Risk Screening for Exposure to Groundwater Pollution in a Wastewater Irrigation District of the Mexico City Region

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Untreated wastewater from the Mexico City basin has been used for decades to irrigate cropland in the Mezquital Valley, State of Hidalgo, Mexico. Excess irrigation water recharges the near-surface aquifer that is used as a domestic water supply source. We assessed the groundwater quality of three key groundwater sources of domestic water by analyzing for 24 trace metals, 67 target base-neutral/acid (BNA) organic compounds, nontarget BNA organics, 23 chlorinated pesticides, 20 polychlorinated biphenyls, and nitrate, as well as microbiological contaminants—coliforms, Vibrio cholerae, and Salmonella. Study participants answered a questionnaire that estimated ingestion and dermal exposure to groundwater; 10% of the sample reported frequent diarrhea and 9% reported persistent skin irritations. Detection of V. cholerae non-01 in surface waters at all sites suggested a potential risk (surrogate indicator present) of diarrheal disease for canal and river bathers by accidental ingestion, as well as potential Vibrio contamination of near-surface groundwater and potential cholera risk, magnified by lapses in disinfection. High total coliform levels in surface water and lower levels in groundwater at all sites indicated fecal contamination and a potential risk of gastrointestinal disease in populations exposed to inadequately disinfected groundwater. Using chemical criteria, no significant risk from ingestion or dermal contact was identified at the method detection limits at any site, except from nitrate exposure: infants and young children are at risk from methemoglobinemia at all sites. Results suggest that pathogen risk interventions are a priority, whereas nitrate risk needs further characterization to determine if formal treatment is needed. The risks exist inside and outside the irrigation district. The method was highly cost-effective. Key words: groundwater, Mexico, nitrate, pathogens, risk, wastewater irrigation. Environ Health Perspect 107:553–561 (1999). [Online 3 June 1999] http://ehpnet1.niehs.nih.gov/docs/1999/107p553-561downs/abstract.html

Mexico City and the Valley of Mexico indisputably provides one of the best examples of a development model in crisis. Of the current average Mexico City wastewater flow of 45 m³/sec, approximately 75% is used, without formal treatment, to irrigate 90,000 ha in the Mezquital Valley, State of Hidalgo (1). The total human exposure implications of this water have yet to be explored. The main epidemiologic research in the region has reported significant diarrheal disease and parasitic infections in farm workers and their families (2). In the most recent review of the environmental impact of using wastewater for irrigation (arguably the largest such region in the world), the lack of attention to drinking water in the zone and potential groundwater pollution from nitrates, dissolved organic matter, and detergents was highlighted (3). Urban wastewater is transported over 80 km and distributed by canals for flood irrigation of cropland in a naturally semiarid region, recharging the local aquifer system that provides domestic water for 170,000 people. Irrigation in the Mezquital Valley was 14,000 ha in 1914–1926; 28,000 in 1950; 42,000 in 1965, and 85,000 in 1994 (3).

A recharge-discharge ratio of approximately 5:1 has been estimated (4), manifesting as a rising water table, waterlogging of some fields, and the appearance of new springs and seeps. The region is considered among the most important in Mexico for the area it covers and its economic value from agriculture.

Mexico City Metropolitan Zone (MCMZ) wastewater is composed of a mixture of domestic, municipal, and industrial wastewater, and stormwater runoff. It receives no conventional treatment (1) and is subject to mixing and natural transformation processes during its transport from the MCMZ to the irrigation region and further biodegradation and sedimentation in a storage reservoir. Approximately 55% of the nation’s industry is located in the MCMZ (paper, food, chemicals, textiles, and automotive), with approximately 43% of the wastewater in the irrigation district of industrial origin, and 57% of domestic and municipal origin (5).

The research hypothesis was that pollutants levels in groundwater represent a health risk. The research objective was to cost-effectively identify priority risks.

Study region. The study region is located 80 km north of Mexico City (Figure 1), between the Rivers Tula and Salado, in and around the Endhó Reservoir. Approximately 10,000 ha receive raw wastewater directly; 35,000 ha receive 80% wastewater + 20% fluvial reservoir water, and 25,000 ha receive naturally treated wastewater from the Requena, Endhó, Rojo Gómez, and Vicente Aguirre storage reservoirs (7).

The elevation is approximately 1,900 m above sea level, the mean temperature is 17°C, and the mean annual precipitation varies from 700 mm in the southeast to 400 mm in the north (1). Rainy season is pronounced—from June to September. Crops are alfalfa and maize (60%), oats, barley, wheat, beans, and some vegetables—chili peppers, Italian squash, and tomatoes. Cultivation of root vegetables or those consumed raw is officially prohibited, yet they are grown in some areas. Irrigation is by flooding or furrow, and rates lie between 1,500 and 2,200 mm/ha/year (1).

Population. The Mezquital population consists of municipalities of small rural villages that depend on agriculture. In the Tula Jurisdiction (irrigation district 03), 16% of the homes do not have piped water, and 45% must collect water from points outside the home. In addition, only 47% of homes have sanitation (3). Domestic water is routinely collected from groundwater wells and springs. Water is disinfected by small chlorination stations that are manually operated and maintained. The areas of focus for the project were the small village of Cerro Colorado, which is adjacent to the springs (population 110) and the area around the spring in the town of Tezonopeteca de Aldama (population 20,000). Because exposure is a function of socio-economic conditions, socioeconomic characteristics of a population...
sample were gathered using a field questionnaire. Such a profile is also important for the design of appropriate interventions and risk communication strategy.

