



Project Summary

Proposed Test Protocol to Determine Toxicant Leaching into Potable Water

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A simple apparatus was constructed from Teflon* to test leachability of contaminants. Plates coated with coal-tar-based material were placed in the Teflon test chamber of the apparatus, and water of controlled parameters was continuously passed through the chamber at a velocity of 2 L/min for a period of 24 hr.

The test apparatus was unique in its ability to perform an accelerated leaching test under flowing water conditions. These tests showed migrations of various component polynuclear aromatic hydrocarbons (PNA) with no detectable aging effect in three successive 24-hr leachates in results that fell in the range of 30 to 400 µg/L.

The possibility of PNA migration from the coal-tar-based material lining pipes in the field was tested at three utilities. No quantitative correlation could be established between the leaching observed under laboratory and field tests. However, the leaching pattern from the field pipes can be quantitatively explained from the results of laboratory leaching tests.

This Project Summary was developed by EPA's Risk Reduction Engineering Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully docu-

mented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Potable water used by large segments of the U.S. population is exposed to direct and indirect additives. The direct additives are chemicals that are deliberately added during the treatment of raw water for coagulation, softening, corrosion control, disinfection, fluoridation, and other purposes. As a result, finished water may contain both intended and unintended residuals from direct additives. Indirect additives are defined as contaminants that are inadvertently introduced into the potable water through paints, coatings, liners, sealants, pumps, and other items used during storage and distribution of potable water to consumers. The change in potable water quality as a result of the presence of direct and indirect additives necessitates an evaluation of the possible health hazards arising from these additives. Through a memorandum of understanding signed by the U.S. Food and Drug Administration and the U.S. Environmental Protection Agency (EPA) in 1979, the responsibility for monitoring and controlling these additives was vested in EPA (44FR42775, July 20, 1979). As one of the initial steps towards meeting this responsibility, EPA, in cooperation with the National Research Council, produced a Water Treatment Chemicals Codex for direct additives only. The Codex recommends a minimum acceptable purity specification as it

* Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

related to health for about 25 commonly present additives in potable water.

Indirect additives, on the other hand, have been monitored through a voluntary program and through the issuance of advisory opinions by EPA or its predecessor agencies. Obstacles to the development of a safety evaluation program for indirect additives include a lack of established maximum contaminant levels in several instances, absence of suitable laboratory simulation data and field studies, and the lack of a general consensus regarding the target parameters to be monitored as indicators of indirect additives. The present investigation was undertaken to provide support for Codex development methodology for indirect additives. The purpose of this research was (1) to develop a comprehensive and realistic laboratory test protocol that would simulate contaminant migration from coal-tar-based materials similar to those that line potable water pipes and tanks in the field, and (2) to correlate the laboratory test results with actual field studies. Coal-tar-based materials were used to represent sources of secondary additives for developing the test protocol because leachates from these materials are known to contain a large number of compounds, some of which are suspected to be carcinogenic.

Experimental

Laboratory Apparatus

The laboratory leaching apparatus was fabricated and assembled inhouse. It consisted of four parts: (1) a leaching compartment of Teflon having a well 20-1/2 by 1-1/2 by 9/20 in. in the midsection and a removable Teflon top plate for the insertion of test plates; (2) Teflon connecting fittings and tubes; (3) a variable speed circulating pump with all Teflon wettable parts; and (4) a flowmeter. A diagram of the laboratory apparatus is shown in Figure 1.

Test plates were fabricated from a stainless steel sheet 0.05 in. thick. Each plate had a dimension of 20 x 1.5 in. These plates were sand-blasted before being coated. Each plate was cleansed with purified deionized distilled water (DDW) and acetone and was dried before the application of the coating material. A one-coat Bitumastic Super Tank Solution (Type I) was used in the experiments as a coating system. The test plates were coated with the suction-feed spraying system at a delivery pressure adjusted to about 60

psi at the gun, as recommended by the manufacturer of the coating material. Two coats of the coating material were evenly applied on both sides of the test plates. The test plates were air dried for 10 days and those plates with total dry thickness ranging from 0.040 to 0.060 in. were selected for further leaching tests.

