metal frame. Two squeezers and two metal frames were operated simultaneously. Pressure was applied to each of the squeezers using a 4 ton car jack. This compressed and partially dewatered the clays. In order to reduce the potential for contamination, approximately the first ml of expelled water was discarded. The additional water obtained was collected directly into a syringe screwed into the squeezer bottom part. The syringes used are discussed below. The syringe allowed the samples to be collected with no headspace, a necessary feature to avoid loss of VOCs. After collection, the sample was expelled from the syringe directly into a borosilicate glass vial which was immediately sealed with a silicon-teflon septum and a screw cap. All the squeezing manipulations and sample transfer steps were conducted in a cold room at 4°C.

Preliminary studies to determine squeezing time showed that water extraction could continue for approximately 6 days, when additional pressure was applied each hour. However, the majority of the liquid (50% to 60%) was obtained during the first 24 hours. Therefore the following methods were adopted for squeezing specific samples.

For VOCs it was important to collect the sample in the shortest possible time, to minimize potential volatilization of compounds and loss, as well as to avoid potential problems resulting from leaving the system unattended overnight. Therefore, for collection of VOCs samples the pressure adjustments were done each 30 minutes, and sample collection occurred in approximately 6 hours. The volume of water obtained in this manner varied with the core segment, presumably because of the variation in compressibility of the clays. If more than 20 ml were obtained, then 20 ml of the water were transferred into a 25 ml vial. If less than 20 ml were obtained, then 4 ml were transferred into a 5 ml vial. Reasons for this choice of sample volumes and vial size are discussed later at the VOC analysis section. VOCs samples were analyzed the same day as obtained.

For surfactant and TOC samples, for which volatilization is not such an important issue, squeezing was completed in 24-48 hours, obtaining 40 ml pore water samples. This was done by applying pressure at approximately 60 minutes intervals for surfactants and TOC. The samples were collected directly into a syringe screwed into the squeezer bottom part. After collection, samples were transferred to 40 ml borosilicate glass vials which were immediately sealed with a silicon-teflon septum and a screw cap leaving no headspace.

Considering the small volumes of water produced by squeezing and the potential sources of contamination, extreme care was taken during squeezer cleaning and assembly as recommended by Rodvang (1987). Between squeezing runs, all squeezer parts, including o-rings, were thoroughly washed and dried. All parts of the squeezers that would be in contact with the clay sample were rinsed with hexane, methanol, nitric acid at 10%, tap water and deionized water. Parts were manipulated with surgical latex gloves previously rinsed with deionized water. Once rinsed, squeezer parts were put in an oven shortly to dry before assembly.

Experimental Methods

Clay Properties

Subsamples of the clayey media were taken from the cores and analyzed for the following characteristics: solid density (ρ_s), porosity (θ), and organic matter content (f_{om}). The methods are described below.

Solid Density. The solid density (ρ_s) was determined at the Soil Mechanics Laboratory, Institute of Engineering, UNAM, following the Soil Mechanics Manual for Soil Analysis (CNA, 1990).

Representative 200 g subsamples of dried soils were sieved through No. 4 (4.69 mm) sieves and put in porcelain dishes. Samples were then crushed and homogenized using a mortar and pestle to a size that could pass a No. 40 sieve (0.420 mm). They were then dried in an oven at 110°C for at least 18 hours, and put in a desiccator to cool to room temperature. Then 60 g subsamples were prepared using a balance; the weight of the dry sample was recorded as W_s.

Several 500 ml volumetric flasks were individually calibrated to determine the exact mass of degassed, distilled water contained in them when they were filled to the inscribed mark (the measurement was made at the temperature of subsequent analysis). The weight of each flask filled with water was recorded.

Sample analysis proceeded as follows. One of the calibrated flasks was partly filled with approximately 100 ml of distilled water, recording the weight as W_m. The dry soil was deposited into the flask using a glass funnel, and the total weight of the flask after adding the solids recorded as W_{ms}. Material adhering to the walls of the flask was washed down into the flask with distilled water. The flask was heated in a water bath to approximately 100°C in order to liberate gases trapped in the soils. The flask was then taken out of the water bath and cooled to room temperature. The total volume was then adjusted to the inscribed line by adding degassed distilled water. Water adhering to the flask neck was dried with absorbent paper. The outside of the flask was cleaned and the flask reweighed, recording W_{mws}.

The solid weight (W_s) is the difference between the flask without solids (W_m) and the flask with solids (W_{ms}). Solid density was calculated as:

$$\rho_s = \frac{W_s}{W_s + W_{mw} - W_{mws}}$$

where:

W_s = weight of dry soil

W_{mw} = weight of flask + water

W_{mws} = weight of flask + water + sample

Porosity and Volumetric Moisture Content. The volumetric moisture content is the ratio of the volume of water to the total volume of the sample, expressed as $\theta_w = V_w/V_T$. Porosity is defined as the ratio of volume of the voids to the total volume of the sample, V_v/V_T. Therefore, for saturated media the volumetric moisture content is equal to the porosity (Taylor, 1948; Freeze and Cherry, 1979). We will use the term porosity hereafter.

To determine the porosity the following procedure was followed. The wet weight of a soil sample was registered as W_w (grams). The sample was then put in an oven at 110°C to dry until a stable weight was obtained, i.e. to ensure complete dryness of the sample. Dry weight was then recorded as W_d. An OHAUS balance (Branweigh B3000D, P/N 76073-00) was used. The difference between wet and dry weight gave the water weight. The water volume was calculated by assuming its density to be 1 g/cm^3. Total volumes (cm^3) were obtained for each sample by measuring the length of each core section and assuming that the tubes were perfectly cylindrical (2" diameter). The porosity (volumetric water content) was calculated as the ratio of the water volume to the total volume.

Organic Matter Content. The organic matter content of a solid sample, previously dried in an oven at 110°C, was assumed to be equal to the mass lost upon ignition in a muffle oven at 550°C. The method was that for determining total solids, fixed solids and volatile solids in solid and semisolid samples (APHA, 1985). The fraction of organic matter (f_{om}) is given by the ignition mass loss divided by the total initial dry mass.

Surfactant Analysis

Pore water samples were analyzed for anionic surfactants following the Anionic Surfactant as Methylene Blue Active Substances (MBAS) method, according to APHA (1989). This method is not specific for linear alkyl sulfonates (LAS) or alkyl benzene sulfonates (ABS), but is used for environmental samples as an indicator of total anionic surfactant concentration. Positive interferences result from other organic sulfonates, organic sulfates, organic carboxylates, phenols, and inorganic ions such as thiocyanates, cyanates, nitrates, and chlorides. Thurman (1992) found that these interferences are generally minimal for environmental samples. Negative interferences can result from the presence of cationic surfactants and cationic materials such as amines, because they compete with the methylene blue in the formation of ion pairs (APHA, 1989; Field et al., 1992a).

In this method, excess methylene blue is added to an acidified sample. The sample is then extracted three times with chloroform. The combined chloroform extracts are backwashed with distilled water and then analyzed by spectrophotometry. The method is applicable to MBAS concentrations as low as 0.025 mg/l (APHA, 1989). Dodecyl benzene sulfonic acid (sodium salt, 80% purity, Sigma Lot 46F0544, D-2525) was used as a standard.

Clarification of the sample was accomplished by adding aluminum hydroxide solution ($Al(OH)_3$) to a selected volume of sample (from 5 ml to 20 ml) until the sample would clear by sedimentation after mixing. A maximum of 3.5 ml of the 156 g/l $Al(OH)_3$ solution was required. Samples were then filtered through Whatman No. 2 paper filters. The samples were shaken to observe foaming in order to select the volume of subsample to use for analysis; this visual technique was recommended by a commercial laboratory, Investigación y Desarrollo de Estudios de Calidad del Agua, S.C. (González, 1991) to ensure the total surfactant mass to be within the appropriate range for analysis. For very abundant observed foaming, 5 ml of sample was assumed to contain a total mass of surfactant that could readily be quantified. For lesser but still abundant foaming, 10 ml to 20 ml of sample were assumed to contain a total mass of surfactant that could readily be quantified. The water samples volumes used were in the range of 5 ml to 20 ml since all samples showed abundant foaming.

Standards and samples were diluted to 100 ml with distilled water. Extractions of this volume were conducted in the separatory funnels. The standard solutions, which produced total masses of ABS ranging from 10 μg to 80 μg, were analyzed using a Spectronics 20 Spectrophotometer, Serial No. 0913539D. Transmittance was determined at 652 nm against a blank of chloroform, from which absorbance can be calculated as the inverse logarithm of transmittance.

VOC Analysis

Pore water samples were analyzed for VOCs, such as 1,1-dichloroethylene (DCE), 1,1,1-trichloroethane (TCA), trichloroethylene (TCE) and tetrachloroethylene (PCE). A static headspace technique for extracting VOCs from samples was used, modified from Method 3810 (U.S. EPA, 1986). This method is recommended for screening samples prior to using the purge and trap method. However, since there was no purge and trap concentrator available for use in Mexico in this work, the headspace technique had to suffice.

As described before, sample was transferred from the syringe in which it was collected into a sealed glass container, leaving a fixed percentage (20%) of the total volume as headspace in either 5 ml or 25 ml borosilicate glass vials. A 20% headspace was selected to allow a high gas concentration while also providing a headspace volume which was significantly greater than the volume to be withdrawn for gas chromatography analysis.

After an equilibration period, analysis of each sample was conducted by withdrawing a known volume of headspace using a gas-tight microsyringe and then injecting the volume into a gas chromatograph (*GC*). On the basis of preliminary tests with standards of the compounds of interest, the U.S. EPA headspace method was modified to accommodate the constraints of the available analytical equipment. The samples were equilibrated in a water bath at 65°C for 40 minutes. The headspace sample volume analyzed was 10 μl, since the largest syringe needle that would fit in the *GC* injection port was that of the available 10 μl gas-tight syringes.

The *GC* was an SRI Instruments Gas Chromatograph, Model 8610, equipped with a DB-624 fused silica capillary column (0.53 mm megabore, 30 m long), and an Electron Capture Detector (ECD) with a ^{63}Ni source. The system was operated with a special mixture of carrier gas, 5% methane in 95% argon (INFRA, Mexico). The *GC* oven temperature was initially held at 30°C for 2 minutes, then ramped at 8°C per minute to 200°C, with a total time for each run of 23.5 minutes.

The ECD output was collected and integrated by a microcomputer running SRI's Peaksimple II chromatography software. The output was also recorded on a dot matrix printer along with the interpretation produced by the software. It was noted that the baseline of the chromatogram was relatively noisy, presumably because of low quality carrier gas, unavailability of gas cleanup traps, and power line fluctuations. However, after considerable work with standards, it was determined that the halogenated compounds could be analyzed reliably, even though with relatively high detection limits.

No formal studies were conducted to determine the detection limit in this work. Nevertheless they were estimated based on analysis of individual and mixed standards of the analytes of interest. These analyses were conducted on different days and at several low concentrations. The resulting chromatograms were carefully examined to estimate the minimum concentration that could be reliably assumed to correspond to actual detection of the analyte (versus occasional integration of baseline noise by the software). The detection limits roughly estimated this way for the procedure outlined above were the following: 10.0 μg/l for DCE, 0.5 μg/l for TCA, 1.0 μg/l for TCE, and 0.1 μg/l for PCE. Controls of distilled water were run every day to demonstrate glassware, reagents, column and detector were interference-free.

Two types of syringes were tested for squeezed water collection. The glass syringes plunger did not seal correctly and the water leaked. It was assumed that this leak would also allow escape of VOCs, so the glass syringes were judged inappropriate for this study. Therefore 20 ml polypropylene body and end plunger with pharmaceutical-grade rubber plunger tip syringes, which were readily available when squeezing had to be completed, were used for water collection.

