
DISTRIBUTION OF VINYL CHLORIDE (VC) IN A LABORATORY COLUMN USING AQUIFER MATERIAL FROM A CONTAMINATED SITE

¹A.R. Fischer, ¹H. Lorbeer, and ²P. Werner

¹²*Dresden University of Technology, Institute of Waste Management and Contaminated Site Treatment, Pratzschwitzer Str. 15, D-01796 Pirna, Germany; ¹Phone: +49-3501-5300-28; ²Phone: +49-3501-5300-21; ¹²Fax: +49-3501-5300-22*

ABSTRACT

This paper investigates distribution behaviour of the carcinogenic compound vinyl chloride (VC) under semi-natural conditions in a three-phase system (air, water, and aquifer material). A stainless steel column was filled with quaternary aquifer material (gritty sand) from a contaminated site (Bitterfeld, Germany). VC-contaminated water with a defined concentration was prepared and pumped in several cycles through the saturated zone of the column. The concentration level of VC in air and water was measured regularly until equilibrium was reached. The amount of VC adsorbed on the aquifer material was calculated by a mass balance consideration. The dimensionless Henry's Law constant (approx. 1.6) and the K_{oc} (approx. 210) of VC were determined. Results agree well with literature values. However, to our knowledge this is the first study to investigate the partitioning of VC experimentally with aquifer material under semi-natural conditions.

Key words: vinyl chloride, aquifer material, contaminated site, K_{oc} , Henry's law constant

INTRODUCTION

Vinyl chloride (VC) is a gaseous carcinogenic substance (b.p. -13.4°C) often found at sites contaminated with volatile chlorinated compounds. Although VC is used as monomer for polymerization, it also appears in the environment as a metabolite during the biodegradation of chlorinated solvents (Adamson et al., 2004).

VC is often found in air samples at disused plastics industries as well as in landfill gas. Due to the possible dehalogenation of the cleaning agent perchloroethylene, VC is also often detected at former dry-cleaning centers. One of the elimination pathways for VC is simple evaporation from groundwater or soil water, which can be estimated from Henry's Law constant. The dimensionless partition coefficient of VC between gas phase and aqueous phase has been reported to be between 0.9 and 2.3 (Hine and Mookerjee, 1975; Wilhelm et al., 1977; Gossett, 1987; Howe et al., 1988). However, the question is, how useful are these values for calculating the evaporation of VC under natural conditions? These data have been determined by theoretical calculations or by partitioning experiments in artificial laboratory systems. In most cases, mixtures of distilled water and methanol— as cosolvents — were used. Additionally, to estimate actual distribution of VC in the environment, data on sorption behavior to particulate matter are also necessary. However, there are no experimental data available that allow for calculating the respective distribution coefficients (WHO, 2004).

In this study, aquifer material (gritty sand) from a contaminated site (Bitterfeld, Germany) was used to determine the distribution of VC under nearly realistic conditions. The groundwater at this site is known to contain many toxic organic compounds and also a low level of VC (approximately 10 µg/L). The fate of VC and other contaminants at this site is important for the risk assessment, because the total volume of the contaminated aquifer is approx. 200 million cubic meters. Therefore, it is of special interest to investigate the distribution of VC with material from that site after addition of VC-contaminated water. For the fast determination of VC below the detection limit of the GC/FID, a semi-quantitative derivatization method was modified and evaluated for the requirements of this study. This method can be used at low concentrations of less than 50 ng/L.

MATERIALS AND METHODS

Laboratory Column

The laboratory column has a cylindrical form (Figure 1). Dimensions of the column are listed in Table 1. Two water inlets were positioned at the bottom and top of the column. The column was filled with aquifer material. The lower 30 cm of the column was saturated with water equating to approximately one-fifth of the total column volume. A pair of opposite sampling ports was located every 15 cm along the unsaturated zone of the column between the water level and the top. Stainless steel split tubes were inserted through the column, fixed in screwed flanges, and sealed at both ends using Viton® gaskets. Each tube contained 32 slots, each 50-mm long and 1-mm wide, placed only on both sides of the tube in order to prevent the interior from clogging up when the column was filled. This enabled the unhampered diffusion of the column air inside the tube and to the sampling points.