The leaching test with coated plates began by pre-exposing the plates in a solution of sodium hypochlorite containing 50 ppm of free chlorine at a pH of 10.5. The plates were allowed to stand in this solution overnight and were subsequently washed with purified DDW. Two plates were placed inside the leaching compartment, and it was sealed. The compartment was filled with test water of controlled parameters, and the flow rate of the circulating water was maintained at the desired value. The entire leaching apparatus was transferred to an environmental chamber where the temperature at which the test was conducted could be controlled. It was experimentally determined that for a flow rate of 2 L/min, the temperature of the environmental chamber had to be set at 12.8°C for the circulating water to attain an equilibrium temperature of 21.5°C and at 25.6°C to attain a temperature of

28.5°C. The system was allowed to run for the desired length of time.

At the end of the run, all of the water from the leaching apparatus was drained into a measuring cylinder. An aliquot of the water (≈ 70 mL) was kept separate for performing alkalinity, hardness, and residual chlorine tests. The residual leachate was solvent extracted with methylene chloride (6 mL of methylene chloride for every 100 mL of water). The extract was concentrated to a final volume of 1 mL using a Kuderna-Danforth apparatus and subsequent blowdown using prepurified N₂ gas at 30°C.

Field Sampler

The field sampler consisted of the following three main components: (1) a two-stage resin column system; (2) variable water pumping consisting of a Masterflex pump with appropriate pumpheads and flow controller; and (3) flowmeter. Chroma extender-type columns of 150 x 25 x 4 mm were used to hold the resin bed. The resin bed consisted of equal volumes of XAD-2 and XE-348 resins separated by glass wool. The length of the resin bed was set at 13 cm. The ends of the Chromaflex columns were plugged

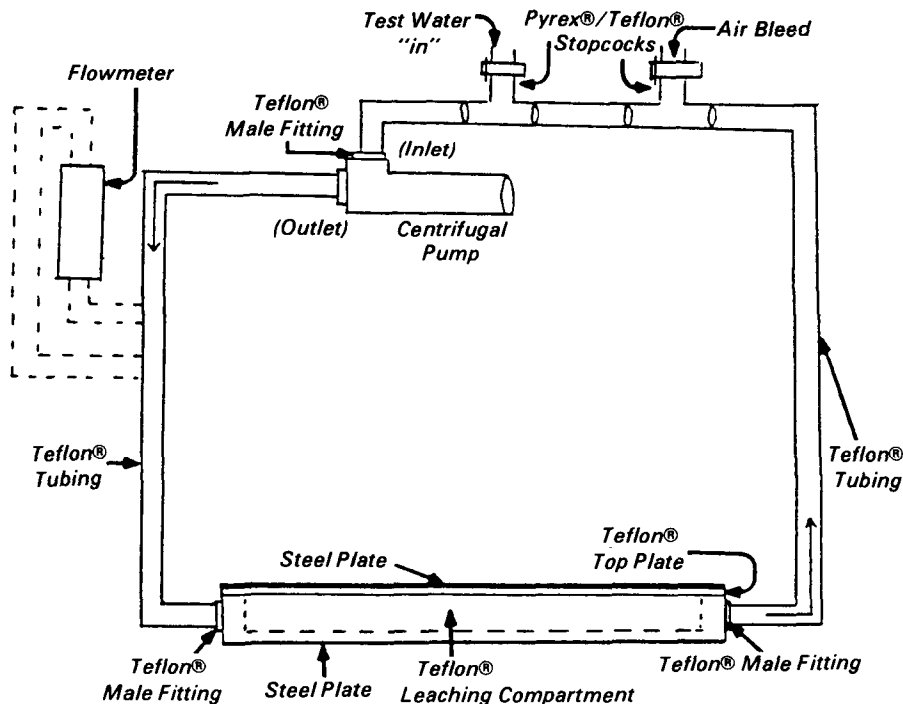


Figure 1. Schematic diagram of leaching apparatus (not to scale).

with clean glass wool and were connected to two tapered column adaptors by "O" rings and clamps. Two such resin columns were connected in parallel to the water to be sampled through a Pyrex glass Y-tube. The other end of the column was connected individually to a variable Masterflex pump. The pump units with their flow controllers allowed water to pass through the resin bed at the desired rate. The outlets of the pumps were connected to calibrated flowmeters to measure the flow rate that was maintained at 40 mL/min. The effluent water was collected in calibrated collapsible plastic carboys. Measurement of the total water collected in each carboy over a known period of time permitted the gross water flow rate through the resin beds to be estimated. All connections along the different components were made with the custom-made 8-mm Pyrex glass tubing of convenient shape and length, and minimum lengths of Tygon tubing were used for interconnecting the Pyrex glass tubing.