The polypropylene syringes were later tested by Dr. R. Allen from the

University of Waterloo, Canada. Stock solutions of DCE, methylene chloride, CTET, TCE and PCE prepared in methanol were used to prepare an aqueous solution containing all compounds. Since the *GC* sensitivity is different for each compound, initial solution average concentration was 2,939.8 μg/l for DCE, 11,912.8 μg/l for methylene chloride, 22.7 μg/l for CTET, 199.2 μg/l for TCE and 43.4 μg/l for PCE. The aqueous solution was placed, using a method to minimize volatilization, into the polypropylene syringes and glass vials. The glass hypovials served as controls. After equilibration for 20.8 hours at 4°C, a liquid-liquid micro-extraction was carried out for samples and controls in 15 ml glass hypovials with 2.5 ml of pentane. The solution was transferred from the syringes to the glass hypovials which were then sealed with aluminum crimp caps and teflon lined septa and analyzed by *GC*/ECD (Varian 3400, column DB-64).

Results and Discussion

Clay Properties

The measured characteristics of the soil matrix are shown in Table 3.1. These include solid density (ρ_s), porosity (θ), and fraction of organic matter (f_{om}).

The measured solid density varies slightly for each site, ranging from 2.10 g/cm^3 to 2.74 g/cm^3. In general, the individual subsample analyses are within one standard deviation of the mean for each site. Furthermore, the

Table 3.1. Soil matrix characterstics, solid density (ρ_s), porosity (θ), and organic matter fraction (f_{om}).

DEPTH (m)	ρ_s g/cm^3	θ %	DEPTH (m)	f_{om} %
GRAN CANAL				
-0.20	--	--	-0.28	26.05
-0.55	2.40	64.33	-0.63	8.40
-0.89	2.23	51.07	-0.97	36.39
-1.22	2.53	65.11	-1.29	9.37
-1.59	2.55	73.78	-1.67	9.41
-1.93	2.57	69.92	-2.02	7.03
-2.28	2.55	84.03	-2.36	11.82
-2.75	2.63	82.34	-2.83	10.43
-3.09	2.71	91.87	-3.17	2.61
-3.44	2.58	77.36	-3.52	15.64
-3.78	2.59	81.20	-3.86	12.63
-4.22	2.55	91.38	-4.31	17.40
-4.57	2.57	93.09	-4.65	13.45
-4.92	2.54	92.45	-5.00	13.30
-5.34	2.59	91.97	-5.42	9.45
-5.69	2.65	73.73	-5.77	7.84
-6.03	2.67	90.51	-6.11	9.67
-6.37	2.47	91.78	-6.45	7.11
MEAN	2.55	80.35		12.67
S.D.	0.11	12.50		7.77
RIO REMEDIOS				
-0.08	2.33	--	-0.16	14.31
-0.41	2.42	71.20	-1.33	5.83
-1.94	2.66	53.00	-2.03	5.53
-2.29	2.65	53.10	-2.37	5.24
-2.76	2.55	89.50	-2.85	8.99
-3.11	2.63	90.80	-3.19	12.17
-3.46	2.59	90.00	-3.54	13.63
-3.80	2.59	91.80	-3.88	16.96
-4.24	2.52	91.50	-4.33	14.89
-4.59	2.56	89.90	-4.67	13.75
-4.93	2.34	89.60	-5.01	10.48
-5.34	2.63	91.50	-5.42	13.28
-5.69	2.57	87.20	-5.77	10.84
-6.03	2.52	85.00	-6.11	10.25
-6.37	2.53	90.00	-6.45	7.52
MEAN	2.54	83.15		10.91
S.D.	0.10	13.78		3.68
URBAN SITE				
-1.46	2.74	42.90	-1.54	2.64
-1.81	2.70	70.30	-1.89	2.63
-2.15	2.10	81.00	-2.23	6.00
-2.49	2.62	87.40	-2.67	7.37
-2.93	2.59	88.60	-3.01	9.01
-3.27	2.59	87.90	-3.35	6.04
-3.62	2.58	82.90	-3.70	8.86
-4.08	2.68	91.30	-4.16	12.15
-4.42	2.70	92.90	-4.50	14.85
-4.77	2.71	91.30	-4.85	12.24
-5.11	2.57	91.60	-5.19	13.69
-5.51	2.65	90.00	-5.59	13.46
-5.86	2.36	90.80	-5.94	20.32
-6.20	2.73	63.60	-6.28	1.74
MEAN	2.59	82.32		9.36
S.D.	0.17	14.24		5.39
ALL MEASUREMENTS				
MEAN	2.56	81.84		11.12
S.D.	0.13	13.21		6.04

mean values of the solid density at each site are within 5% of each other. The mean values of solid density of the lacustrine materials are 2.55 g/cm^3, 2.54 g/cm^3 and 2.59 g/cm^3 at the Gran Canal, Rio Remedios and Urban sites respectively. Pooling all measurements for all three sites, the mean solid density is estimated as 2.56 g/cm^3. These values are close to the mean of 2.42 g/cm^3 reported for the Upper Clay Formation in Mexico City, and the mean of 2.70 g/cm^3 reported for the Upper Clay Formation at Texcoco (Marsal and Mazari, 1990).

Based on field and laboratory observations of the soil matrix and detailed core logging conducted by Pitre (1992) it was evident that the following depth intervals were composed of fill material rather than the lacustrine material: from ground surface to 2.26 m depth next to the Gran Canal, from ground surface to 2.50 m next to Rio Remedios (part of which are compacted materials), and from ground surface to 2.39 m at the Urban Site.

According to Pitre (1992) the water table is at 30 cm depth at the Gran Canal site and at 1.5 m at the Urban Site. The water table probably fluctuates slightly at these sites, but this was not confirmed in this work.

Porosity in the lacustrine clay matrix is high, generally ranging from 74% to 93% near the Gran Canal. In the sample taken at 5.69 m, the observed sand lenses explain the relatively lower porosity. Porosity is quite uniform in Rio Remedios, with values in the range of 85% to 92% below the fill zone. The same is true for the Urban Site, where values ranged from 82% to 93% except at 6.20 m where a lower porosity is observed for strata in which layers of sand alternated with clay.

Porosity in unconsolidated clay deposits generally ranges from 40% to 70% (Freeze and Cherry, 1979). Nevertheless, porosities of the clays in the Basin of Mexico have been reported between 80% and 90% (Marsal and Mazari, 1969). Specifically, in the Upper Clay Formation porosities are approximately 87% in the Mexico City area and 80% in the Texcoco area (Marsal and Mazari, 1990). Pooling all measurements from this work, the average porosity for the three study sites is 82%, which is in the range reported for previous work in the Basin of Mexico.

The organic matter content of the solids (f_{om}) in this study ranges from 2.6% to 36.4%, with an average of 12.7% for the Gran Canal site, 10.9% for the Rio Remedios site, and 9.4% for the Urban Site. Pooling all measurements, the average for the three study sites is 11%. In previous work, the f_{om} of the lacustrine sediments, in a different location within the basin, has been reported to range between 1% to 7% in most cases, with a maximum of 28% recorded at 71 m depth (Marsal and Mazari, 1969). It appears that the f_{om} values in the current work are higher than most of the values reported previously for the Basin. It is possible that this enhanced organic matter content results from inputs of organic matter from the canals. The Gran Canal has been in operation since the beginning of the century, and thus might be expected to have the most enhanced organic matter content. The Rio Remedios was a natural river used in recent years to dispose industrial and domestic wastes. It originally flowed from the west through an aqueduct that discharged in Lago de Texcoco. Due to subsidence problems the course was changed in the 1970s to its current location. Therefore comparing the average f_{om}, Rio Remedios is expected to be somewhat lower than the Gran Canal site, since exposure to sewage has been shorter. This is also the case of the Urban Site, at which the average f_{om} is lower than at the other two sites.

The TOC results are not presented or discussed in this dissertation. High concentrations of such determinations suggest interference by suspended solids due to improper filtration.

Estimated Sorption and Retardation

Organic carbon fraction (f_{oc}) estimates, average bulk density (ρ_b), and average porosity (θ) determinations are reported in Table 3.2. Also included in the table are estimated sorption distribution coefficient (K_d) and retardation factors (R) for DCE, TCA, TCE and PCE. Porosity and bulk density were not determined for the same core sections analyzed for organic matter content. Therefore the average value for these parameters in the sections immediately above and below the organic matter section were used in the retardation calculations.

Table 3.2. Measured parameters, fraction of organic carbon (f_{oc}), average bulk density (ρ_b), average porosity (θ), and estimated parameters, sorption distribution coefficient (K_d), and retardation factor (R).

DEPTH (m)	f_{oc}	ρ_b	θ	K_d DCE	R DCE	K_d TCA	R TCA	K_d TCE	R TCE	K_d PCE	R PCE
GRAN CANAL											
-0.28	0.15	0.43	0.32	9.52	13.79	19.04	26.59	19.65	27.40	47.76	65.17
-0.63	0.05	0.98	0.58	3.07	6.20	6.14	11.41	6.33	11.74	15.39	27.10
-0.97	0.21	0.99	0.58	13.30	23.59	26.60	46.17	27.44	47.61	66.71	114.29
-1.29	0.05	0.78	0.69	3.43	4.85	6.85	8.69	7.07	8.94	17.18	20.30
-1.67	0.05	0.72	0.72	3.44	4.46	6.88	7.92	7.09	8.14	17.25	18.37
-2.02	0.04	0.59	0.77	2.57	2.97	5.14	4.94	5.30	5.06	12.89	10.88
-2.36	0.07	0.44	0.83	4.32	3.26	8.64	5.53	8.92	5.67	21.67	12.36
-2.83	0.06	0.34	0.87	3.81	2.49	7.62	3.98	7.86	4.07	19.12	8.47
-3.17	0.02	0.40	0.85	0.95	1.45	1.91	1.90	1.97	1.93	4.79	3.27
-3.52	0.09	0.54	0.79	5.71	4.87	11.43	8.74	11.79	8.98	28.66	20.41
-3.86	0.07	0.36	0.86	4.62	2.91	9.23	4.81	9.53	4.93	23.16	10.56
-4.31	0.10	0.20	0.92	6.36	2.38	12.71	3.76	13.12	3.85	31.89	7.93
-4.65	0.08	0.19	0.93	4.91	1.98	9.83	2.95	10.14	3.02	24.65	5.90
-5.00	0.08	0.20	0.93	4.86	2.05	9.72	3.10	10.03	3.17	24.38	6.27
-5.42	0.05	0.46	0.83	3.46	2.89	6.91	4.79	7.13	4.91	17.33	10.50
-5.77	0.05	0.48	0.83	2.87	2.65	5.73	4.30	5.91	4.41	14.38	9.28
-6.11	0.06	0.23	0.92	3.53	1.87	7.07	2.74	7.29	2.79	17.72	5.36
-6.45	0.04	0.23	0.92	2.60	1.64	5.20	2.27	5.36	2.31	13.04	4.19
MEAN	0.07	0.48	0.79	4.63	4.79	9.26	8.59	9.55	8.83	23.22	20.03
S.D.	0.04	0.25	0.16	2.84	5.47	5.67	10.95	5.85	11.29	14.23	27.45
RIO REMEDIOS											
-0.16	0.08	0.63	0.27	5.23	13.34	10.46	25.67	10.79	26.45	26.23	62.87
-1.33	0.03	1.25	0.53	2.13	6.00	4.26	11.01	4.40	11.33	10.69	26.10
-2.03	0.03	1.24	0.53	2.02	5.73	4.04	10.45	4.17	10.75	10.13	24.70
-2.37	0.03	0.76	0.72	1.92	3.02	3.83	5.05	3.95	5.17	9.61	11.15
-2.85	0.05	0.26	0.91	3.29	1.93	6.57	2.85	6.78	2.91	16.48	5.64
-3.19	0.07	0.25	0.91	4.45	2.23	8.90	3.46	9.18	3.54	22.31	7.16
-3.54	0.08	0.24	0.91	4.98	2.29	9.96	3.57	10.27	3.65	24.97	7.45
-3.88	0.10	0.21	0.92	6.20	2.41	12.40	3.83	12.79	3.92	31.09	8.10
-4.33	0.09	0.24	0.91	5.44	2.41	10.88	3.81	11.23	3.90	27.30	8.05
-4.67	0.08	0.25	0.90	5.03	2.40	10.05	3.79	10.37	3.88	25.21	8.00
-5.01	0.06	0.23	0.91	3.83	1.97	7.66	2.94	7.91	3.00	19.22	5.86
-5.42	0.08	0.28	0.90	4.85	2.49	9.70	3.98	10.01	4.08	24.34	8.48
-5.77	0.06	0.35	0.86	3.96	2.61	7.92	4.22	8.17	4.33	19.87	9.09
-6.11	0.06	0.31	0.88	3.75	2.33	7.49	3.65	7.73	3.74	18.79	7.66
-6.45	0.04	0.31	0.88	2.75	1.97	5.50	2.94	5.67	3.00	13.79	5.86
MEAN	0.06	0.45	0.80	3.99	3.54	7.98	6.08	8.23	6.24	20.00	13.74
S.D.	0.02	0.36	0.20	1.35	2.99	2.69	5.98	2.77	6.17	6.74	15.00
URBAN SITE											
-1.54	0.02	1.19	0.57	0.96	3.02	1.93	5.05	1.99	5.17	4.84	11.15
-1.89	0.02	0.60	0.76	0.96	1.76	1.92	2.53	1.98	2.58	4.82	4.83
-2.23	0.03	0.37	0.84	2.19	1.95	4.39	2.91	4.53	2.97	11.00	5.78
-2.67	0.04	0.31	0.88	2.69	1.95	5.39	2.90	5.56	2.96	13.51	5.76
-3.01	0.05	0.30	0.89	3.29	2.12	6.58	3.23	6.79	3.30	16.51	6.60
-3.35	0.04	0.38	0.86	2.21	1.98	4.42	2.96	4.56	3.03	11.08	5.92
-3.70	0.05	0.34	0.87	3.24	2.26	6.47	3.53	6.68	3.61	16.24	7.34
-4.16	0.07	0.21	0.92	4.44	2.01	8.88	3.03	9.16	3.09	22.28	6.08
-4.50	0.09	0.22	0.92	5.43	2.27	10.86	3.54	11.20	3.62	27.23	7.36
-4.85	0.07	0.23	0.92	4.47	2.12	8.95	3.25	9.23	3.32	22.44	6.64
-5.19	0.08	0.23	0.92	5.00	2.26	10.01	3.52	10.32	3.59	25.09	7.31
-5.59	0.08	0.23	0.91	4.92	2.24	9.84	3.49	10.15	3.56	24.67	7.23
-5.94	0.12	0.61	0.78	7.43	6.80	14.85	12.59	15.32	12.96	37.24	30.07
-6.28	0.01	0.61	0.78	0.64	1.50	1.27	1.99	1.31	2.03	3.19	3.49
MEAN	0.06	0.42	0.84	3.42	2.45	6.84	3.89	7.06	3.98	17.15	8.26
S.D.	0.03	0.27	0.10	1.97	1.30	3.93	2.60	4.06	2.68	9.87	6.51
ALL MEASUREMENTS											
MEAN	0.06	0.45	0.81	4.00	3.73	7.99	6.51	8.25	6.68	20.05	14.87
S.D.	0.03	0.29	0.16	2.21	3.90	4.41	7.80	4.55	8.05	11.07	19.56