Mortality data from 1995 (6) show the top five causes of death in the State of Hidalgo (population of 2.11 million in 1995) for adults as (a) heart diseases (incidence rate 61/10^5); (b) cirrhosis and other chronic liver diseases (46/10^5); (c) malignant tumors (44/10^5); (d) accidents (40/10^5); and (e) diabetes mellitus (31/10^5). For infants younger than 1 year of age the top five causes were (a) perinatal problems (rate 780/10^5); (b) congenital anomalies (257/10^5); (c) pneumonia and influenza (234/10^5); (d) gastrointestinal infectious diseases (101/10^5); and (e) accidents (48/10^5). All of these causes of death, except accidents, may be directly or indirectly related to environmental pollution.

**Water quality assessment.** Although in Mexico water quality standards are arguably the most complete in Latin America, institutional weaknesses mean they are rarely monitored and enforced (7). Growing needs for environmentally responsible wastewater reuse worldwide calls for the inclusion of a wider range of parameters that, although currently unregulated, are potentially toxic as suggested by their structure–activity characteristics: the organic fraction of known or potential toxic and mutagenic effects is the base/neutral/acid fraction (8), such as polyaromatic hydrocarbons.

The screening parameters consisted of 24 trace metals, 67 semivolatile BNA target organic compounds (those included in drinking water tests by U.S. Environmental Protection Agency (EPA) methods 525 and 625 (9, 10)), nitrate, 23 chlorinated pesticides, and a custom 21-congener PCB suite (Table 1).

Criteria pathogens were the bacteria *Vibrio cholerae* and *Salmonella*. The *V. cholerae* enterotoxin produces mild to profuse diarrhea, vomiting, and rapid fluid loss. Morphologically and physiologically similar to *V. cholerae* 01, the non-01 vibrios produce either cholera toxin (CT) or CT-like toxin, although the diarrheal illness from their ingestion in contaminated food or water is milder (11). Only *V. cholerae* 01 has been shown to produce cholera (12). *Salmonella* can cause typhoid and paratyphoid fever (13), as well as severe diarrhea and dysentery. The indicator organisms used to detect fecal pollution were total coliforms and *Escherichia coli*. Total coliforms include *E. coli*, *Enterobacter*, *Klebsiella*, and *Citrobacter*, and are one of the best indicators of water treatment effectiveness. Of the fecal coliforms, *E. coli* is the most reliable indicator because it is specifically of fecal origin (12).

**Methods**

**Exposure assessment.** Table 2 shows the conceptual matrix used to identify groundwater ingestion and dermal contact as local priority pathways. Exposure was estimated by applying a field questionnaire to 210 families in the Tehuantepec and Cerro Colorado regions. The questionnaire asked specific questions related to ingestion and bathing in the home to quantify ingestion and dermal contact.

Exposure statistics used in the United States (e.g., adult ingestion 2.0 L/day) were not assumed because climatic and cultural differences between the United States and Mexico were expected to influence values. Drinking and bathing habits were captured for two age groups: 0–15 and 16–70 years of age. All drinks and soups containing water were considered, and frequency and duration of bathing was estimated. This type of questionnaire to quantify exposure had not previously been applied in the region. Living conditions and perceptions of water problems were also captured.

Exposure to contaminants in domestic water was estimated using the pathway exposure factor (PEF) method of McKone and Daniels (14). The relationship between risk and PEF is given in Equation 1. The PEFS for ingestion and dermal contact are the exposures per unit contaminant concentration for these pathways (Equation 2). The PEFS for ingestion, $PEF_i$, and dermal
contact, \( PEF_D \), are given by Equations 3 and 4, respectively. Additional infant (0–3 months) and young children (≤ 10 kg) groups were used for nitrate exposure. Body weight (BW), ingestion (\( I_g \)), and dermal contact time (\( T \)) statistics were estimated from the population questionnaire. A Monte Carlo method was used to probabilistically estimate the PEFs.

\[
R = (CDI - RfD) \times p
\]  

where \( R \) = individual risk (unitless probability); \( CDI \) = chronic daily intake of contaminant (mg/kg/day); \( RfD \) = reference daily intake (assumed 0 for carcinogens) (mg/kg/day); and \( p \) = contaminant toxicity or potency (mg/kg/day)^{-1}.

\[
CDI_{ij} = C_j \times PEF_f
\]  

where \( CDI_{ij} \) = chronic daily intake of contaminant by exposure to medium \( i \) by pathway \( j \) (mg/kg/day); \( C_j \) = concentration of contaminant in exposure medium \( i \) (mg/L); and \( PEF_f \) = pathway exposure factor by pathway \( j \) (L/kg/day).

\[
PEF_f = I_{w/BW}
\]  

where \( I_{w/BW} \) = drinking water daily intake per unit body weight (L/kg/day).

\[
PEF_D = T \times f_j \times SA / BW \times K_f
\]  

where \( T \) = exposure duration (hr); \( f_j \) = fraction of skin surface immersed in contaminated water (unitless); \( SA \) = skin surface area (m²); \( BW \) = body weight (kg); and \( K_f \) = contaminant permeability constant across the stratum corneum (L/m²/hr).