Gas from the unsaturated zone was sampled using Mininert® valves (crimp-top type, 13mm, Valco Instruments Co. Corp.). Valves were inserted and fastened directly into the protruding ends of the split tubes. Opposite ends of the split tubes were sealed by Swagelok screw connections and blind plugs. Gas samples were taken from inside the split tube at one-third of the column diameter by gas-tight syringes equipped with valves and extra-long needles.

The Mininert® valves were in contact with column air only through a 1.94-cm² Teflon® surface. Seals at the bottom and top of the column were Viton ring gaskets. All other connections were of the gasket-free Swagelok type. Water was pumped by means of a rotary piston pump (MCP-CPF Process, Ismatec) equipped with a QPQ1.CSC pump head. All connections between the storage tank, pump, and column were stainless steel capillary tubing.

Before the column was used for the experiments, pressure tightness of the laboratory

column was checked by applying excess pressure of 100 kPa for 24 hours. Experiments were conducted at room temperature (20–24°C). Table 1 contains additional data on vinyl chloride and the experimental conditions.

The column was filled with the aquifer material and washed with 140 L (about two column volumes) of tap water, which emerged from outlets in a manifold perforated tube over the top of the column. The pore volume within the column was therefore completely saturated with water. This treatment also compressed the material and the fill-level sank by 0.1 m. Compaction was 7.5%. This was taken into account in further calculations. Grain-size distribution and hydraulic conductivity of the aquifer material were determined by sieving according to German Industry Standards DIN 18123 and DIN 19368, respectively. Total organic carbon content (TOC) was determined using a Shimadzu TOC-5000 analyser. Ten samples of aquifer material were homogenized and analysed in parallel (0.1 g each).

Spiking Procedure

A gas-tight pressure tank (Sartorius, 6.16 L) was filled with 5 L of distilled water, and VC was added through a connection from a gas cylinder. The tank was then shaken on a rotary shaker for 48 hours in order to ensure a complete homogeneous solution. After the tap water had been removed, 3.6 L of the spiking solution containing VC were filled into the column and pumped in cycle overnight (76 mL/min). The extraction point was horizon 0 (Fig. 2).

The measured initial concentration of the aqueous VC solution within the column was 440 mg/L as determined at the column inlet sampling point. Over the next few weeks, the VC concentrations in air and water were determined until equilibrium had been reached. The total water volume within the column was estimated to be approx. 10.2 L and the calculated air volume approx. 17.5 L (see Table 1).

VC Water Analysis

For the VC calibrations, a vinyl chloride stock solution of 200 µg/mL in methanol (Supelco) was purchased. Aqueous VC solutions were prepared by a step-wise dilution of the stock solution with water until the preferred concentration was reached. This was accomplished by using gas tight syringes with which the VC solution was immediately injected through a septum into a head-space vial (22 mL) containing water. Overall liquid volume in each headspace vial was 10 mL.

VC water samples (1 mL) from the laboratory column were taken in duplicate from two horizons (0 and -1) with lockable, gas tight syringes. Samples were injected through septa into head space vials containing 9 mL of distilled water. The head-space vials were thermostatted at 85°C for 1.5 hours, followed by analysis of the head-space with an HP 6890

gas chromatograph (Agilent) equipped with a split/splitless injector and flame ionisation detector (FID). The GC system was connected to a Perkin-Elmer HS 40XL autosampler. A HP-PONA capillary column (50 m, 0.2 mm i.d., 0.5 µm film thickness) was used for separation. Helium was used as carrier gas (1.0 mL/min, constant flow) and nitrogen as make-up gas (25 mL/min), along with hydrogen (35 mL/min) and oxygen (65 mL/min) as detector gases. One hundred µL of head space was injected (split ratio: 1:0.3). Temperature settings were injector temperature 150°C, oven temperature programme: 30°C (5 min) → 10°C/min → 150°C (5 min), and detector temperature 300°C. Calibration was performed from 20 µg/L to 2000 µg/L with a correlation coefficient of >0.996. Detection limit was approximately 10 µg/L.