Field Sampling Analyses

Potable water samples from three water supply systems on the West Coast of the United States were analyzed as field samples. The rationale for selecting these systems was that they represented three large public water utilities and all contained transmission pipes lined with coal-tar-based material. The expected occurrence of secondary additives in this water make it well suited to test whether or not the designed laboratory leaching apparatus, upon which the proposed test protocol is based, could be successfully used.

At each water supply, water samples were collected at three points. The first point was the water at the treatment plant before it was exposed to lined transmission pipes or tanks. The second and third sampling points were near the beginning and near the end of a transmission system that had pipes lined with coal-tar-based materials.

The sampling unit was transported to each sampling location by packing the individual components in suitcases. For the convenience of transportation, the Masterflex pumps with the flow-controllers and pumpheads were carried in a separate suitcase provided by the manufacturer. A total of 20 L of water was collected from each sampling point. At the end of the sampling, the ends of the resin columns were sealed with polyurethane foam plugs, parafilm, and

masking tape. The columns were wrapped in aluminum foil, cooled with non-wettable ice packs, and then transported to the laboratory. In the laboratory the resin beds were warmed and separated, and only the XAD-2 portions were spiked with a known amount of C¹⁴-fluorene. Only the XAD-2 resins were subjected to the elution method. The XE-348 beds containing more polar compounds were not further analyzed.

The XAD-2 resin bed was washed with about 20 to 25 mL of acetone. The vacuum from an aspirator removed excess acetone from the resin bed. The dry XAD-2 bed was removed to a clean thimble, and the resin was Soxhlet-extracted for 24 hr with methylene chloride. The acetone wash was diluted with purified DDW and extracted with methylene chloride. The two methylene chloride layers were combined and concentrated to 1 mL for radioactive counting and analysis using a gas chromatography-mass spectrometry-data system combination (GC-MS-DS). Before the radioactive counting, a solvent exchange of methylene chloride to toluene was performed on 500 μ L of the above concentrated extract. The collection efficiency of seven PNA's with this sampling apparatus averaged 84% in the laboratory.

To increase the sensitivity of the GC-MS-DS analysis, several modifications were made in the original system. The injection port of the original packed column GC was replaced according to the manufacturer's instructions with an on-column (capillary) injection system. The interface of the exit end of the column with the MS was also altered; the jet separator and its associated accessories were completely removed and the exit end of the capillary column was introduced directly into the ion source. The conditions used for the operation of the GC-MS were as follows:

Column:	30 m x 0.25 mm DB-1 fused silica capillary
Column program:	50°C for 4 min; 8°C/min to 270°C; Hold at 270°C for 20 min
Carrier gas He linear velocity:	35 to 45 cm/sec
Source temperature:	170°C

Analyzer temperature:	200°C
MS delay:	4 min following sample injection
Scan:	50 to up to 500 amu
Scan time:	1.2 sec/scan

In the specific ion mode, the parent ion and two other fragment ions with the highest intensities were monitored for a period of 150 millisecon each.

The performance characteristics of the MS were verified by frequently injecting 50 ng decafluorotriphenylphosphine (DFTPP) into the GC-MS system. When the performance characteristics fell below the recommended levels, the source of the unacceptable performance characteristics were corrected either by cleaning the ion source, plugging possible leaks, or changing the sorbent traps for the carrier gas.

The GC-MS system produced a total ion chromatogram of each sample. Since the chromatograms contained large numbers of peaks, the MS data system was used to identify the peaks and locate the individual peaks when necessary. The tentative identification of each peak was by NBS Spectral Library search. The final identification of a compound was made by matching the relative retention time (with respect to anthracene-d₁₀) and the MS fragmentation pattern with an authentic standard. A peak was quantified by comparing its area with that of the anthracene-d₁₀ internal standard. This method of quantification assumes a linear response of peak area with the concentration.

Results and Discussion

The 24-hr laboratory leaching experiments conducted with plates coated with a coal-tar based material and water of controlled parameters (aggressive index, 8.6; free residual chlorine, 3.3 \pm 0.03; and temperature 21.5 \pm 0.5°C) showed the migration of the following components at the specified concentrations (μ g/L): indene, 73; naphthalene, 36; quinoline, 213; indole, 45; acenaphthalene, 77; fluorene, 79; phenanthrene/anthracene, 298; carbazole, 399; pyrene, 117; and triphenylene/chrysene, 81. The results of three consecutive 24-hr washings, each performed to determine the aging effect of the coated plates, failed to show any difference in the concentrations of the individual PNA's in the successive leachates. The increase of residual chlorine level in water from 0.93 to 3.3 mg/L, resulted in decreased concen-

trations of some of the PNA's, particularly the levels of phenanthrene/anthracene, purene, and fluorene in the leachates, possibly because of the formation of more chlorinated PNA's at higher chlorine level. No clear trend resulting from the leachability of PNA's was observed by changing the water temperature from 21.5°C to 28.4°C.