Skin surface area (SA) was calculated from the relationship published by the International Commission on Radiological Protection (15), given in Equation 5.

\[
SA = (4BW + 7)/(BW + 90)
\]  

A value of 10 L/m²/hr for \( K_f \) was used in Equation 4, following McKone and Daniels’ (14) assumption that the \( K_f \) estimate for volatile organic compounds can also be used as a first-order estimate for the soluble phase of other waterborne contaminants. An estimate of 0.6 (± 0.1) for skin fraction (\( f \)) immersed was used for those who bathed themselves in groundwater springs. For those who bathed using cups or buckets, dermal contact was assumed not to be a significant pathway.

**Environmental sampling.** Three groundwater sampling locations were chosen (Figure 1). Tezontepec is a rural town approximately 45 km from the point where

| Table 1. Chemical water quality parameters.  
|-----------------|---------|---------|---------|
| **BNA target organic compounds** | **Metals** | **Chlorinated pesticides** |
| **Name** | **MDL (ppb)** | **Name** | **MDL (ppb)** | **Name** | **PCBs** |
| Acenaphthene | 0.06 | Aluminum | 0.15 | 1,2-DDE | 0.64 |
| Acenaphthylene | 0.06 | Arsenic | 0.14 | 4,4'-DDD | 0.64 |
| Anthracene | 2.1 | Barium | 0.35 | 4,4'-DDE | 0.64 |
| Benzo(a)anthracene | 0.07 | Beryllium | 0.3 | 4,4'-DDT | 0.64 |
| Benzo(b)fluoranthene | 0.14 | Benzene | 0.3 | 5-BCD | 0.64 |
| Benzo(j)fluoranthene | 0.15 | Black | 0.64 | 5-BCD | 0.64 |
| Benzo(a,h)pyrene | 0.37 | Benzyl alcohol | 0.14 | 7-BCD | 0.64 |
| Benzo(e)pyrene | 0.07 | Benzylic alcohol | 0.14 | 7-BCD | 0.64 |
| Bis-(2-chloroethoxy)methane | 0.33 | Bisphenol A | 0.14 | 7-BCD | 0.64 |

**Abbreviations:** BHC, benzenehexachloride (isomers); BZ, Bartschmieter-Zell classification of 209 PCB congeners; MDL, method detection limit in ppb; ppb, parts per billion; **4** indicates the chlorinated pesticide. **5** indicates the PCBs.

*Except nitrate (standard method 4110C) (18).* U.S. EPA methods 525 (drinking water) (9), 625 (wastewater) (10).

*Standard method 3120B (18).* U.S. EPA method 608 (18).
the wastewater enters Hidalgo. It has a local spring (site TZG) derived from the infiltration of irrigation water. Cerrro Colorado is the main spring in the valley, supplying domestic water to 170,000 people (Table 3). The spring (site CCG) is approximately 35 km from the wastewater entry and was the second sampling location. The third location was a natural spring derived from upland precipitation approximately 8 km from the wastewater entry. This site (ESG) near the River El Salto was the control site for near-surface groundwater quality and was a natural near-surface aquifer discharge point located outside the irrigation district. Because groundwater in the valley is either of the wastewater-derived near-surface aquifer or the deeper (50–100 m) hydrothermal aquifer, it was important to carefully choose a control for the near-surface aquifer.

Each sample set included one sample for metals, one for organics, and one for pathogens. Four sets of samples of groundwater were taken at each site once per month during the dry season, when dilution of contaminant concentrations was expected to be lowest (December 1996–March 1997). Samples of adjacent surface water were also taken for pathogens. Samples from a house tap at Tezontepac (site TZH) were taken only once. The sampling regime was considered optimal for the resource constraints, although some samples were lost in transit.

Microbiological testing. Water samples were collected in 200-ml plastic containers for microbiological testing at each site and at surface water sites adjacent to the groundwater sites (TZS, CCS, and ESS). Biochemical determinations of the presence/absence of V. cholerae and Salmonella were carried out at the State Public Health Laboratory (Hidalgo). Results of suspected positives were sent to the National Institute of Epidemiological Diagnosis and Reference (Santo Tomas, Mexico City, Mexico) for polymerase chain reaction confirmation. A semiportable device for quantitatively measuring total and E. coli levels, Autoanalysis Collert (Idexx Laboratory, Inc., Westbrook, ME), was used on one sampling day. This method is also called the minimal media method (17).

Physicochemical and chemical testing. Physicochemical parameters—temperature, pH, dissolved oxygen, and conductivity—were measured in the field using portable monitors from Yellow Springs Instrument Company, Inc., Yellow Springs, Ohio. At each sampling point, amber glass bottles with Teflon (E.I. Du Pont de Nemours and Co., Wilmington, DE) caps were used to take 1 L of water for metals analysis and 1 L for organics analysis. Travel blanks consisted of 1 L water purified using a Millipore complete purification system (Millipore Corp., Bedford, MA), consisting of reverse osmosis and reagent grade purification. Samples were kept in ice and shipped by express courier for next day delivery to the University of California, Los Angeles (Los Angeles, CA) laboratory.

Nitrate levels in water were determined by standard method 4110C (18). Simultaneous metal analysis of the filtered aqueous phase was carried out by standard method 3120B (18), an inductively-coupled plasma/atomic emission (ICP/AE) method, on a Perkin-Elmer Optima 3000 DA ICP-AES Spectrometer (Perkin-Elmer, Norwalk, CT). Water samples were analyzed for EPA target drinking water BNA contaminants using an expanded list of analytes, based on EPA Methods 525 (drinking water) (19) and 625 (wastewater) (18). Method 625 was modified by a capillary column. Method detection limits are given in Table 1. Samples were analyzed for chlorinated pesticides and PCBs using methods based on EPA method 608, Pesticides and PCBs [polychlorinated biphensyls (19)].