The mean values for estimated f_{oc} are 7% at the Gran Canal, 6% at the Rio Remedios, and 6% at the Urban Site. The mean value for all measurements was 6%. These results are high as compared to the mean value of 3.6% of organic carbon reported by Marsal and Mazari (1969) for the Mexico City soils.

Measured porosities in the sections immediately above and below the organic matter section range from 70% to 90% if the fill strata are ignored. The measured porosities are typical of the clay formation in the Basin of Mexico.

In order to compare the sorption potential of the various organic compounds of interest a crude calculation was done. For surfactants it was assumed that sorption is purely hydrophobic, that K_d can be calculated as $K_d = f_{oc} K_{oc}$, and that K_{oc} for ABS is similar to that for C-12 LAS (6400 l/kg as reported by Brownawell et al., 1991), since no reported K_{oc} values for ABS were found. Using the sorption coefficient equation, the estimated K_d for surfactants is in the order of 384 cm^3/g. Retardation is in the order of 217, based on mean values for ρ_b, θ, and estimated K_d.

The estimated K_d values for VOCs vary significantly at the sites due to the variation in the measured properties. Pooling all estimates of K_d (in cm^3/g), the mean values are 4.0 for DCE, 8.0 for TCA, 8.3 for TCE, and 20.0 for PCE. Estimated mean retardation factors are 3.7 for DCE, 6.5 for TCA, 6.7 for TCE and 14.9 for PCE.

Average K_d estimated values of the organic compounds of interest show the compounds that sorb more are the surfactants, followed by the VOCs in a decreasing order: PCE, TCE, TCA, and DCE. Comparing the retardation factor estimated for surfactants and VOCs, the surfactants retardation is about 15 times larger as compared to PCE, 32 times larger as compared to TCE, 33 times larger as compared to TCA, and 59 times larger as compared to DCE.

Tritium and Chloride Distribution

Depth profiles of two tracers, tritium and chloride (data kindly provided by Pitre, 1992), are shown on Figure 3.6 for the Gran Canal and Figure 3.7 for the Urban Site. No tritium or chloride were measured for the Rio Remedios site. At the Gran Canal site, the bottom of the canal is at approximately 2.95 m depth. The tritium peak has migrated deeper than the bottom of the canal and approximately coincides with the chloride peak. Therefore it was inferred by Pitre (1992) that ^3H was probably introduced to the ground from the canal. The chloride peak coincides with the bottom of the canal and also suggests a minimal downward movement has occurred, approximately 1.0 m.

At the Urban Site the tritium peak was observed at approximately 3.5 m depth and the water table at this site is typically at 1.5 m depth. Therefore the tritium peak has moved approximately 2.0 m from the water table. The

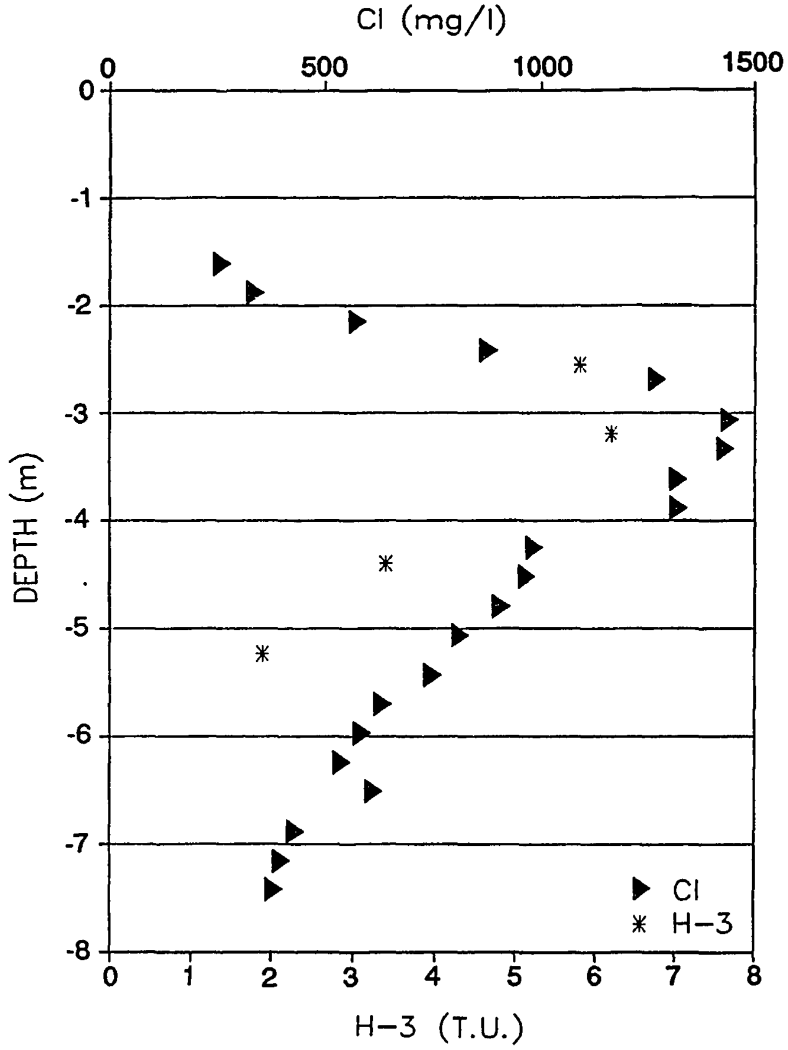

Figure 3.6. Depth profile of tritium units and chloride concentration versus depth at the Gran Canal site (Pitre, 1992).

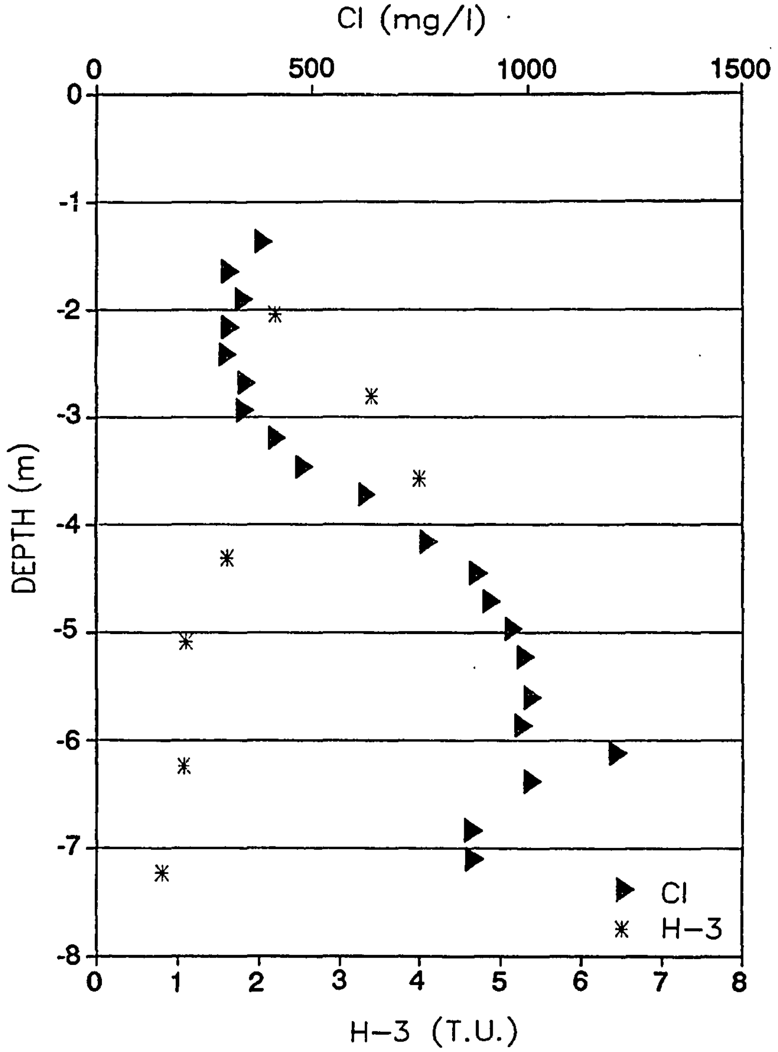

Figure 3.7. Depth profile of tritium units and chloride concentration versus depth at the Urban Site (Pitre, 1992).

chloride peak is located at approximately 5.0 m, 3.5 m below the water table. It has been inferred by Pitre (1992) that if the chloride peak has moved as a result of infiltration, then the peak in the tritium profile at the Urban Site seems to reflect the atmospheric tritium peak which occurred in 1953 in the northern hemisphere. This means that approximately 3.5 m of infiltration occurred.

The chloride data have not been described in more detail since it's distribution depends on the original concentrations as constituents of the natural lacustrine area. Some inferences will be made once this information is modelled by Pitre (1992). The tritium and chloride data (Pitre, 1992) show slight infiltration (25 cm) from the Gran Canal and migration of approximately 3.5 m and 5.5 m of tritium and chloride peaks respectively in the urban area as a result of infiltration.

Surfactant Distribution

A one-day sampling of the canal water at the Gran Canal showed MBAS concentrations in the range of 1.3 mg/l to 35.0 mg/l, with a mean value of 13.1 mg/l from triplicate analyses at four different times during a 12 hour period. The one-day sampling of the Rio Remedios canal water showed concentrations in the range from 0.4 mg/l to 50.9 mg/l. The mean value for the Rio Remedios water was 12.8 mg/l.