VC Gas Analysis

VC was purchased in a gas cylinder (Sigma-Aldrich). Defined VC air samples with known concentrations were prepared using a small gas-collecting vessel (100 mL) equipped with two ground-in stopcocks and a discharging device with PTFE-coated silicone septum. The vessel was evacuated and flushed several times, alternating with water-jet vacuum pump and VC gas from the gas cylinder. After filling had been completed, excess pressure was allowed to drop to atmospheric pressure by opening one stopcock for 1 second (under an extractor hood). The amount of VC was controlled by weighing (density of VC at room temperature is approximately 2.5 µg/µl). The vessel was used as stock VC gas for further dilutions. For dilutions, defined VC gas volumes were taken through the septum with gas-tight syringes and injected through a septum into gas-tight vials of different volumes in order to obtain defined dilutions. Analyses were conducted with gas-tight syringes by direct injection into a GC/FID.

VC air samples (50 µL) from the laboratory column were taken in duplicate from the seven different horizons of the unsaturated zone with lockable gas-tight syringes and analyzed immediately with the GC/FID system described above for the water samples. Injections were performed (split ratio: 1:10). Temperature settings were injector temperature 200°C, oven temperature programme: 35°C (5 min), postrun (200°C) for 5 minutes, and detector temperature 300°C. Calibration was performed from 20 ng to 200 ng with a correlation coefficient of >0.999. Detection limit was approximately 5 ng.

VC Derivative Analysis

In this work, low VC concentrations in air and water had to be analyzed that were below detection limits of the standard method described. For this reason, a derivatization method (Wittsiepe et al., 1993, 1996) for low VC concentrations was modified. VC reacts very rapidly with bromine to form 1,2-dibromochloroethane, which can be determined with

sensitivity by a gas chromatograph coupled with an electron capture detector (GC/ECD). Results were compared in parallel with underivatized VC gas and water samples determined by GC/FID. VC air samples (500 μL) and water samples (50 μL) were taken in duplicate with gas-tight syringes. Each sample was injected through a septum into a 10-mL head-space vial containing the internal standard 1-bromo-3-chloro-propane (1.6 $\text{ng}/\mu\text{L}$) dissolved in 2 mL of decane and 5 mL of bromine water (0.1%). Decane (Fluka, Switzerland) was used as a solvent because it is of minor toxicity and is available free of olefins, which could unfavorably affect bromination by the formation of by-products. Moreover, diluted VC solutions can be stored in decane at -15°C without freezing. The head-space vial was shaken for 15 minutes. A reddish phase was concentrated at the top of the reaction vial due to the higher solubility of bromine in decane. After shaking, the reaction was stopped by adding 2 mL of aqueous sodium thiosulphate solution (10%) and excess bromine reacted to bromide. Afterwards, 1 μL of the decane phase was sampled through the septum with a gas-tight syringe and analyzed with GC/ECD as described above.

The derivatization method was used for routine analyses in order to estimate the distribution behavior of VC during the elapsed time. This was important, particularly within the first days of the experiment, because the VC air concentrations were too low for detection with GC/FID. For later samples that exceeded the detection limit of the FID, results of the derivatization method were controlled by the GC/FID method.

Synthesis of the VC Derivative

1,2-dibromochloroethane as reference compound was synthesized as described by Wittsiepe et al., 1990. Afterwards, defined dilutions were produced with carbon disulphide (Merck, Germany) as solvent using gas-tight syringes. The derivative was analyzed with GC/ECD and calibrated for concentrations from 10 pg up to 100 ng . An HP 6890 with split/splitless injector and ECD detector (Hewlett-Packard) and an HP-PONA capillary column (50 m, 0.2 mm i.d., 0.5 μm film thickness) was employed with helium as carrier gas (1.0 mL/min , constant flow) and nitrogen as make-up gas (40 mL/min). Approximately 1 μL was injected (split ratio: 1:20). Temperature settings were injector temperature 250°C , oven temperature programme: 40°C (1 min) $\rightarrow 10^\circ\text{C}/\text{min} \rightarrow 115^\circ\text{C}$ (3 min) $\rightarrow 20^\circ\text{C}/\text{min} \rightarrow 300^\circ\text{C}$ (1.25 min) and detector temperature 300°C . The correlation coefficient was >0.999 ; 1-bromo-3-chloro-propane was used as an internal standard.