Semivolatile BNA compound, organochlorine pesticide, and PCB analyses were carried out by concentrating the water sample using standard method 3520A (Liquid–Liquid Extraction) (18). The extraction used a 1-L sample for metals analysis and 1 L for BNA. A batch extractor was used with dichloromethane as the active agent. Samples were dried on a sodium sulfate column, concentrated to 1 mL by Kuderna-Danish evaporation, and analyzed with a Finnigan 4000 (Finnigan, San Jose, CA) gas chromatography/mass spectrometer (GC/MS). The GC column was a DB-5MS, 30 m × 0.25 mm. Six internal standards were injected into the sample at 40 ng/μL before GC/MS analysis. These standards were 1,4-dichlorobenzene-D4, naphthalene-D8, acenaphthene-D10, phenanthrene-D10, chrysene-D12, and perylene-D12.

Chlorinated pesticides and the selected PCB suite analyses were carried out using GC/electron capture detection (ECD) on a Varian 3500 instrument (Varian, Walnut Creek, CA) and dual columns. Method detection limits for aqueous samples of PCBs and chlorinated pesticides were 0.005–0.010 μg/L.

BNA organic analysis included distinguishing and approximately quantifying nontarget trace organics, using GC/MS profiling (20,21). Nontarget compounds were tentatively identified when possible by visually inspecting sample spectra and comparing them against closest matches from the 42,000-compound EPA/National Institutes of Health Mass Spectral Database Library (22). Because response factors were unknown for nontarget compounds, each compound’s concentration was approximately quantified by comparing ratios of its spectral area to the spectral area of the closest internal standard of known concentration. Each compound has a specific scan number from the GC total ion current, which is mainly a function of molecular weight (MW) and boiling point (BP). The GC/MS output total ion chromatograms were cleaned of peaks found in travel blanks and phthalates known to be experimental artifacts. A list of target and tentatively identified nontarget compounds was compiled for each sample for data comparison.

Results and Discussion

Socioeconomic population profile. Using the questionnaire results, the sampled population of 210 families was characterized by education level, living conditions, bathing habits, drinking habits, and health signs (Table 4). The illiteracy rate was 10% in male heads of the family and 14% in mothers. Most houses had cement floors (89%) and water closets (inside 30%, outside 46%). The percentage of families without drainage was 17%; without piped water, 11%. Springs were popular bathing places (39%) of

| Medium | Pathway | Airp | Airg | SW | GW | Soil | Sed | Biota |
|--------|---------|------|------|----|----|------|-----|------|
| Inhalation | e11 | e21 | e31 | e41 | e51 | -   | e72 |
| Ingestion  | e12 | e22 | e32 | e42 | e52 | e62 | e72 |
| Dermal contact | e13 | e23 | e33 | e43 | e53 | e63 | -   |

**Table 2. Conceptual matrix of exposure pathways.**

| Medium | Pathway | Airp | Airg | SW | GW | Soil | Sed | Biota |
|--------|---------|------|------|----|----|------|-----|------|
| Cerro Colorado | 7 | 145,000 | 200 | 36 | Gravity | Chlorination |
| C. Colorado-Huitul | 23 | 35,000 | 130 | 7.5 | Gravity | Chlorination |
| Total | 30 | 170,000 | 330 | 42.5 | - | - | - |

**Table 3. Domestic water supply from Cerro Colorado spring.**

Abbreviations: L, length (km); NS, number of settlements supplied. Data from Comisión Nacional del Agua (18).
Table 4. Socioeconomic population profile.*

| Characteristic | %& |
|---------------|----|
| 1.1 Age of head of family 20–30 years | 22 |
| 1.2 Age of head of family 30–40 years | 24 |
| 1.3 Age of head of family 60–70 years | 15 |
| 2 Education | |
| 2.1 Family head reads and writes | 89 |
| 2.2 Family head neither reads nor writes | 10 |
| 2.3 Mother reads and writes | 83 |
| 2.4 Mother neither reads nor writes | 14 |
| 2.5 Family head did finish primary school | 29 |
| 2.6 Family head did not finish primary school | 37 |
| 2.7 Family head did finish secondary school | 12 |
| 3 Living conditions | |
| 3.1 House floor cement | 27 |
| 3.2 House floor earth | 6 |
| 3.3 House roof is tin | 31 |
| 3.4 House roof is cement | 68 |
| 3.5 House roof is cardboard | 2 |
| 3.6 House has WC inside | 30 |
| 3.7 House has WC outside | 46 |
| 3.8 House has no WC | 24 |
| 3.9 House has waste drainage | 74 |
| 3.10 House has septic tank | 8 |
| 3.11 House has no sanitation | 17 |
| 3.12 House has piped water inside | 27 |
| 3.13 House has piped water outside | 62 |
| 3.14 House has no piped water | 11 |
| 4 Bathing habits | |
| 4.1 Family bathes inside with shower | 25 |
| 4.2 Family bathes with small bowl | 29 |
| 4.3 Family bathes in spring | 39 |
| 5 Drinking habits | |
| 5.1 Drinking water from tap | 28 |
| 5.2 Drinking water from spring | 65 |
| 5.3 Drinking bottled water | 4 |
| 5.4 Boil water >10 min before drinking | 24 |
| 5.5 Boil water <10 min before drinking | 7 |
| 5.6 Do nothing to water before drinking | 65 |
| 6 Health signs | |
| 6.1 Frequent diarrhea among family | 10 |
| 6.2 Persistent skin irritations | 9 |

*WC, water closet.*

*n = 210 families; important export data in bold.