Figures 3.8, 3.9 and 3.10 show the depth profiles of surfactants at the

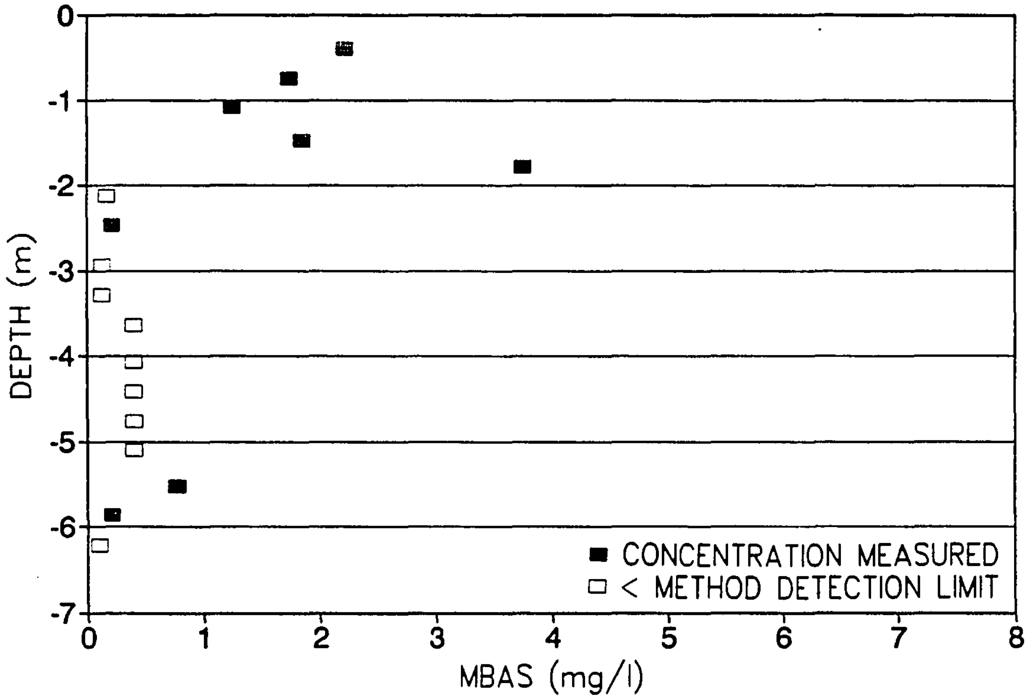

Figure 3.8. Depth profile of MBAS at the Gran Canal site. Hollow symbols are analyses of samples with concentrations at or below the MDL.

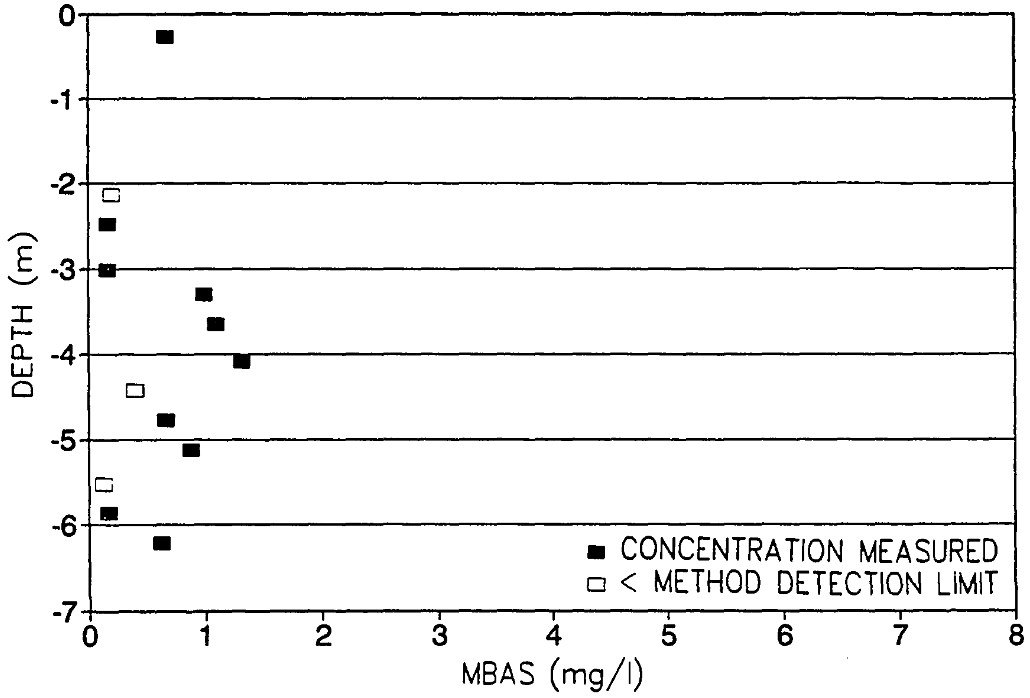

Figure 3.9. Depth profile of MBAS at the Rio Remedios site. Hollow symbols are analyses of samples with concentrations at or below the MDL.

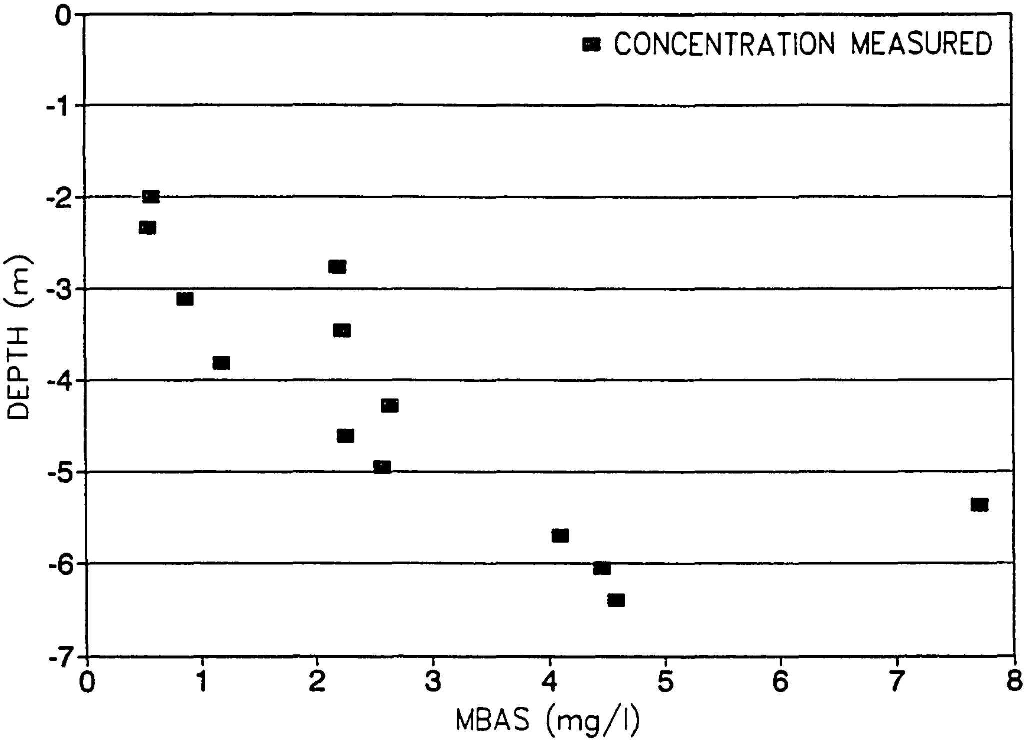

Figure 3.10. Depth profile of MBAS at the Urban Site.

Gran Canal site, the Rio Remedios site and the Urban Site, respectively. Filled symbols indicate the measured concentrations; the hollow symbols indicate the method detection limit (MDL) for analyses that were below the MDL. The MDL is not constant due to variability in the volume used for the surfactant analysis.

The profile beneath the Gran Canal shows variable but significant concentrations from surface to approximately 2.0 m depth, with values in the range of 1.3 mg/l to 3.7 mg/l. A smaller peak of MBAS is noted at approximately 5.5 m, with relatively low but detectable concentrations. The average concentration of MBAS for the upper 2.0 m at the Gran Canal site is 2.2 mg/l. Based solely on one-day sampling of the canal, the canal water appears to have surfactant concentrations about 10 times higher than found in the underlying pore water.

At the Rio Remedios site the surfactant profile shows more variation. MBAS concentration at the surface is about 0.7 mg/l, and below some hard strata in which it was not possible to core, sample concentrations varied in the range of 0.1 mg/l to 1.3 mg/l. Two conspicuous peaks were noted, one between 3.0 m and 4.0 m, and another at approximately 5.0 m depth. There is a slight increase in concentration at the bottom of the core, which suggests that the maximum penetration depth of these compounds is deeper than sampled in this work. The surfactant mean value at Rio Remedios is 0.6 mg/l. As at the Gran Canal site, the surfactant concentrations in the Rio Remedios one-day sampling are about an order of magnitude higher than the maximum concentrations found in the clay pore water.

At the Urban Site the surfactant profile is extremely variable, presenting distinct peaks at approximately 2.8 m, 3.5 m, 4.3 m, and 5.4 m. The general tendency of the profile is to increase in concentration with depth as shown in Figure 3.8. The MBAS concentration is in the range of 0.6 mg/l to 7.7 mg/l, showing in general higher concentrations than the pore waters at the canal sites. The mean MBAS concentration is 2.8 mg/l. The high concentrations may be due to leaking sewers, septic tanks or other pipelines that cross close to the sampling site. The soil matrix at this site is more heterogeneous than at the two canal sites, with several sand layers. At approximately 5.0 m, samples had a particularly fetid smell; this coincides with various sandy layers from 4.0 m to 6.3 m which may have been transporting sewage or septic tank effluent, both of which would be expected to have relatively high surfactant concentrations.

Three additional samples from the Urban Site (8.3 m, 9.4 m, and 12.7 m) were squeezed and analyzed for MBAS by Environmental Laboratories Inc., a commercial laboratory in Ontario, Canada. These work was conducted in July 1992, 12 months after the cores were collected. The measured concentrations at these depths were 1.9 mg/l, 2.0 mg/l and 1.6 mg/l respectively. Thus, assuming all MBAS data are correct and comparable, the MBAS profile at the Urban Site strongly resembles the chloride curve (Figure 3.7.).

The depth profiles differ from site to site, probably due primarily to variation in the soil properties (organic matter content, hydraulic conductivity patterns, etc.). The MBAS concentrations found in the clay pore waters adjacent to the sewage canals are in the range reported for similar studies of sewage impacts on groundwater in other parts of the world.

This study confirms that surfactants are present in the sewage canals that cross the MCMA, although this finding is by no means surprising. The surfactants have penetrated downwards into the adjacent clay matrix. Although at relatively low concentrations, these data are significant as they show the presence and migration of these chemicals into the clay formation which has generally been considered impermeable.

VOC Distribution

A limitation for the VOC determinations were the syringes used to collect the pore water samples, as mentioned in the VOC analysis section. Given that errors arising from sorption or desorption of compounds to the sampling or extraction materials have been reported (Reynolds et al., 1989; Gillham and O'Hannesin, 1990), some experiments were conducted with polypropylene syringes. These were done to check for potential sorption and/or desorption of organic compounds to or from the syringe material.

It should be noted that in the sorption experiments, standard solutions were in the syringes for approximately 20 hours, while the actual samples were in the syringe for a maximum of 6 hours. The experiments showed a removal of 51% of DCE, 16% of methylene chloride, 55% of CTET, 61% of TCE, and 77% of PCE.

According to Reynolds et al. (1989) the period between 10 minutes and 1,000 minutes (16 hours) is a critical sorption period since the difference in relative concentration could decrease from less than 10% in the first 10 minutes to approximately 30% in 1,000 minutes. No exact correlation between periods of time with the syringe test and the sample extraction was obtained since the materials and compounds tested by Reynolds et al. (1989) did not include hard polypropylene materials or pharmaceutical-grade rubber like the ones used in this study.

The tests conducted for desorption of compounds from the syringe material or the rubber plunger tip revealed no detectable concentration of the compounds of interest.

Although use of the polypropylene syringes is likely to have biased the measured results, the bias is clearly negative. This implies that if any VOCs are detected, then they are present in the analyzed pore water at a concentration which is equal to or possibly considerably greater than the measured concentration. Thus, the results reported below are primarily of use for determinations of presence of VOCs and identification of general trends.