RESULTS

Determination of Henry's Law Coefficient

Once the whole system is in equilibrium, the concentration ratio of VC in the gas phase and in the aqueous phase provides an estimate of the dimensionless air-water partition

coefficient that can be translated into the standard Henry's Law coefficient by temperature correction.

The VC concentration in the water phase of the column decreased rapidly from 440 mg L⁻¹ in the beginning to 290 mg L⁻¹ (after 1 day) and to ca. 9 mg L⁻¹ after a few days, indicating that VC evaporated quickly from the water phase. During the experiment, the pH decreased from 7.0 to approx. 4.0. Figure 3 shows the development of the VC concentrations in the water phase (horizon 0) and in the air phase (horizons 1+2, horizon 4 and horizon 6).

Each data point represents the mean value of two samples. Variations of the analytical replications were small (< 10%) and are not displayed for better clarity. Time course of the VC concentrations was similar for all horizons. Therefore, a detailed illustration of the other horizons was dispensed with. Assuming that equilibrium was reached at the end of the experiment (45 days), average VC concentrations in air (14 mg L⁻¹) and water (9 mg L⁻¹) were used to estimate the dimensionless Henry's Law constant H to be 1.6, which agrees well with existing literature values (Hine and Mookerjee, 1975; Wilhelm et al., 1977; Gossett, 1987; Howe et al., 1988).

Determination of K_{oc}

A mass balance calculation indicated that large amounts of VC (approximately 70%) sorbed on the gritty sand during the experiment. Thus, chemical fate of VC in the environment is obviously affected by sorption, although literature values for the K_{oc} are often small (< 10 L kg⁻¹). The K_{oc} is the partition coefficient of the contaminant between water and the organic fraction of the solid material and is defined as

$$K_{oc} = K_d \cdot 100 \cdot (OC)^{-1}$$

K_{oc} (L kg⁻¹) = organic carbon normalized sorption coefficient

K_d (L kg⁻¹) = distribution coefficient sorbent/water

OC (%) = organic carbon content of the sorbent (here: gritty sand)

Total VC within the column was 440 (mg L⁻¹) × 3.6 (L) = 1.584 g. The VC amount in air at equilibrium was 14.0 (mg L⁻¹) × 17.5 (L) = 245 mg and VC in water was 9.0 (mg L⁻¹) × 10.2 (L) = 91.8 mg. This leads to a calculated VC concentration on the aquifer material of 1247 (mg) 132⁻¹ (kg⁻¹) = 9.45 mg kg⁻¹. With the resulting K_d value for VC of approximately 1.1 L kg⁻¹, a K_{oc} of 210 (log K_{oc} = 2.32) was estimated by normalization with the organic carbon content, which was 0.5% with a range of variation between 0.45% and 0.55%.

DISCUSSION

K_{oc} values in the literature span a wide range from 0.8 to 240 (Lyman et al., 1982; Mabey, 1982; Liljestrand and Charbeneau, 1987; Jury et al., 1990; Yeh and Kastenber, 1991; Harmon et al., 1992; WHO, 2004). However, all these values were calculated without

experimental data. Our experimental results are at the upper end of these values and suggest that sorption of VC is more important in the environment than estimated using the low K_{oc} values from literature. However, given the very low organic carbon content of 0.5%, the uncertainty in K_{oc} is quite high.

VC could be adsorbed on Teflon® or Viton® surfaces. However, the sum contact area of all the Teflon® valves amounts to less than 0.002 m², while that of the Viton® seals is about 0.003 m². Then again, the specific surface of the aquifer material must also be considered. A common value for the specific surface of sand is approximately 100 cm²/g (Bugueva and Deryugin, 1986; Dundulis and Gadeikis, 2006). The column was filled with dry matter representing a specific surface of more than 800 m². Therefore, the Teflon® and Viton® surfaces are unlikely to significantly influence results of the VC adsorption experiment.