*Percentage of sampled families with characteristic.

families) and sources of drinking water (65%). Most families did not sterilize their drinking water (65%), and only 4% used bottled water. Ten percent of families reported frequent diarrhea. Nine percent reported persistent skin irritations, which could be effects of dermal contact with wastewater. Almost all families questioned stated that the main advantage of treating wastewater before irrigation would be “cleaner crops.”

Observations of barefoot farm workers, children bathing in canals, and livestock ingesting wastewater suggest human dermal exposure to wastewater (c33, Table 2) and ingestion (c72, Table 2) of the food products of animals exposed to wastewater should be assessed—cow’s and goat’s milk, beef, and sheep’s meat.

**Groundwater pathway exposure factors.**

The children’s mean groundwater ingestion was 1.6 ± 0.48 L/day (standard deviation (SD)), and the adult mean was 2.0 ± 0.45 L/day (Table 5). Mean dermal contact times (∼SD) for children and adults were 11 ± 3.6 and 11 ± 3.3 min/day, respectively. The mean PEFs (±SDs) for ingestion for children and adults were 0.092 ± 0.076 and 0.033 ± 0.010 L/kg/day, respectively (Table 6). The mean PEFs (±SDs) for dermal contact for children and adults were 0.035 ± 0.017 and 0.024 ± 0.010 L/kg/day, respectively. In children, the ingestion rate (I(w)) contributed 70% of the uncertainty in the ingestion PEF and BW 30%, whereas for dermal contact 54% of the uncertainty was accounted for by uncertainty in contact time (T) and 31% by skin fraction immersed (f). For adults, the ingestion rate contributed 66% of the uncertainty in the ingestion PEF and BW 34%, whereas for dermal contact 55% of the uncertainty was accounted for by uncertainty in contact time and 34% by skin fraction immersed.

**Microbiological indicators.** Of the March 1997 surface water samples TZS, CCS, and ESS (adjacent to the groundwater sites TZG, CCG, and ESG), only the TZS sample was positive for the *V. cholerae* serogroup non-01. All surface water site samples taken in December 1996 were positive for *V. cholerae* non-01. Samples taken in December 1996 were negative for *Salmonella* at all sites. The March 1997 coliform counts were greater than the instrument maximum > 2,419/100 mL for total coliforms and *E. coli* in all surface water sites. The March 1997 groundwater samples TZG, CCG, and ESG registered total coliforms at 770; 1,730; and 37/100 mL, respectively, and *E. coli* at 7, 4, and 0/100 mL, respectively. The March 1997 house sample (TZH) had values of 0 for total coliforms and *E. coli*.

The presence of *V. cholerae*-non 01 in all surface water sites is a red flag; the near-surface groundwater supplies are potentially at risk from contamination, with a resultant potential cholera risk. Because this bacterium is almost exclusively transmitted by water (13), prevention of epidemic cholera depends on providing a safe drinking water supply that is chlorinated and free from sewage contamination; lapses in disinfection that occur during the manual changeover of chlorine tanks magnifies the risk. Coliforms suggest a potential risk of gastrointestinal diseases at all sites, with total coliforms and *E. coli* counts above the Mexican standard (23) of 2/100 mL and 0/100 mL, respectively. World Health Organization (WHO) guidelines (12) for fecal coliforms in drinking water were exceeded (includes *E. coli*), as were the WHO guidelines (24) for wastewater reuse for the irrigation of crops likely to be eaten uncooked—limits for fecal coliforms were ≤ 1,000 per 100 mL (geometric mean). Unlike studies with wastewater reservoirs in Israel, where fecal coliforms are removed by up to five orders of magnitude after retention (25), the comparison of the site before retention in the Endhô Reservoir (Figure 1, ESS/ESS) with the site after retention (TZG/TZS) did not show this effect. This may be because the Tula River receives fecal pollution after retention, along the 20 km between the reservoir and the sampling site.

**Nitrate data.** Table 7 shows means and SDs of nitrate ion concentration (NO3−). Mean nitrate in groundwater ranged from 47 to 69 mg/L, whereas the health standard is 50 mg/L. The single sample at the house (TZH) was highest at 73 mg/L. ESG (control site) nitrate levels of 47 mg/L are not attributable to wastewater infiltration: manure from grazing cattle and horses, and fertilizers are likely sources. Using PEF values from Table 6, mean CDI for the children ranged from 4.3 mg NO3−/kg/day at ESG to 6.3 mg NO3−/kg/day at CCG. The TZH value was 6.7 mg NO3−/kg/day. Corresponding values for the adult group were 36% of the child values. Assuming a risk group of young children of BW 10 kg and ingestion 1 L/day (PEF = 0.1 L/kg/day), the CDI ranges from 4.7 mg NO3−/kg/day at ESG to 6.9 mg NO3−/kg/day at CCG. For the highest risk group of infants assuming a BW of 4 kg and ingestion of 0.6 L/day (20) —PEF; on the order of 0.15 L/kg/day—the CDI ranges from 7 mg NO3−/kg/day at ESG to 10 mg NO3−/kg/day at CCG.