The maximum VOC concentrations detected in a one-day sampling of the canal water were: 3 μg/l for PCE and 48 μg/l for TCE in the Gran Canal surface water. Concentrations of 5 μg/l for DCE, 2 μg/l for PCE, and 1 μg/l for TCE were detected in Rio Remedios surface water.

Profiles of the VOC concentration versus depth below ground surface at the Gran Canal represent the distribution of DCE (Figure 3.11), TCA (Figure 3.12), and PCE (Figure 3.13). TCE was not detected. VOC determinations below the Gran Canal were carried out down to 5.09 m depth. DCE was at or below the detection limit for the deepest twelve determinations, while TCA was at the detection limit for the deepest six determinations, and PCE for the deepest two analyses. It was assumed that no VOCs were present deeper than the sections analyzed, which might not be true due to a bias caused by sorption of the VOCs to the syringes used as described before.

The VOC results show penetration of some of these compounds down to approximately 5.0 m depth for PCE, specifically in the sampling site adjacent to the Gran Canal, where the concentration appears to decrease with increasing depth. The maximum concentration detected was 0.4 μg/l at approximately 1.80 m depth. TCA was detected down to about 4.0 m depth and DCE was detected at various depths down to about 3.0 m.

The general trend of the surfactants and PCE at the Gran Canal site is

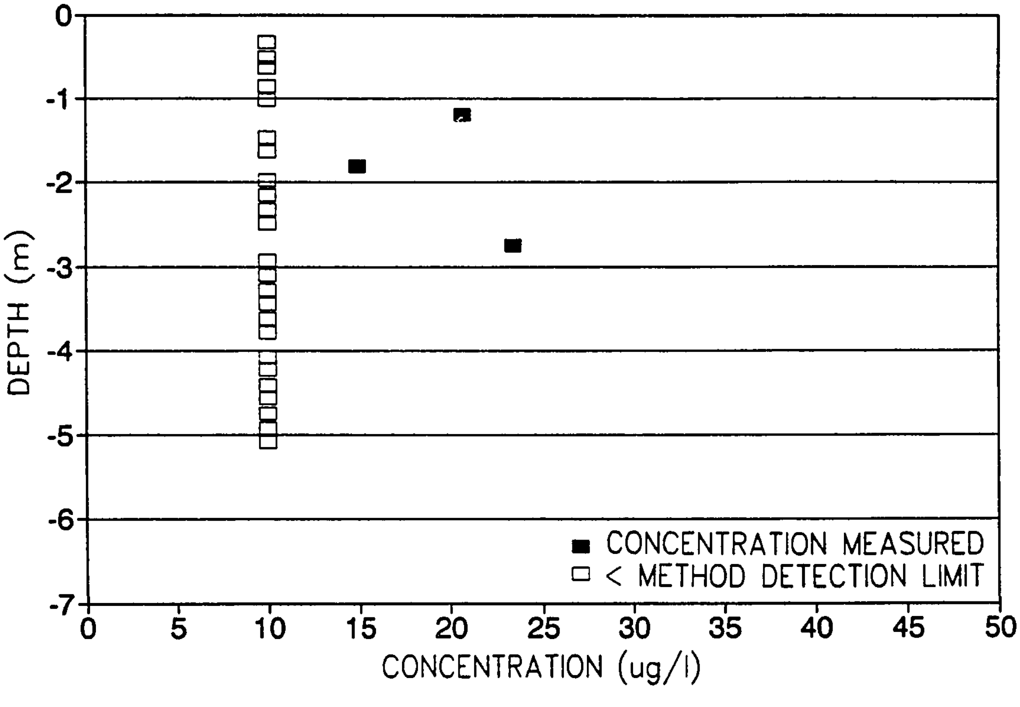

Figure 3.11. Depth profile of 1,1-DCE concentration versus depth at the Gran Canal site. Only three samples (solid symbols) had concentrations above the estimated detection limit of 10 μg/l (hollow symbols).

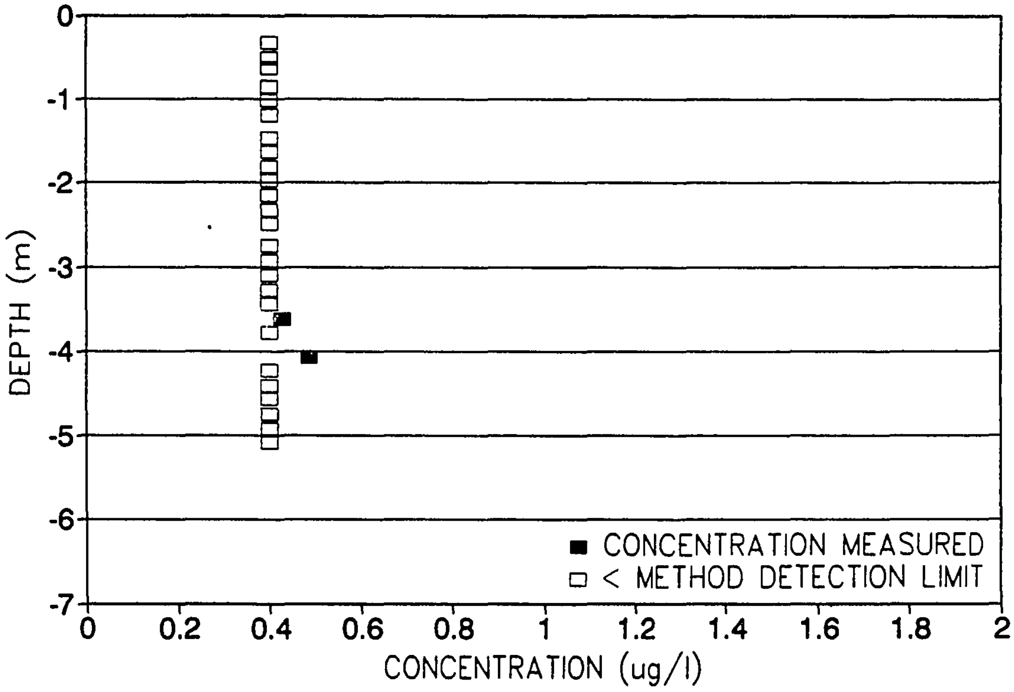

Figure 3.12. Depth profile of 1,1,1-TCA concentration versus depth at the Gran Canal site. Only two samples (solid symbols) had concentrations above the estimated detection limit of 0.4 μg/l (hollow symbols).

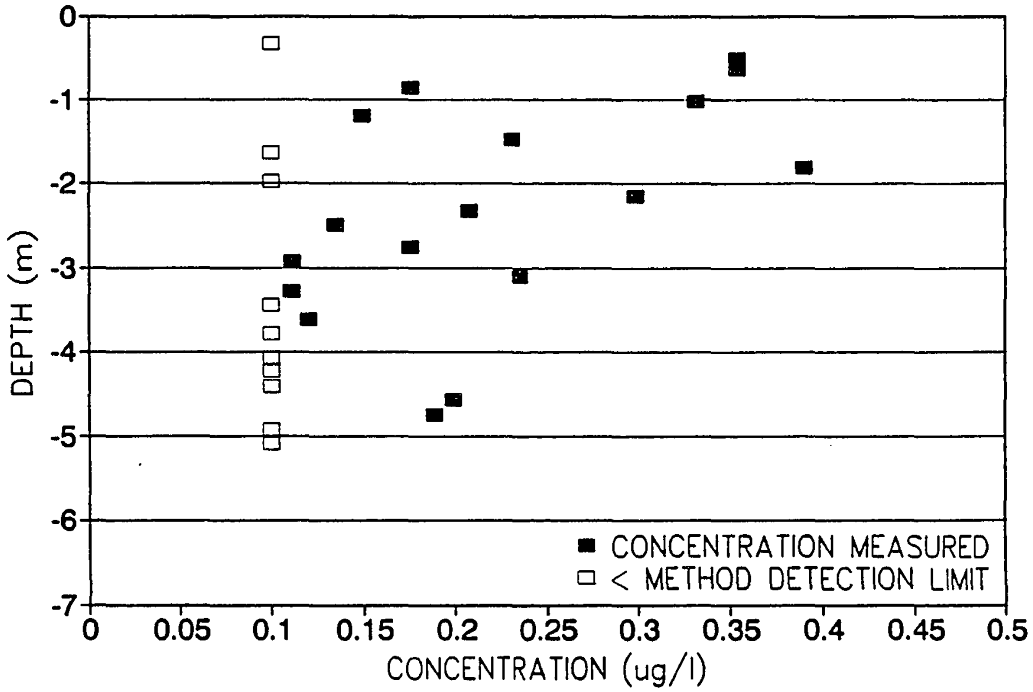

Figure 3.13. Depth profile of PCE concentration versus depth at the Gran Canal site. Estimated detection limit is 0.1 μg/l (hollow symbols).

similar, with higher concentrations in the first 2.0 m, which coincides with the fill strata. A peak was observed for PCE and surfactants at approximately 1.80 m, which coincides with a peak of DCE. Therefore, it is assumed that this is a permeable layer, composed of fill that allows the various compounds to migrate downwards until they reach the clay formation.

At the Rio Remedios site, DCE was noted at only 0.12 m depth, at a concentration close to the detection limit (Figure 3.14). TCA and TCE were not detected. Figure 3.15 presents the depth profile of measured PCE concentrations which were at or close to the detection limit. The analyses were conducted down to 2.43 m depth below ground surface at Rio Remedios, getting concentrations at the detection limit for the deepest three determinations done for PCE and the deepest eight determinations for DCE.

The Rio Remedios site was a particularly difficult site for sampling since some consolidated material (rock) was found from 0.54 m to 1.52 m and from 1.75 m to 2.13 m depth. The angle at which the coring was done due to space constraints had some influence on the core distance from the bottom of the canal. The closest point sampled below the Rio Remedios was at approximately 0.90 m, while the minimum distance from core to canal bottom at the Gran Canal was 0.40 m. Comparing the Gran Canal and the Rio Remedios site, some apparent differences were noticed. Rio Remedios presented a thin rock lining at the bottom of the canal in the sampling site, which the Gran Canal did not have. Fractures identified in the Gran Canal

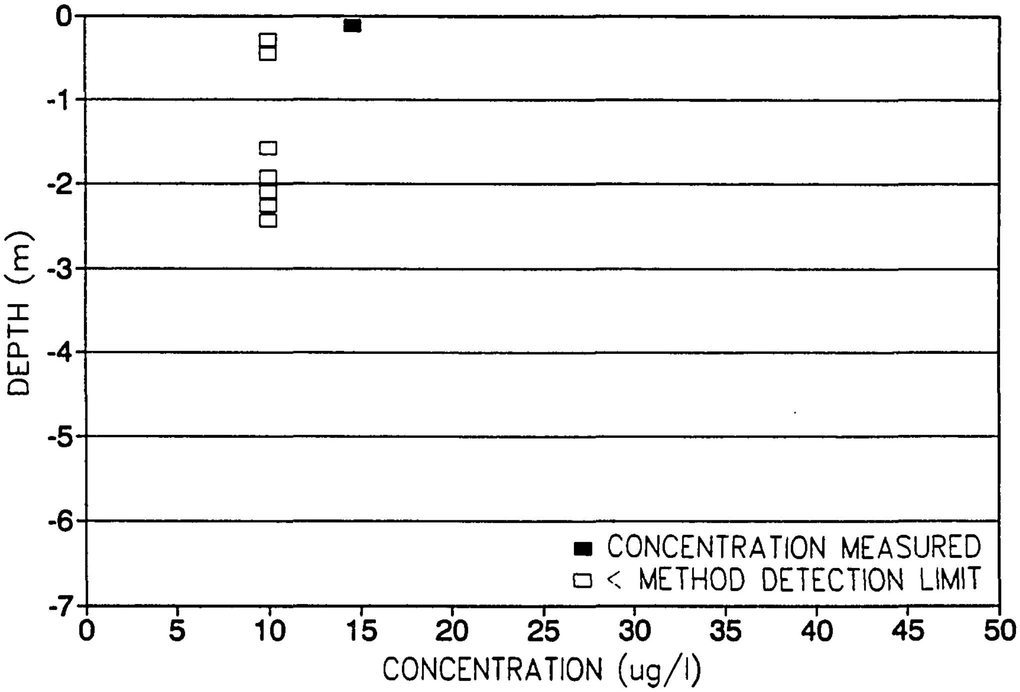

Figure 3.14. Depth profile of 1,1-DCE concentration versus depth at the Rio Remedios site. Only one sample (solid symbol) presented a concentration above the estimated detection limit of 10 μg/l (hollow symbols).