Field test results of water collected from one utility showed that the concentrations of a few PNA's noticeably increased as a result of finished water passing through transmission pipes/tank lined with coal-tar-based material. For example, the concentration of indene, fluoranthene, and pyrene increased from 0.12 µg/L, 0.06 µg/L, and none detected to 0.17, 0.11, and <0.05 µg/L, respectively. No noticeable difference in the level of PNA's in water originating from pipes lined with coal-tar-based material was observed, however, when compared with levels from the other two utilities. This is probably because the transmission pipe used for sampling water in one utility was relatively new (≈ 5 yr) and the transmission pipes in the other two utilities were older (≈ 10 years old). Probably a difference of PNA concentrations in the two other systems would have been observed if the detection limit for the PNA's had been lower (<0.05 µg/L). No quantitative correlation could be established between the leaching observed under laboratory and field tests. This is not surprising considering that, among the many differences between the two cases, laboratory plates leach at about 4 orders of magnitude higher than do the field pipes. However, the leaching pattern from the field pipes can be qualitatively explained from the results of laboratory leaching tests.

Summary and Conclusions

The Laboratory leaching apparatus and the test protocol developed in the present study have been successfully used to determine the leachings of major individual components from plates lined with coal-tar-based material. The test

protocol was developed to identify and quantify the major individual contaminants in the leachates. This is an important improvement over the previously available protocols because it will permit the assessment of possible health hazards arising from the individual leached components. The developed test protocol accelerates the leaching of components from coated surfaces and permits measurement of the level of major leachables in short-term leaching tests.

The leaching study shows that PNA's are the major contaminants that will leach into water from surfaces lined with coal-tar-based material. Evidence is provided that PNA concentrations in leachates depend on the free residual chlorine in the water and that an increase in chlorine level will decrease the level of some PNA's in the leaching water. The study also demonstrates that short-term laboratory leaching tests are not suitable for studying the aging effect in the field of pipes lined with coal-tar-based materials.

Results of a few field tests with potable water after their passage through pipes lined with coal-tar-based material demonstrate that no quantitative correlation can be made between the laboratory and field leaching tests. The leaching of components from lined pipes in the field will be about four orders of magnitude lower than laboratory leaching from coated plates. To establish the possible PNA leaching in the field from transmission pipes lined with coal-tar-based material older than 5 yr, therefore, the detection limit for PNA quantification should be ≤50 ng/thousand liters. The results of laboratory leaching tests are useful in field tests aimed at predicting and rationalizing the observed leaching of contaminants from transmission pipes lined with coal-tar-based material.

Recommendations

Based on our experience with the present project, we recommend that the following ideas be considered for implementation of further research:

1. Proper interlaboratory verification undertaken so that the test apparatus and the test protocol developed in this study can be used by EPA as standard method for the approval of materials intended to be used in contact with drinking water.
2. The verified test protocol be used to identify and quantify the major individual components for subsequent toxicological testing to determine which of those identified are causative factors in leachates found to be toxic.
3. The verified test protocol be used to further establish the effect of water quality parameters on the migration of contaminants into the water.
4. A guideline based on the toxicity of the individual contaminants be established to specify the minimum acceptable detection limit of the contaminants for the verified test protocol.
5. Further research be conducted to verify the applicability of the present test protocol to other materials used in the transmission of potable water.
6. Further research be conducted to establish a possible correlation between the leaching observed under laboratory conditions and those under field conditions.

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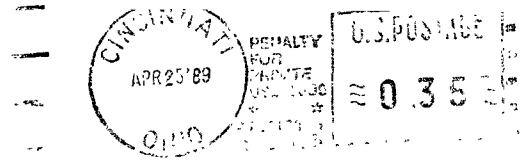
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Alan A. Stevens is the EPA Project Officer (see below).

The complete report, entitled "Proposed Test Protocol to Detect Leaching into Potable Water," (Order No. PB 89-125 959/AS; subject to change) will be available only from:

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