In infants, the drinking water no observed adverse effect level (NOAEL) and lowest observed adverse effect level (LOAEL) for methemoglobinemia have been given in dose terms as 1.6 mg nitrate-nitrogen/kg/day and 1.8–3.2 mg/kg/day, respectively (26,27), equivalent to approximately 7 mg NO3−/kg/day and 8–14 mg NO3−/kg/day. The NOAEL is also the oral reference dose (oral RFD) in equation 1 (uncertainty factor of 1). The infant group is at risk at all sites because CDI ≥ RFD. Using the acceptable daily intake (ADI) of 3.65 mg NO3−/kg/day, young children of BW ≤ 10 kg and ingestion ≥ 1.0 L/day are also at risk because CDI ≥ ADI. In methemoglobinemia, nitrate reduced to nitrite oxidizes hemoglobin to methemoglobin, impairing oxygen transport to tissues. Although experiments with animals suggest neither nitrate nor nitrite acts directly as a carcinogen, it may increase cancer risk in humans by endogenous formation of N-nitroso compounds whereas evidence implicating high nitrate in drinking water with...
other end points such as congenital malformations, cardiovascular effects, and thyroid effects are inconclusive (12).

**Physicochemical data.** Table 7 shows means and standard deviations of temperature at site (7), site pH, conductivity (C), dissolved oxygen (DO). Mean T was approximately 20°C, with pH ranging from 7.1 to 7.6. Conductivity ranged from 1,200 to 1,850 µhos (TZH) and DO between 5.2 and 6.9 mg/L, with coefficients of variation at CCG and ESG of 0.45 and 0.23, respectively.

**Metals, BNA organics, chlorinated pesticides, and PCBs.** Mean levels of the 24 target heavy metals did not exceed U.S. Safe Drinking Water Act (29) maximum contaminant levels and maximum-level goals or Mexican standards (23) at any site; therefore, no significant risk was identified by these criteria (Table 8). No target BNA organics were detected in the samples; therefore, no significant risk was identified by these criteria at the method detection limit, whereas several nontarget BNA compounds were detected in samples, most of which could not be identified (Table 9). The number of tentatively identified compounds in the sampled groundwater ranged from 0 (ESG) to 2 (CCG), and unidentified compounds from 2 (TZG) to 9 (CCG). All tentatively identified compound levels were ≤ 2 µg/L, and all detected compounds were ≤ 6 µg/L. Tentatively identified and unidentified compounds are of unknown but potential toxicity, so an unknown risk exists by this criterion.

Only one chlorinated pesticide was detected from the list, γ-chlordane in ESG, on 12 March 1997 at approximately 30 pg/L (on the order of 10^{11} g/L). There is no evidence this compound is a human carcinogen (31). Levels in water in previous studies in Hawaii (32) were on the order of 1 ng/L, and levels of magnitude 10^{11} g/L are considered low. Therefore, risk by this pollutant was considered insignificant.

Several PCB congeners were detected from the PCB list (Tables 1 and 9). The main transport medium is air, with strong sorption to suspended particles and soil. For this reason, leaching is limited and groundwater levels low (33). PCBs are classified as suspected carcinogens by the EPA on the basis of animal tests. They have a potential to cause developmental and fetotoxic effects in humans, and there is evidence that they may cause hepatic toxicity (34). However, typical levels between 0.1 and 0.5 ng/L found elsewhere in drinking water represent negligible contributions to body burden as compared to food intake (35). For these reasons, the low levels detected (≤ 36 pg/L) were not considered a risk factor. Tables 10 and 11 summarize chemical and microbiological health risks, respectively, identified at method detection limits.

**Removal processes.** The chemical contaminant levels in near-surface groundwater were lower than expected considering the short infiltration depth of a few meters for raw wastewater. However, because the sampling sites are springs, the water has also been subject to horizontal groundwater flow over distances up to several tens of kilometers. Degradation and dispersion processes, organic sorption to soil and trapping of suspended solids, and Endhò Reservoir retention (Figure 1) appear to effectively remove BNA organic contaminants. During the 80–100 km journey of wastewater from Mexico City to the Irrigation District, it is likely that metals and organics associated with suspended matter settle out, whereas the soluble fractions of metals and organics sorb to bottom sediments and soils during infiltration. Biodegradation of xenobiotics is probably active in the canals, reservoir, and soil (36). Despite the apparent efficiency of natural treatment processes, if the water table continues to rise and fields become saturated (4), the bioavailability of wastewater-borne contaminants will increase, creating different exposure conditions. This is one argument for reducing the incoming wastewater flow from Mexico City, and this would also free up the wastewater for recycling within the Mexico City basin, where water is scarce. Using cleaner local groundwater and more efficient irrigation would reduce environmental health impacts and allow higher value crops to be grown.

Direct exposure to surface wastewater through inhalation and dermal contact, and indirectly through ingestion of milk, beef, sheep's meat, and crops may be important and should be evaluated: Dairy cattle and sheep drink directly from sewage canals because no other surface water is available.