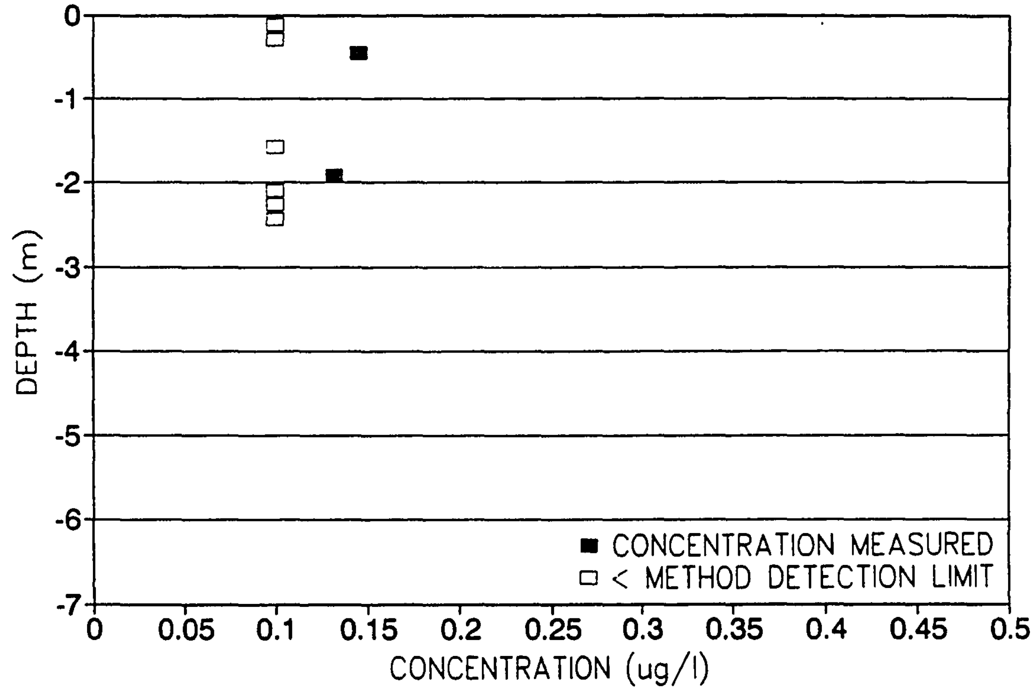

Figure 3.15. Depth profile of PCE concentration versus depth at the Rio Remedios site. Only two samples (solid symbols) had concentrations above the estimated detection limit of 0.1 μg/l (hollow symbols).

ranged from about 20/m to 100/m, no data are available from the Rio Remedios site for comparison. Fractures at the Urban Site ranged from absent to about 20/m, which let us assume fracturing in the Rio Remedios might be different than in the Gran Canal. More information on fracturing is needed to confirm this.

VOCs concentrations in Rio Remedios were expected to be higher than in Gran Canal since the former crosses one of the main industrial zones at the northern part of the MCMA, and receives a lot of the industrial wastewater with no previous treatment. Despite these expectations, the measured VOCs concentrations in Gran Canal pore waters were higher than in the Rio Remedios.

In the Urban Site only three core sections were analyzed (1.45 m to 1.79 m depth), since the first 1.50 m was fill. Halogenated organics were not detected in the three subsamples analyzed. No additional analyses were carried out.

At the Urban Site there are too few VOCs results to shed much insight. However, VOCs and surfactants appear to have completely different distributions. Surfactants were detected at the highest concentrations of the three sampling sites, whereas VOCs were not detected even at low concentrations. Fractures present in the US range from absent to about 20/m, which would have an influence on the movement of the compounds present.

At the Urban Site the surfactants followed the same trend than the chloride and no retardation was observed, the maximum peak for both type of compounds was between 5.0 m and 6.0 m depth. Three additional analyses confirmed these two compounds follow the same trend. There is no complete set of data, only three VOC measurements were done, not detecting any VOCs. The anionic surfactant data seem to contradict the hypothesis because the concentration rises with depth and this rise occurs below the tritium peak. Assuming surfactants were used since the 1940s while the other compounds were released until the 1950s, it is possible to say that surfactants accumulated in the lacustrine plain due to their higher sorption capacity and the high organic content of the soil matrix, when the hydraulic gradients were still upwards, and they started migrating with the other compounds when the gradients were reversed, which occurred in the 1970s (Pitre, 1992).

Furthermore the Urban Site is closer to the edge of the lacustrine clay plain, and the clay aquitard is thinner in this site, reflecting the negative hydraulic trends more drastically than the canal site, posing a more stronger downward force for the migration of these compounds.

Comparison of Surfactant, PCE and Tritium

The Gran Canal site is the site for which there is a complete set of data, and seem to be the only site that behaves as expected in this study.

Therefore, the surfactant, PCE and ^3H data were replotted to illustrate the movement of the different compounds.

When comparing the surfactant and PCE with the tritium profiles (Figure 3.16) some retardation was observed for the organics at this site. Anionic surfactants peak is at approximately 1.8 m depth and PCE maximum concentrations occurred between surface and 2.3 m depth as compared to tritium for which a peak was detected at 3.2 m depth. Retardation of these compounds may be occurring due to sorption, which may be driven by the fraction of organic carbon content. Tritium seems to have moved further than PCE, which has moved further than surfactants. This behavior is consistent with the general expectation, since tritium is non-sorbing, VOCs are predicted to sorb and surfactants are predicted to sorb even stronger based on literature values and estimates from f_{oc}. Therefore the Gran Canal site is consistent with the hypothesis of contaminants moving downwards influenced by the downward gradients. There appears to be evidence of differential retardation of VOCs and surfactants, but this interpretation is compounded by our uncertainty regarding the timing of the release of these compounds in the MCMA.

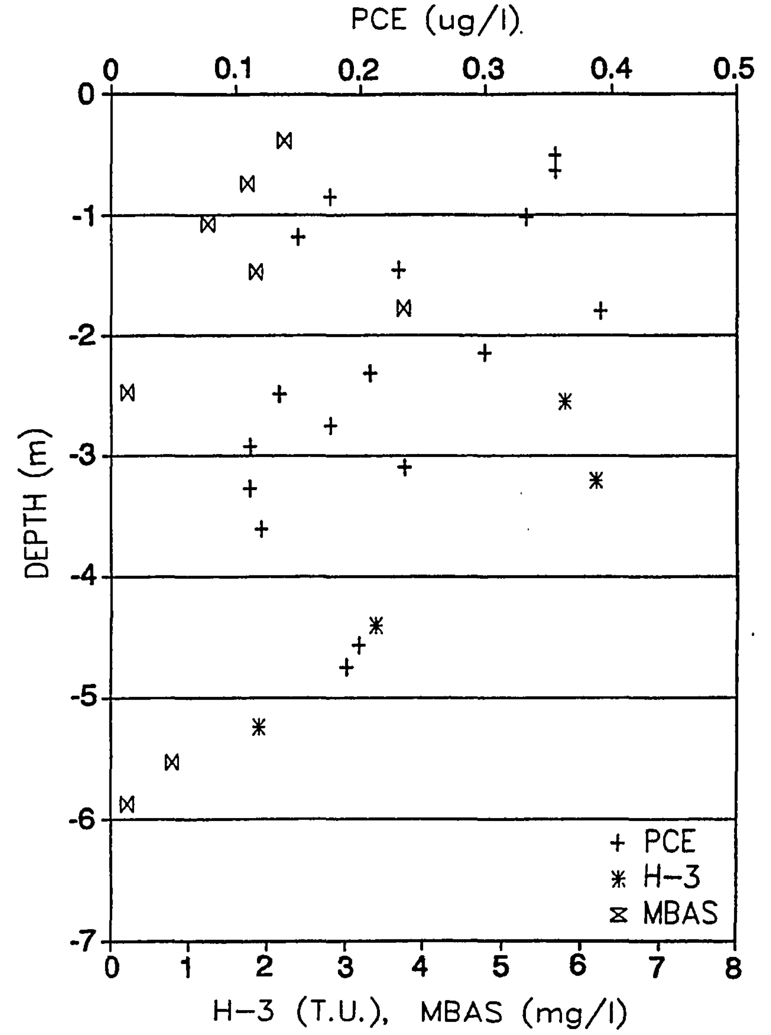

Figure 3.16. Depth profile of PCE, MBAS concentrations and tritium units versus depth at the Gran Canal site.

Conclusions

The various aspects examined in this field study conducted in the lacustrine area of the Basin of Mexico leads us to the following conclusions:

1. Several man-made organic chemicals including anionic surfactants (ABS) and volatile organic compounds (VOCs) (1,1-DCE, 1,1,1-TCA, and PCE), have penetrated downwards into the clay aquitard.

2. Although at relatively low concentrations, these data are significant since they show the presence and migration of organic compounds into the clay formation which has generally been considered impermeable.

3. Chemical distribution at the Gran Canal site is consistent with the hypothesis of downward migration of contaminants due to downward gradients.

4. The data for the Rio Remedios and Urban Site are not complete for the same depths, therefore the evidence of downward movement of organic compounds is weak.

5. Organic compounds appear to have been retarded during migration. No definite conclusions can be driven since the history of input and releases of the different compounds to the canals are not known precisely.

6. The inconsistencies observed with the surfactant data could be due to either positive (Urban Site) or negative (Gran Canal) interferences in the clays of the Basin of Mexico. Therefore the MBAS technique may have limited application for analysis of organic compounds of anthropogenic origin in this geographical area. Strongest reliable tracers of man-made chemicals appear to be the VOCs, especially PCE.

7. It is evident that there is a potential for downward migration of organic compounds. It has been confirmed at present and is likely to increase in rate with the overexploitation of the aquifer which affects the aquitard and contributes to downward migration of these contaminants.

This study gives an insight to a potential environmental problem, transport of organic compounds in the clay aquitard that could threaten the groundwater resources in the Basin of Mexico. The utilization, manipulation and disposal of organic compounds is more likely to increase in a metropolitan area like the MCMA and the likelihood of environmental problems related to these compounds will increase. Therefore more detailed, careful and diverse studies are needed regarding this issue in the Basin of Mexico in order to prevent more than remediate some of the potential environmental problems.

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Chapter 4

Policy Implications for Water Management

Introduction

Water resources have always been an important component of the ecosystem within the Basin of Mexico. During different historical periods water has played a fundamental role from the social, economic, and environmental perspectives. The area has changed from a lacustrine system to an urban area, that surpassed the natural capacity for water extraction in 1964 (Ramírez, 1990).

Nevertheless, at present Mexico City derives 75% of its water supply from an aquifer system that underlies the metropolitan area. Water withdrawal is exceeding water recharge by 45%, which is likely to be affecting water quality as well as causing subsidence problems in the urban area.

Downward migration of organic contaminants from the unlined sewer canals was investigated in a field study. Our results indicate that although concentrations of organic compounds are low, and the penetration distances shallow, these compounds are present and are moving downwards into the clay aquitard, which should represent a forewarning for governmental agencies regarding the groundwater reservoirs.

Master plans for water management in the Basin of Mexico have been suggested during different administrations, according to immediate needs. A well defined and continuous overall water management plan with long-term objectives is needed for the Basin of Mexico. Water management is under the jurisdiction of multiple agencies, with conflicting authority. In this chapter the local and federal authorities involved in management of the water resources are discussed, focusing on some of the main attributions and responsibilities of each agency. Some general policies and conclusions related to water management and monitoring are discussed within a framework for improving long-term water management in the Basin of Mexico.