The strong decrease of the pH (from pH 7 to approx. 4.0) indicates that biodegradation may have affected the VC level in the experiment, because it is well known that hydrochloric acid is produced during the biodegradation of volatile chlorinated compounds (Gälli and Leisinger, 1985). However, a significant impact of biodegradation on the VC levels within the time period of the experiment (6 weeks) seems unlikely. The observed pH drop could be explained by generation of approximately 0.001 moles of hydrochloric acid, which implies degradation of only 0.063 g VC (4% of total VC). A buffering effect, e.g. by carbonate, which would decrease the acidic influence of the metabolite hydrochloric acid, cannot be completely ruled out but seems to be unlikely, due to the composition of the used soil and use of distilled water throughout the experiment.

CONCLUSIONS

In this study, distribution of vinyl chloride (VC) in the air, water, and solid phases of quaternary aquifer material was determined in a laboratory column experiment. Henry's Law coefficient and K_{oc} value were calculated from experimental data. Henry's Law coefficient was in good agreement with literature values. The K_{oc} value was at the upper limit of existing values from literature. However, in contrast to literature values, it was calculated from experimental data. Significant adsorption of VC was observed which amounted to approximately 78% of the total VC mass in the used column. This, to our knowledge, is the first study to experimentally determine the K_{oc} of VC with natural material. Future research will continue with materials having different organic carbon content and at different temperature conditions to eliminate uncertainties.

The sorption of VC in the environment seems to be a widely underestimated factor. Sorption of VC could well be an important sink, which should not be ruled out. It is known that chlorinated hydrocarbons are often recalcitrant compounds. They are not

easily biodegradable, and sorption additionally hinders both abiotic and biotic degradation processes of organic compounds. Therefore, after discharge of VC to the environment, e.g. by accident, it should be taken into account that a complete mass balance requires consideration of sorbed VC and not only analysis of water and air.

ACKNOWLEDGMENTS

This work was kindly funded by the German State Department of the Environment and Geology in Dresden (Landesamt für Umwelt und Geologie), grant no. 13-8802.3523/99. Additional financial support was kindly provided by the UFZ Centre for Environmental Research Leipzig–Halle under Project SAFIRA (Search for Natural Attenuation Forces in Regionally Contaminated Aquifers).

REFERENCES

- Adamson D.T., D. Y. Lyon, and J.B. Hughes, 2004. Flux and product distribution during biological treatment of tetrachloroethene-dense, nonaqueous-phase liquid, *Environ. Sci. Technol.* **38:7**, 2021-2028.
- Bugaeva, N.K., and L.M. Deryugin, 1986. Experience in using sands of different grain size for concretes of the Sayano-Shushenskoe hydroelectric station. *Hydrotech. Construction* **20:4**, 199-203.
- Dundulis, K., and S. Gadeikis, 2006. Influence of morphometric characteristics of sand particles on the strength parameters of sand soils in Lithuania. *Geologija. Vilnius.* **53**, 52-56.
- Gälli, R., and T. Leisinger, 1985. Specialised bacterial strains for the removal of dichloromethane from industrial water. *Conserv. Recycling* **8:1-2**, 91-100.
- Gossett, J.M., 1987. Measurement of Henry's Law constants for C1 and C2 chlorinated hydrocarbons, *Environ. Sci. Technol.* **21:2**, 202-208.
- Harmon, T.C., L. Semprini, and P.V. Roberts, 1992. Simulating solute transport using laboratory-based sorption parameters. *J. Environ. Eng.* **118:5**, 666-689.
- Hine, J., and P.K. Mookerjee, 1975. The intrinsic hydrophilic character of organic compounds. Correlations in terms of structural contributions. *J. Org. Chem.* **40**, 292-298.