**Conclusions and Recommendations**

**Risks.** Our results suggest that pathogens are priority agents as compared to chemicals for groundwater ingestion, and they are not restricted to the wastewater irrigation district. By the coliform criterion, a potential risk of gastrointestinal disease was identified with total coliforms and E. coli counts above the Mexican standard (23), particularly because disinfection can be intermittent when chlorine tanks run dry and changeover is not efficient. No risk by Salmonella was identified. The presence of V. cholerae non-01 in surface waters including the river (TZS) indicates a

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**Table 5. Ingestion and dermal contact statistics.**

| Age group | BW | v1 | v2 | v3 | v4 | v5 | v6 | vT | T |
|-----------|----|----|----|----|----|----|----|----|---|
| 0–15 years | Avg | 22.6 | 1.02 | 0.11 | 0.17 | 0.02 | 0.14 | 0.16 | 1.62 | 10.8 |
| SD | 11.4 | 0.39 | 0.08 | 0.19 | 0.05 | 0.06 | 0.05 | 0.48 | 3.6 |
| n | 1038 | 161 | 161 | 161 | 161 | 161 | 161 | 161 | 161 |
| 16–70 years | Avg | 63.4 | 1.37 | 0.11 | 0.22 | 0.02 | 0.13 | 0.16 | 2.02 | 10.8 |
| SD | 10.1 | 0.35 | 0.10 | 0.18 | 0.05 | 0.06 | 0.09 | 0.45 | 3.3 |
| n | 1348 | 210 | 210 | 210 | 210 | 210 | 210 | 210 | 158 |

**Table 6. Pathway exposure factor statistics.**

| Children 0–15 years of age | Adults 16–70 years of age |
|-----------------------------|---------------------------|
| PEF | PEF_D | PEF | PEF_D |
| **Statistical value** | | |
| Mean | 0.092 | 0.035 | 0.033 | 0.024 |
| Median | 0.070 | 0.034 | 0.032 | 0.023 |
| Mode | 0.057 | 0.034 | 0.030 | 0.017 |
| Standard deviation | 0.076 | 0.017 | 0.010 | 0.010 |
| **Sensitivity** | | | | |
| Ingestion (L) | 70 | – | 66 | – |
| Body weight (BW) | 30 | 10 | 34 | 3 |
| BAT (h) | 54 | – | 55 | – |
| Skin fraction (f) | – | 31 | – | 35 |
| Permeability (K_D) | – | 5 | – | 7 |

**Abbreviations:** PEF, pathway exposure factor for ingestion (L/kg/day); PEF_D, pathway exposure factor for dermal contact (L/kg/day); PEF, pathway exposure factor for ingestion (L/kg/day).
potential risk of diarrheal disease for people bathing and accidentally ingesting this water. A potential risk of cholera exists because of possible near-surface groundwater contamination by *Vibrio* in surface water, a risk increased by lapses in sanitation. Ten percent of families of the sample population reported frequent diarrhea.

By the nitrate criterion, the infant and young children groups are at risk from methemoglobinemia at all sites and are not restricted to the wastewater irrigation district. This risk warrants further characterization that includes a focused epidemiologic study before the investment of scarce resources in source control and/or treatment technology can be justified. Any future treatment should be appropriate for the rural context. No risk was identified using the metals criteria at method detection limits. By the criteria of BNA target compounds, chlorinated pesticides, and PCBs, no significant risk was identified at method detection limits. An unknown risk exists from tentatively identified and unidentified BNA compounds, although all detected compounds were at levels ≤ 6 μg/L. Nine percent of the sample reported persistent skin irritations, which could be effects of dermal contact with wastewater chemicals in canals and fields.

The screening method proved cost-effective in identifying priority risks in a complex pollution situation, a valuable tool in the search for health interventions that are efficient. The screening method is less costly than traditional epidemiologic studies and projects such studies, an approach particularly appropriate in less-developed countries where resources are scarce.

**Potential treatment options.** Microbiological risk agents require better control, with improvements sought for manual chlorination, such as low bank and irregular dose warnings, systematic tank replacement, better operator training, and/or simple automated, low-cost systems. Major plans to treat the wastewater leaving Mexico City and entering Mezquital are under review, with new primary treatment and disinfection targeted at pathogen removal (7).

Major treatment/disinfection options require full cost-effectiveness and impact assessment, and an understanding of the resistances of different pathogens, not merely consideration of the most studied risk from helminth eggs (7). However, even with major treatment, local pathogen risk sources would still need attention by improving basic hygiene and low-cost rural sanitation.
Table 9. BNA organics, chlorinated pesticides, and polychlorinated biphenyl data.

| Parameter/site | Before | After | Before | After | Before | After | Before | After |
|---------------|--------|-------|--------|-------|--------|-------|--------|-------|
| BNA organics  |        |       |        |       |        |       |        |       |
| Number of site | 0      | 0     | 0      | 0     | 0      | 0     | 0      | 0     |
| Mass targets (%) | 0      | 0     | 0      | 0     | 0      | 0     | 0      | 0     |
| Number of nontarget compounds | 6     | 3     | 3      | 6     | 11     |       |       |       |
| Number tentatively identified | 1     | 0     | 1      | 0     | 2      |       |       |       |
| Number unidentified | 5     | 3     | 2      | 3     | 5      | 9     |       |       |
| Mass non targets (%) | 100   | 100   | 100    | 100   | 100    | 100   | 100    | 100   |
| Estimated amounts (µg/L) |        |       |        |       |        |       |        |       |
| Non-target compounds (tentatively identified)* | 1     | 2     | -      | -     | 1      | -     | -      | -     |
| Cyclotrisiloxane, hexamethyldisiloxane | -     | -     | -      | -     | -      | -     | -      | -     |
| Propanoic acid, 2-methylbutyl ester | -     | -     | -      | -     | -      | -     | -      | -     |
| 1-dodecene | -     | -     | -      | -     | -      | -     | -      | -     |
| Chlorinated pesticides (µg/L) |        |       |        |       |        |       |        |       |
| γ-Chlorodane | -     | 30    | -      | -     | -      | -     | -      | -     |
| Polychlorinated biphenyls (µg/L) |        |       |        |       |        |       |        |       |
| BZ-28 | -     | -     | -      | -     | -      | -     | -      | -     |
| BZ-66 | 26    | 20    | 16     | 10    | 36     |       |       |       |
| T-Norachlor | 4     | 19    | -      | -     | 11     |       |       |       |
| BZ-105 | 2     | -     | 6      | -     | -      |       |       |       |
| BZ-153 | 2     | -     | 36     | -     | -      |       |       |       |
| BZ-190 | 14    | 25    | 35     | -     | 22     | 7     |       |       |
| BZ-187 | 6     | -     | 13     | -     | -      | 4     |       |       |