Mexican Governmental Agencies

At present the main governmental agencies which manage water in the Mexico City Metropolitan Area (MCMA) include Departamento del Distrito Federal (DDF, Federal District Department), the main local agency with jurisdiction in México, D.F., and the Comisión de Aguas y Saneamiento del Estado de México (CASEM, Commission for Water and Sanitation of the State of Mexico) with jurisdiction in the Estado de México. The various federal agencies involved are: Secretaría de Agricultura y Recursos Hidráulicos (SARH, Ministry of Agriculture and Hydraulic Resources) through a decentralized commission, Comisión Nacional del Agua (CNA, National Water Commission) created in 1989, and the Secretaría de Salud (SS, Ministry of Health). In 1992 a new ministry was created Secretaria de Desarrollo Social (SEDESOL, Ministry of Social Development), which incorporates the previous Secretaria de Desarrollo Urbano y Ecologia (SEDUE, Ministry of Urban Development and Ecology). This new ministry will be in charge of urban development, ecology, and social development, and will manage some of the water resource related issues. The ministries have jurisdiction in the whole country, including the MCMA, where activities related to the water resource are coordinated with the local authorities. These agencies are involved in one or more of the following activities related to the water resources: extraction, distribution, supply, wastewater, treatment, and reuse.

DDF represents the most important water management agency in the MCMA. In practice this agency controls water extraction, supply and drainage. Within DDF the specific office in charge of the complex hydraulic system is DGCOH, Dirección General de Construcción y Operación Hidráulica (Office of Construction and Hydraulic Operation), created in 1978 (DDF, 1982).

The Mexican regulatory agencies involved in the management of water resources in the Basin of Mexico and the main attributions for establishing the technical standards for the various water uses, as well as surveillance and enforcement activities are summarized in Table 4.1.

Table 4.1. Mexican regulatory agencies regarding water issues.

	STANDARDS	SURVEILLANCE	ENFORCEMENT
Drinking water	SS	DDF + SS	SEDESOL[2,3]
Supply sources	SEDESOL[1]	DDF + SARH	SEDESOL[2,3]
Wastewater	SEDESOL[1] + SS + SARH	DDF + SARH	SEDESOL[2,3]
Industrial effluents	SEDESOL[1]	DDF + SARH	SEDESOL[2,3]
Hazardous waste	SEDESOL[1] + SS	SS + SEDESOL	SEDESOL[2,3]

DDF, Departamento del Distrito Federal = Federal District Department
SARH, Secretaria de Agricultura y Recursos Hidráulicos = Ministry of Agriculture and Hydraulic Resources
SEDESOL, Secretaria de Desarrollo Social = Ministry of Social Development
[1] Instituto Nacional de Ecologia = National Institute of Ecology
[2] Procuraduria Federal de Protección Ambiental = Environmental Enforcing and Prosecuting Branch
[3] Include other ministries if decided by [2]
SS, Secretaria de Salud = Ministry of Health

Mexican Legislation and Regulations

Water reservoirs are considered in the Mexican legislation as one of the nation's natural resources. Specific aspects of management of the resource and water quality issues are briefly discussed.

The principle of conservation of natural resources was integrated into the Constitución Política de los Estados Unidos Mexicanos (Political Constitution of the Mexican United States) in 1917. Water is considered one of the natural resources that belongs to the nation. Article 27 establishes that this resource is under the nation's authority, and that exploitation, use or development by individuals or corporations should be made in accordance with the Mexican laws (CPEUM, 1988).

From the environmental point of view, article 73, fraction XVI, refers to prevention and control of environmental contamination. This idea was incorporated into the Constitution in 1971. Article 25 refers to the protection of the environment, regarding the regulation of productive resources for the social and private sectors. This idea was integrated into the Constitution in 1983 and it is the only place where the environment is specifically cited in it (Brañes, 1987).

In Mexico three laws regarding environmental issues have been proposed and amended since the 1970's. The Ley Federal para Prevenir y Controlar la Contaminación Ambiental (General Law to Prevent and Control Environmental Contamination) enacted in 1971, was superseded in 1983 by the Ley Federal de Protección al Ambiente (Federal Law for the Protection of the Environment). In 1988 the Ley General del Equilibrio Ecológico y la Protección al Ambiente (General Law of Ecological Equilibrium and Environmental Protection) superseded the previous laws and continues to be valid (DOF, 1988a).

The Ley Federal de Aguas (General Law on Water) is the major legal order for water protection. It includes principles on equitable distribution and conservation of the hydraulic resources. It also regulates the exploitation, use and development of surface water and groundwater for the following uses: domestic, public services, industrial, agricultural, electricity generation and aquaculture (LFA, 1989).

In the Ley General de Salud (General Law on Health) the authority is given to SS to establish the technical standards for treatment of natural waters intended for human use and consumption, as well as enforcement of such regulations (LGS, 1987).

Drinking Water

SS amended and expanded drinking water regulations in 1988. These are part of the Reglamento de la Ley General de Salud en Materia de Control Sanitario de Actividades, Establecimientos, Productos y Servicios (Regulations for the General Law on Health about Sanitary Control of Activities, Establishments, Products and Services) (DOF, 1988b). A specific chapter on water and ice for human consumption is included. This considers 27 parameters, mainly bacteriological and inorganic determinations, including metal determinations. The only organic determinations incorporated in this regulation are phenols, MBAS, organic carbon extractable with chloroform and organic carbon extractable with alcohol. No other aromatic or aliphatic compounds are considered in the 1988 drinking water standards. In 1992 a technical standard regarding water sampling in public and private water systems for use and human consumption was issued by SS (DOF, 1992). This adds a few parameters to the drinking water standards, such as color, conductivity, carbon dioxide and pesticides. The only specific sampling procedures for organics mentioned are MBAS, phenols and pesticides.

Although organic compounds are not considered in the drinking water standards, several organic compounds are included in the Criterios Ecol6gicos de Calidad del Agua (Ecological Criteria for Water Quality) issued by SEDUE in 1989 (DOF, 1989a). This agreement considers 126 bacteriological, inorganic and organic parameters in supply sources for drinking water. It is specified that these are standards to be applied to water extracted from a water source that would require treatment before being used for human consumption. Organic compounds included in these standards are: organochloride and organophosphate pesticides, polychlorinated biphenyls (PCBs), polynuclear aromatic hydrocarbons such as toluene, dichlorobenzene, as well as dichloroethane, dichloroethylene (DCE), trichloroethylene (TCE), perchloroethylene (PCE), and carbon tetrachloride (CTET), among others. No specific sampling procedures for these compounds are mentioned. Existing standards for some VOCs, including the organic compounds of interest in this study, are summarized in Table 4.2.

Wastewater

During 1988 several standards were issued regarding maximum permissible limits for the disposal of industrial wastewaters (DOF 1988c,d,e,f), and are summarized in Table 4.3 by industry and parameters required. (Organic compounds considered in these regulations are marked with an asterisk).

From Table 4.3 it is possible to observe that organic compounds are parameters considered in the wastewater effluents of a few industries, i.e. copper and alloy laminated, extrusion and stretching, and sawmill products treatment. Even though other industries are likely to be using and disposing organic compounds, not all are considered in the technical standards, e.g. for the crude oil refining derivates and petrochemistry the organics considered are mercaptans; for the plastic products and synthetic polymers, polyamides, phenols and acrylic resins are considered among other parameters; in the textile industry no organics are mentioned.

Table 4.2. Mexican standards for selected VOCs in water supply sources (DOF, 1989a).

Compound	Maximum concentration (μg/l)
Benzene[a]	10 [b]
Carbon tetrachloride[a]	4 [b]
Chlorobenzene	20
1,2-Dichloroethane[a]	5
1,1-Dichloroethylene[a]	0.3
1,2-Dichloroethylene[a]	0.3
Methylene chloride	2 [b]
Tetrachloroethylene[a]	8 [b]
Toluene	14300
1,1,1-Trichloroethane[a]	18400 [b]
1,1,2-Trichloroethane[a]	6 [b]
Trichloroethylene[a]	3 [b]

[a] Persistent compound, bioaccumulates or carcinogen. Human exposure should be restricted to the minimum.

[b] Level extrapolated using a mathematical model. In future revisions this level may be modified.

Table 4.3. Mexican standards for industrial wastewater effluents (DOF, 1988c,d,e,f).

Standard code	Industry	Parameters
NTE-CCA-001/88	conventional thermoelectric stations	1,2,3,4,5,6,*7,8,9,10,67
NTE-CCA-002/88	sugar cane production	1,3,8,11,12,13,14,15,67
NTE-CCA-003/88	crude oil refining, derivates and petrochemistry	1,2,3,4,5,8,10,11,13,16, 17,18,*19,20,21,*22,23,24, 25,26,27,28,29,30,31,67
NTE-CCA-004/88	fertilizers manufacturing	1,2,6,8,13,15,20,21,32,33, 67
NTE-CCA-005/88	plastic and synthetic polymers	1,2,3,6,8,10,11,12,13,*19, 32,33,*34,35,*36,37,*38,67
NTE-CCA-006/88	flour	1,2,6,8,10,11,12,13,15,67
NTE-CCA-007/88	beer and malt	1,2,3,8,10,11,12,13,14,39, 40,67
NTE-CCA-008/88	construction asbestos	1,2,3,5,10,11,*19,29,67
NTE-CCA-009/88	milk and derivates	1,2,6,8,11,15,39,67
NTE-CCA-010/88	flat glass	1,2,3,6,8,11,13,41,67
NTE-CCA-011/88	gloss and blow glass	1,2,3,8,10,13,25,32,42,67
NTE-CCA-012/88	synthetic rubber, tires and inner tubes	1,2,3,8,10,11,13,14,18,41, 67
NTE-CCA-013/88	iron and steel	1,2,3,8,19,21,25,29,32,37, 42,43,44,67
NTE-CCA-014/88	textile	1,2,4,8,11,12,13,18,*19,40, 67
NTE-CCA-015/88	cellulose and paper	1,2,3,8,10,11,12,13,14,*19, 33,40,42,45,67
NTE-CCA-016/88	soft drinks	1,2,3,8,11,12,13,*41,67
NTE-CCA-017/88	metallic finishing	1,2,3,4,5,8,10,12,13,17, 18,25,27,28,29,30,32,43, 44,46,67
NTE-CCA-018/88	copper and alloy laminated, extrusion, and stretching	1,2,3,4,8,18,23,25,28,29, *47,*48,*49,*50,51,*52,*53, *54,*55,56,*57,67
NTE-CCA-019/88	sawmill products treatment	1,2,3,4,11,12,18,*19,23,25, 26,27,29,*47,*52,*58,*59, *60,*61,*62,*63,*64,*65,*66, 67
NTE-CCA-020/88	textile asbestos, friction and sealing materials	1,2,6,8,10,11,13,15,*19,33, 67
NTE-CCA-021/88	leather tanned and finishing	1,2,3,10,11,12,13,14,15,16, 17,18,67
NTE-CCA-022/88	animal slaughter and meat packaging	1,2,3,6,11,12,13,15,39,40,67
NTE-CCA-023/88	preserved foods bottling and canning	1,2,3,6,10,11,13,14,15,67
NTE-CCA-024/88	products from virgin cellulose	1,2,3,8,10,11,12,13,14,33,40, 67
NTE-CCA-025/88	paper fabrication from recycled cellulose	1,2,3,6,8,10,11,12,13,14,27, 33,39,40,67

Table 4.3. (cont.). Parameters.

1, pH
2, total suspended solids
3, oils and grease
4, copper
5, iron
6, phosphates
*7, PCB
8, temperature
9, chloride
10, COD
11, BOD
12, settleable solids
13, dissolved solids
14, alkalinity
15, total nitrogen
16, sulphide
17, hexavelent chrome
18, total chrome
*19, phenols
20, chloride
21, sulphate
*22, mercaptans
23, arsenic
24, cobalt
25, lead
26, mercury
27, nickel
28, cadmium
29, zinc
30, aluminum
31, vanadium
32, fluoride
33, heavy metals
*34, polyamides
35, silicates
*36, phenolic compounds
37, nitrogen compounds
*38, acrylic resins
39, turbidity
40, color
*41, surfactants (MBAS)
42, ammonia
43, cyanide
44, manganese
45, sulfite
46, barium
*47, benzene
*48, chloroform or trichloromethane
*49, 2,6-dinitrotoluene
*50, ethylbenzene
51, beryllium
*52, naphthalene
*53, anthracene
*54, toluene
*55, 1,1,1-trichloroethane
56, antimony
*57, methylene chloride
*58, benzofluoranthene
*59, dibenzanthracene
*60, benzanthracene
*61, benzopyrene
*62, phenanthrene
*63, fluoranthene
*64, fluorene
*65, pyrene
*66, indene
67, total coliforms
* organic compound

Hazardous Waste Disposal

Several criteria and procedures for hazardous waste disposal site installation and operation were issued by SEDUE in 1988. These contain the technical standards for the determination of hazardous waste, including: the list of hazardous waste (DOF, 1988g), the procedure to determine hazardous waste toxicity to the environment (DOF, 1988h), and the procedure to determine incompatibility between two or more wastes considered as hazardous (DOF, 1988i). Issues related to hazardous waste disposal site construction and operation are summarized in Table 4.4.