- Howe, G.B., M.E. Mullins, and T-N. Rogers, 1988. Air-water partitioning coefficients of organics in dilute aqueous solutions. *J. Hazard. Mater.* **18**, 25-36.
- Jury, W.A., D. Russo, G. Streile, and H. El Abd, 1990. Evaluation of volatilization by organic chemicals residing below the soil surface. *Water Resour. Res.* **26:1**, 13-20.
- Liljestrand, H.M., and R.J. Charbeneau, 1987. Analysis and interpretation of batch equilibrium and column studies of the partitioning of chlorinated hydrocarbons to soil materials from the PPG Lake Charles Site, Environmental and Water Resources Engineering, Department of Civil Engineering, The University of Texas at Austin. (<http://www.dtsc.ca.gov/AssessingRisk/Upload/12dca.pdf>).
- Lyman, W.J., W.F. Reehl, and D.H. Rosenblatt, 1982. Handbook of chemical property estimation methods: environmental behavior of organic compounds, American Chemical Society, Washington, DC.
- Mabey, W.R., 1982. Aquatic fate process data for organic priority pollutants. Final report, EPA-440/4-81-014 U.S. Environmental Protection Agency, Washington, DC, NTIS PB87-169090 5 Fiche.
- WHO, 2004. World Health Organization, United Nations Environment Programme, International programme on chemical safety. Environmental Health Criteria **215**: Vinyl Chloride, 1999 with incorporated corrigenda, published by November 30, 2004), http://whqlibdoc.who.int/ehc/WHO_EHC_215.pdf, cited September 2006.
- Wilhelm, E., R. Battino, and R. Wilcock, 1977. Low-pressure solubility of gases in liquid water. *Chem. Rev.* **77**, 219-262.
- Wittsiepe, J., D. Wallschläger, and F. Selenka, 1990. Gas-chromatographic determination of trace amounts of vinyl chloride in water and air after derivatization to 1,2-dibromochloroethane. *Fresenius J. Anal. Chem.* **336:4**, 322-327.
- Wittsiepe, J., D. Wallschläger, F. Selenka, and E. Jackwerth, 1993. Gas-chromatographic determination of trace amounts of vinyl chloride and dichloroethanes in water after purge-and-trap preconcentration and conversion into their dibrominated derivatives. *Fresenius J. Anal. Chem.* **346:12**, 1028-1034.

Wittsiepe, J., D. Wallschläger, and F. Selenka, 1996. Gas chromatographic determination of trace amounts of vinyl chloride and dichloroethenes in landfill gas, *Fresenius J. Anal. Chem.* **354:7-8**, 910-914.

Yeh, H.C., and W.E. Kastenber, 1991. Health risk assessment of biodegradable volatile organic chemicals: A case study, *J. Hazard. Mater.* **27**, 111-126.

Table 1. Physical-chemical properties of Vinyl Chloride, sediment and column experimental conditions. Laboratory column with flow path for washing of aquifer material with tap water.

| VC properties | |
|---|--------------------|
| Henry coefficient (dim'less) | 0.9–2.3 (25°C) |
| Boiling point [°C] | –13.4 |
| Water solubility [g/L] | 1.1 (28°C) |
| K_{oc} [L/kg] | 0.8–240 |
| Aquifer material | |
| Type | quaternary aquifer |
| Grain-size distribution [mass %]: | |
| Gravel (>2 mm) | 37.5 |
| Sand (0.063–2 mm) | 62.5 |
| Silt and potter's clay (≤ 0.063 mm) | 0 |
| Volume with pores [L] | 71 |
| Pore volume [%-vol] | 30 |
| Pure material volume [L] | 49.7 |
| Water content [%] | 5 |
| Water volume [L] | 6.6 |
| Hydraulic conductivity [m/s] | 0.0045 |
| Mean bulk density (dry matter) [kg/m ³] | 1850 |
| Pure density [kg/m ³] | 2650 |
| Total dry mass [kg] | 132 |
| Organic carbon content [%-wt] | 0.5 ± 0.05 |
| Column experimental conditions | |
| Length [m] | 1.5 |
| Inner diameter [m] | 0.25 |
| Total volume [L] | 73.6 |
| Total VC amount [g] | 1.58 |
| (based on measurement at input) | |
| Total air volume [L] | 17.5 |
| Added water volume [L] | 3.6 |
| Total water volume [L] | 3.6 + 6.6 = 10.2 |
| (VC stock solution + material water content) | |