Abbreviations: BNA: base/neutral/acid; BZ: Ballschmiter-Zell classification of 209 PCB congeners; CCG: Cerro Colorado River groundwater site; ESG: El Salto River groundwater site; TSG: Tezontepec de Aldama groundwater site.

*Scan numbers 496; 1,392, and 2,059, respectively.

Table 10. Summary of chemical risks (at method detection limits).

| Parameter | No. | Level | Risk |
|-----------|-----|-------|------|
| Target BNA organics | 0 | 0 | No |
| Non-target BNA organics | 3–11 | ≤ 2 µg/L | No |
| Chlorinated pesticides | 1 | 30 pg/L | No |
| Polychlorinated biphenyls | 2–5 | ≤ 36 pg/L | No |
| Nitrate | 7–10 mg/kg/day, a > 3.65 mg/kg/day b | Yes c |
| Trace metals | < drinking water standard | No |

Abbreviations: ?, unknown risk; ADI, acceptable daily intake; BNA, base/neutral/acid; CCI, chronic daily intake; No., number of compounds detected. Determinations of risk apply to all sampling sites Tezontepec de Aldama, Cerro Colorado River inside wastewater irrigation district, and El Salto River outside.

*Infant group CDI; Young children CDI. aMethemoglobinemia risk in infants (CDI > reference dose) and young children (CDI > ADI).

Table 11. Summary of microbiological risks (at method detection limits).

| Parameter | Presence | Risk |
|-----------|----------|------|
| Vibrio cholerae | V. cholerae non-01 | Potential d cholera |
| Salmonella | None | No |
| Total coliforms | 37–770/100 mL | Potential e GI disease |
| E. coli | 0–7/100 mL | Potential f GI disease |

GI: gastrointestinal. Determinations of risk apply to all sampling sites Tezontepec de Aldama, Cerro Colorado River inside wastewater irrigation district, and El Salto River outside.

*Superscript indicates risk agent detected.

If further risk characterization proves nitrate management is needed, source identification and control should be the primary techniques. If control is impractical, low maintenance, village-scale denitrification of rural groundwater supplies would be appropriate. Such a method has been demonstrated by Silverstein et al. (37) using a novel packed tower biofilm reactor to a removal efficiency of 80–90% with influent flow at 38 L/min, 88–110 mg/L NO−3. Noyola and Morgan (38) in Mexico designed an anaerobic–anoxic–aerobic process to eliminate organic matter and nitrate in municipal and domestic wastewaters. When organic matter is low, as in Mezquital, the first-stage anoxic-activated sludge reactor is excluded, which leaves two main components: an anoxic activated sludge denitrifier with upward flow, and a packed nitrifier, with recirculation between the two. For the Mezquital conditions, a second, smaller denitrifier can be placed after the first, in which methanol is dosed stochiometrically as the external carbon source. This method can achieve 95% removal of total nitrogen for flows on the order of 1.5 L/sec.

Institutional and educational interventions. Pathogen risks should be mitigated by a vigorous campaign that encourages hand-washing after defecation and before preparing and eating meals, and the boiling of drinking water from springs. Nitrate risk should be mitigated by breast-feeding infants instead of using water-based formula, and the consumption of low cost, certified purified water (an 18-L container costs $6.00 to purchase and half a field worker’s daily wage to renew—$1.50). In developed countries, treatment plants would be installed to mitigate risk, but because physical intervention is often deemed too costly and is slow to appear in poor, rural communities of developing countries, active institutional and educational intervention to combat the nitrate and microbiological risks must precede it—and often substitute it. This should be a collaboration between public health officials (the local Sanitary Jurisdiction in Tula and the State Public Health Office in Pachuca), community leaders, and water resource agencies (local utility companies and the state-level National Water Commission, CNA-Hidalgo). Public health officials need to effect a more persistent campaign of risk communication with basic hygiene education that is culturally accepted, whereas the water resource agencies need to work more closely with researchers to design and help install sanitation that is economically and technically feasible for the rural, agricultural context of Mezquital. Environmental health problems are slowly beginning to fuel much-needed multidisciplinary collaboration at the technical level, but inter-institutional collaboration, community participation, and the transfer of knowledge into cost-effective solutions to priority problems are still the major challenges in Mexico—collective responsibilities for health professionals, engineers, and politicians to assume.

Research recommendations. Applied research should first address priority interventions for pathogen risks. Secondary topics include a fuller characterization of nitrate risk—an adequate, focused case-control epidemiologic study using a new control site exposed to low nitrate; improved surveillance (any infant death from methemoglobinemia is presently unidentified in local health records); direct and indirect human exposure to wastewater in canals and flooded fields, especially dermal contact for bathing children and barefoot farmworkers; and indirect human exposure by ingestion of crops, cow’s milk, beef, and sheep’s meat.

References and Notes

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