

**Energy and Environmental Research Emphasizing
Low-Rank Coal -- Task 1.7
Hot-Water Extraction of Nonpolar Organic
Pollutants from Soils**

Topical Report

Steven B. Hawthorne

January 1995

Work Performed Under Contract No.: DE-FC21-93MC30097

For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, West Virginia

By
University of North Dakota
Grand Forks, North Dakota

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**ENERGY AND ENVIRONMENTAL RESEARCH EMPHASIZING
LOW-RANK COAL -- TASK 1.7
Hot-Water Extraction of Nonpolar Organic Pollutants from Soils**

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SUBTASK 1.7 HOT-WATER EXTRACTION OF NONPOLAR ORGANIC POLLUTANTS FROM SOILS

EXECUTIVE SUMMARY

Supercritical water extraction of organic pollutants from solids is extremely effective because supercritical water has a low dielectric constant and can, therefore, efficiently solvate organics. However, the decrease in the dielectric constant of water can be achieved at much milder conditions (pressures of a few bar and temperatures of ca. 200°–250°C) than the conditions used for supercritical water (pressure > 221 bar and temperature > 374°C) extractions. Polycyclic aromatic hydrocarbons (PAHs) were extracted from a highly contaminated soil using water at temperatures ranging from 50° to 400°C, and pressures from 5 to 600 bar. Most PAHs could not be extracted at 50°C but were completely removed at a temperature of 250°C. Additional increases to 300°C (still subcritical conditions) and 400°C (supercritical water) did not increase the recoveries significantly. The removal of PAHs had very little dependence on pressure when the temperature was 250°C, except that steam extraction (at 5 bar) yielded lower recoveries than the liquid water extractions (at 50, 350, and 600 bar). Therefore, the optimal conditions for extracting PAHs using water were 50 bar and 250°C (hot water). Based on the extraction rates obtained for several of the PAHs, the solubility of high molecular weight PAHs increased at least several thousandfold by increasing the water temperature to 200°–300°C.

Polychlorinated biphenyls (PCBs) were extracted from an industry soil and a sediment using hot-water (subcritical) extraction at 50 bar and 250°C. Although the PCB concentration in the sediment was nearly a thousand times lower than that in the industry soil, all the individual PCB congeners studied were quantitatively removed from both samples. The high removal efficiencies of PCBs from soil and sediment agree very well with those obtained for PAHs from highly contaminated soil at the same extraction conditions, demonstrating that water is a potentially useful extraction solvent for many organics.

1.0 INTRODUCTION

While water is an environmentally acceptable solvent, it has not yet received attention as a subcritical extraction solvent for environmental solids because water is too polar (at ambient conditions) to efficiently dissolve most of the nonionic organics associated with environmental solids.

At ambient temperature and pressure, water has a dielectric constant (ϵ) of ca. 80 (polar), but the dielectric constant is decreased to ca. 8 (nonpolar) in steam or supercritical water conditions (temperature $> 374^{\circ}\text{C}$ and pressure > 221 bar). Therefore, water has been used to extract soils contaminated with organic pollutants either by steam stripping or under supercritical conditions. Both techniques are severely limited for environmental remediation, i.e., steam stripping is only effective on relatively volatile organics, and the high-corrosivity, high-temperature, and high-pressure requirements of supercritical water makes its use unrealistic.

However, the conditions that make supercritical water effective (e.g., lowering of the water's dielectric constant so that it behaves like an organic solvent) do not require supercritical conditions, and can be achieved at relatively "engineering-friendly" conditions of only a few atmospheres of pressure and temperatures as low as $200^{\circ}\text{--}250^{\circ}\text{C}$. Surprisingly, these mild conditions have not been investigated as a remediation technique. Preliminary studies in our laboratory using water at 50 atm and 250°C have shown nearly quantitative removal of creosote polycyclic aromatic hydrocarbons (PAHs) from a highly contaminated soil. This study determined the feasibility of subcritical water to extract nonpolar organic pollutants, such as PAHs and polychlorinated biphenyls (PCBs), from contaminated soils and sediments.