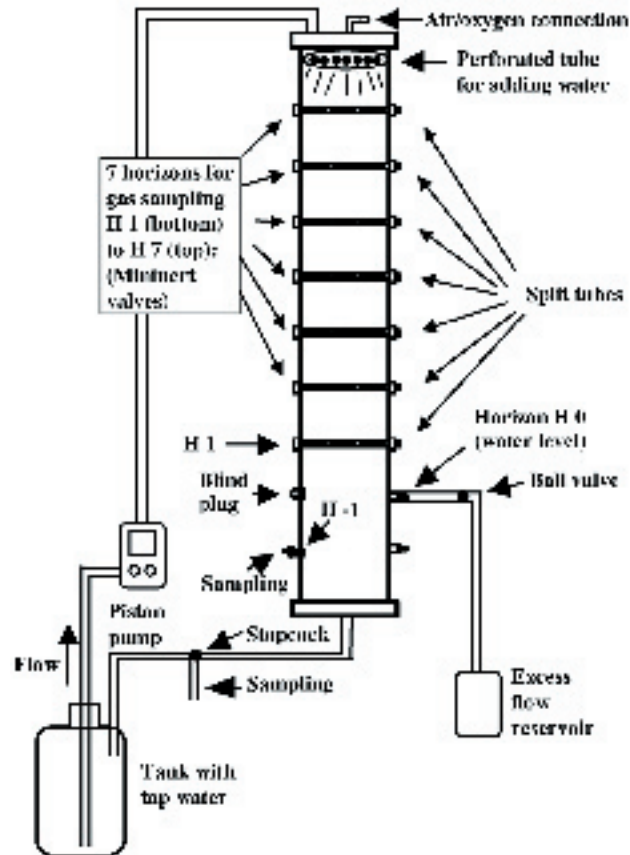


Figure 1. Laboratory column with flow path for washing of aquifer material with tap water.

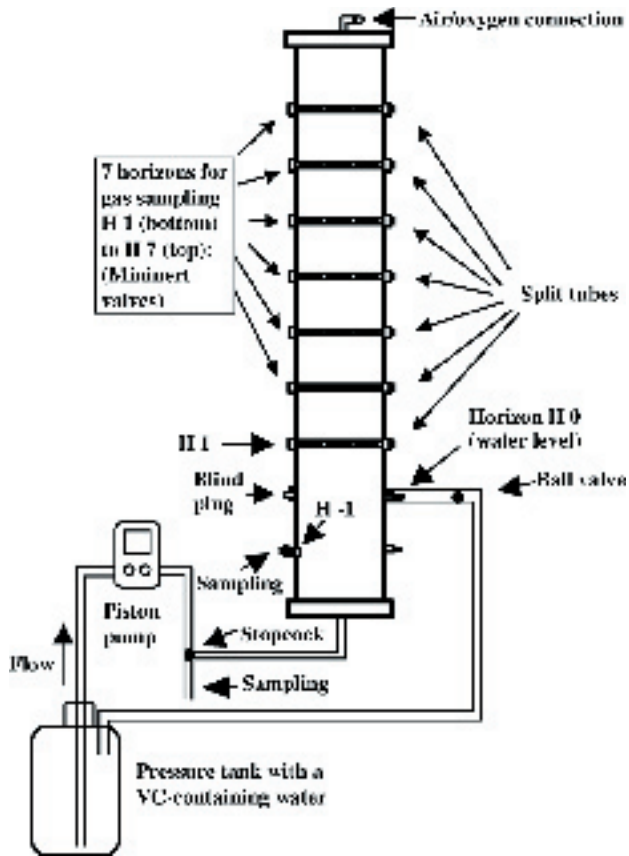


Figure2. VC charging of the column (pumping in circular flow).

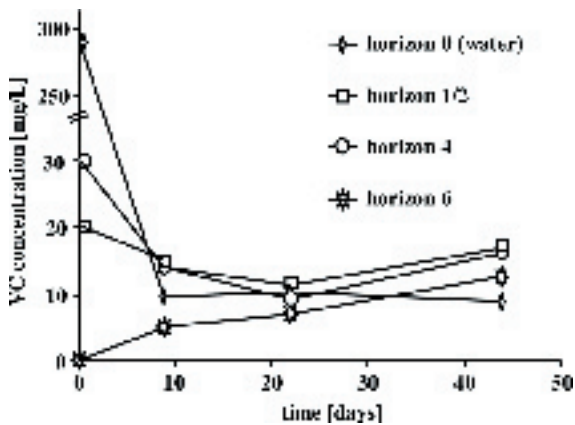


Figure3. VC distribution in water (horizon 0) and air (horizons 1/2/4/6) within a model unsaturated zone.

Original Manuscript Received: November 20, 2006

Revised Manuscript Received: February 26, 2007