Policy Implications

The various governmental institutions responsible for water management in the Basin of Mexico have generated relevant information about different aspects of the water resources, but neither the information nor its implications have been made available to the public. The information we were able to compile and analyze for this project shows there is little knowledge on present and potential contamination of the soils or groundwater in the Basin of Mexico. There is no comprehensive examination of the potential routes by which contaminants may reach the groundwater resources that supply the MCMA.

The aquifer system in the Basin of Mexico is known to be overexploited by about 45%. The effect of this is reflected on water quality

Table 4.4. Standards related to hazardous waste disposal facility construction and operation in Mexico (DOF, 1988j,k,l, 1989b).

Standard code	Topic
NTE-CRP-008-88	Requirements for the site intended for hazardous waste disposal facility construction, excluding radioactive wastes
NTE-CRP-009-88	Requirements for hazardous waste disposal facility, complementary sections, design and construction
NTE-CRP-010-88	Requirements for the design, construction, and operation of confinement cells for hazardous wastes
NTE-CRP-011-88	Requirements for the operation of hazardous waste disposal facilities

degradation and subsidence problems. Water quality monitoring in the Basin of Mexico has been oriented towards surface water, water in the distribution system, and wastewater. Water quality has been based on traditional parameters such as indicator bacteria and inorganic compounds. There is a tremendous lag on organic compound monitoring. Some organic chemicals are regulated in the supply source for drinking water, for which analysis has been initiated. But, since organics are not included to date in the Mexican drinking water standards (DOF, 1988b), these parameters are not considered in the routine drinking water analyses. Lack of testing, however, does not indicate their absence in drinking water.

Mexico City is similar in major respects to other metropolitan areas throughout the world, where serious soil and groundwater contamination problems by organic compounds have been observed. It is very likely that these types of problems can occur or are already occurring in the MCMA.

This work shows some of the first indications of the presence of organic compounds of anthropogenic origin in wastewater and the clay aquitard in the MCMA. Anionic surfactants, and VOCs, such as 1,1-DCE, 1,1,1-TCA, TCE and PCE, are present in the open sewer canals. These compounds, except TCE, have penetrated the clay formation to a depth of 6.5 m. The hydraulic gradients in almost all the Basin of Mexico are downwards, due to the overexploitation of the aquifer. This represents a potential for migration of water and organic contaminants towards the groundwater reservoirs. Furthermore, the clay formation seems to behave as a fractured porous media, which would represent a more serious threat to the groundwater resource.

The maximum concentrations at which organic compounds were detected in this study were as follows. Anionic surfactants in canal water were detected at concentrations as high as 35 mg/l, while in pore water the maximum concentration was 7.7 mg/l at the Urban Site. These concentrations are one or two orders of magnitude higher than the water standards for water sources, which is 0.5 mg/l (DOF, 1989a).

In the case of VOCs the maximum concentrations detected in a one-day sampling of the canal water were: 3 μg/l for PCE and 48 μg/l for TCE in the Gran Canal surface water. Concentrations of 5 μg/l for 1,1-DCE, 2 μg/l for PCE, and 1 μg/l for TCE were detected in Rio Remedios surface water. Comparing these concentrations to the standards in Table 4.2, PCE is 3 to 4 times lower than the standard for water sources, TCE is 1.6 times higher than the recommended standards, and 1,1-DCE is more than 15 times higher than the recommended standard. In pore water PCE was detected at the Gran Canal site at a concentration of 0.4 μg/l, value 20 times lower than the water source standard. For 1,1,1-TCA the maximum concentration detected was 0.5 μg/l, at a much lower concentration than the existing standard. 1,1-DCE was detected at concentrations higher than 20 μg/l, as compared to the water source standard, a concentration about 65 times higher than the existing standard.

Some of the organic compounds such as surfactants, 1,1-DCE, and TCE have been detected in canal water and pore water at higher concentrations than the existing standards for water sources. This represents a potential risk for the downward migration of some compounds at concentrations higher than the recommended towards the water reservoirs. Production wells withdraw water from depths below 50 m, therefore it would take some time for these compounds to reach this depth. Nevertheless, this represents a risk for contamination of clandestine wells which are generally shallower than the large production wells.

Even though technical standards for wastewater discharges of industrial effluents have been issued, they are not complete. These standards have to be revised, especially for organic compounds, which are likely to be used by some of the industries and are not currently considered.

Analytical work on organics in surface water and some areas such as landfills has been initiated. Even though DDF has some of the analytical equipment and facilities to perform such kind of analyses, there is a need to develop modern laboratories with state-to-the-art equipment in order to cope with a diversity of environmental samples.

This study focused on a limited number of organic compounds due to financial, analytical and practical constraints. The results are limited to the subsurface of the lacustrine area in the Subbasin of Texcoco within the Basin of Mexico. Although limited in scope, it is the first time a problem related to organic contaminants in the area of influence of the sewage canals that traverse Mexico City has been identified. There have been other efforts oriented towards the understanding of landfill leakage and contaminant migration in other areas.

Current environmental problems require an interdisciplinary approach and multi-institutional, well-coordinated effort in order to prioritize present and future problems and to implement solutions. There is a need for coordination between government and higher education and research institutions for setting priority areas for development. It should be the task of academic institutions to provide the guidelines on this matter. These institutions would require financial support to conduct programs, develop modern analytical facilities, and train personnel. There is a need for interdisciplinary groups to work on these type of projects. Academic institutions are currently the best prepared institutions to undertake this task.

A mechanism should be developed to increase support from the industrial sector for environmental programs. Current regulations and enforcement have elicited some support from the industrial sector, but there is a need to incorporate them into the financial support for some of the most immediate needs related to environmental management, such as development of analytical facilities, landfill construction and operation, water treatment plant construction and operation, and recycling plants.

International agencies have put much of their attention and support in the Mexico City air pollution problem, which is obvious and visible. Water contamination is an area that has not been fully recognized as a priority area, in part due to its less obvious manifestation. According to the analysis presented in this work, the magnitude of the potential problem, and the lack of basic information about it suggests that water is an issue as critical as air pollution, that deserves immediate attention.

One of the major limitations of the governmental system in Mexico is the lack of continuity in policy actions and the incessant change. The very complex system of local and federal agencies involved in management of the hydraulic resources, and the overlapping of functions have been some of the drawbacks as related to environmentally sound actions. An integral view of the water resources is needed, water quality issues and water reuse must be considered in addition to quantity.

Although first steps towards legislation and regulation of potential organic contaminants have been given, limited analytical facilities and personnel in the governmental agencies restricts the enforcing capability to verify such regulations. One of the next steps would be to efficiently carry out the activities related to surveillance and enforcement. In this areas there is a clear need for specific training and education at different levels, technical, professional and graduate.

Once an aquifer is contaminated it is costly and a long-term undertaking if feasible to clean at all (Gillham and Rao, 1990). It would be more cost-efficient to prevent contamination of the groundwater reservoir than to try to apply remedial actions of high cost and questionable efficacy in the Basin of Mexico.

Conclusions

Information disclosure to the public and research institutions is urgently needed. There is also a need for creating a database on water issues in the MCMA. These would help in the evaluation of monitoring activities and current policies, as well as to plan for the future in a more comprehensive way.

Due to the importance of the groundwater resource in the Basin of Mexico, which represent 75% of the water used in the MCMA, particular attention should be given to groundwater monitoring. It would be prudent for Mexico to begin a serious monitoring program, similar to those initiated in other countries such as the United States and the United Kingdom. Such a program must go beyond water supply monitoring. Water supply wells are generally designed to maximize water delivery, not information on contaminant distribution. For this reason, screen sections in wells may present large vertical intervals which can cause dilution of the contaminant below its detection limit (Mackay and Smith, 1992). For a better understanding of the groundwater reservoir quality installation of a network of monitoring wells is essential.

More detailed and broader projects are required in the Basin of Mexico to evaluate in a more comprehensive way the potential for groundwater contamination by organic compounds. Special attention should be devoted to the transition area in the Basin of Mexico, where significant recharge is know to occur and thus represents the most important area for development of groundwater contamination.

A coordinated effort between governmental agencies with authority in specific areas regarding water management and with a long-term view of the problems and their possible solutions needs to take place in the short-term, before the water management problems get completely out of control.

In the Basin of Mexico it is imperative to apply modern and efficient wastewater treatment systems and to implement a much more stronger water reuse policy, especially for the industrial sector. Wastewater treatment should be one of the priority areas for research and technological development.

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Chapter 5

Conclusions and Recommendations

The potential routes by which contaminants may reach the aquifer system in the Basin of Mexico were analyzed. Vulnerable areas were identified in specific locations. These include the lacustrine area composed of relatively impermeable clays, and the transition zone with more permeable materials. Sensitive areas were identified where electronics manufacturing industries are located in or near the transition zone in the northern part of the Mexico City Metropolitan Area (MCMA), as well as along the sewage system, an areally extensive potential source.

A field study was conducted adjacent to the open sewer canals that traverse the MCMA. The techniques used were exclusively portable, hand-operated methods, developed at the University of Waterloo. The study showed that contrary to previous assumptions the lacustrine clay aquitard is not completely impermeable to penetration by water and contaminants, at least in one location. Organic contaminants, including anionic surfactants (MBAS) and VOCs (1,1-DCE, 1,1,1-TCA and PCE) have penetrated 6.5 m downward into the clay aquitard. From monitoring of tritium, a non-reactive radioactive tracer, there is evidence of migration of contaminants due to slow penetration of water. The results show the presence and migration of low concentrations of organic compounds into the clay aquitard.

This study focused on a limited number of organic compounds. More research is needed in order to understand the behavior and potential transformation of these and other compounds in the subsurface in specific areas within the Basin of Mexico. In addition to organic compounds such as aromatic hydrocarbons and other chlorinated solvents, inorganic compounds, pathogenic bacteria, and viruses should be studied. The potential threat that these compounds represent for the groundwater resource in the Basin of Mexico should be also investigated. Monitoring wells should be installed in the most vulnerable areas, complemented with drinking water monitoring to search for evidence of contaminants.

This study focused on a few organic compounds that have been widely implicated in groundwater contamination throughout the world. Future activities should be oriented towards a more detailed identification and examination of contaminants in the most vulnerable areas for contamination. Actions should be taken as soon as possible to prevent further migration of contaminants and degradation of the groundwater resource.

More detailed and broader projects are required in the Basin of Mexico to further evaluate the potential for groundwater contamination by organic compounds. Monitoring programs oriented towards identification and distribution of contaminants should be initiated. Special attention should be devoted to the transition area which represents the most important area for development of groundwater contamination.

There are no alternative water sources within the Basin of Mexico. An option at present has been to import water from other basins. Besides being extremely expensive, this option deprives other areas of water needed for agriculture and electric power generation. Monitoring and maintaining groundwater quality, therefore, should be a top priority within the Basin of Mexico.

In the Basin of Mexico it is imperative to apply modern and efficient wastewater treatment systems and to implement a strong water reuse policy, especially for the industrial sector. Wastewater treatment should be one of the priority areas for research and technological development.

In the last decade there has been a tightening of legislation and regulations for drinking water, water supply sources, industrial wastewater, and hazardous waste disposal. This will certainly prove to be beneficial over the long term. However, the current regulatory infrastructure is unlikely to be able to implement these regulations effectively for some time.

A well defined and continuous overall water management plan with long-term objectives is needed for the Basin of Mexico. Environmental problems require an interdisciplinary approach and multi-institutional effort in order to prioritize present and future approaches to the water problem.