2.0 OBJECTIVES

The objective was to determine the ability of hot water (subcritical water) to extract PAHs and PCBs from contaminated soils. Specific objectives were:

- Determine the optimal pressure and temperature for removal of PAHs from real-world contaminated soils.
- Determine the minimum pressure and temperature required for reasonable removal rates of PAHs.
- Perform preliminary determinations of the use of hot (subcritical) water to remove other organic contaminants, i.e., PCBs from contaminated soils and sediments.

3.0 ACCOMPLISHMENTS

3.1 Water Extraction Removal Efficiencies of PAHs at Several Temperatures and Pressures

The effects of water temperature (at a constant pressure of 350 bar) on the extraction of PAHs from a highly contaminated soil (purchased from Fisher Scientific) are summarized in Table 2 in the attached publication (Appendix). As would be expected on the basis of the high dielectric constant of

water, extractions at 50°C failed to yield significant recovery of any of the PAHs. As the temperature was increased to 200°C, the removal of all the PAHs increased substantially. Further increases in removal were achieved by increasing the temperature to 250°C, and the recoveries at 250°C compared very favorably with the certified concentrations. Additional increases to 300°C (still subcritical conditions) and 400°C (supercritical water) did not increase the recoveries significantly despite lowering the dielectric constant to about 22 and 8, respectively.

Because the dielectric constant of water depends primarily on temperature and much less on the pressure (Figure 1 in the attached publication, see Appendix), the removal of PAHs had very little dependence on pressure (as shown in Table 3 in the attached publication, see Appendix) when the temperature was 250°C. However, steam extraction (at 5 bar) yielded lower recoveries than the liquid water extractions (at 50, 350, and 600 bar).

3.2 The Optimized "Mild" Conditions for Obtaining High Extraction Efficiencies

As discussed above, the optimal pressure and temperature for removal of PAHs from real-world contaminated soils were 50 bar and 250°C. The optimal condition could be even "milder" (lower) for obtaining the same (high) extraction efficiencies if longer extraction times are used. As shown in Table 2 in the Appendix, the extraction at 200°C for 15 min yielded low recoveries of high molecular weight PAHs. However, when the extraction time was increased to 60 min, the removal of all PAHs was as high as those obtained at 250°C (see Figure 3 in the Appendix). Therefore, the lowest (mildest) extraction temperature to quantitatively remove PAHs from contaminated soils is 200°C if the extraction is performed for 60 min.

Figure 1 in the Appendix shows the pressure-temperature diagram of water. For the extractions at 250°C, the minimum pressure required to keep water as a liquid (not steam) is ca. 30 bar. Based on the results in Table 2 in the attached publication (see Appendix), any pressure that can keep hot water as a liquid could give almost the same removal of PAHs. Therefore, the lowest pressure for the extractions at 250°C is ca. 30 bar. When the extractions are performed at 200°C, the minimum pressure could be decreased to ca. 12 bar (still keeping water in liquid condition).

3.3 Solubility Enhancement of PAHs in Subcritical Water

The PAH solubility in ambient water is very low, on the order of ppm to ppb concentrations. However, the solubilities could be dramatically increased by increasing the water temperature (lowering the dielectric constant of water). The minimum enhancement in solubility was calculated based on the quantity of each individual PAH in the contaminated soil that was extracted under the various subcritical water conditions. This enhancement factor is very conservative, because we were extracting a real-world sample, and thus, the amounts of PAHs were limited. If larger quantities of PAHs, or if pure PAHs, were available, the enhancement in solubility would be even larger.

As shown in Table 1, the solubilities of the high-molecular-weight PAHs in subcritical water are increased by at least three orders of magnitude by simply increasing the temperature. This enhancement in solubility should apply to organics that have low solubilities in ambient water (e.g., PCBs and most fuel hydrocarbons).

TABLE 1

Minimum Enhancement in PAH Solubility in Subcritical Water					
PAH	Conc. In Soil, mg/kg	PAH Solubility, mg/L (1 bar, 20°C)	Minimum Enhancement in PAH Solubility @ 350 bar		
			120°C	200°C	300°C
Anthracene	425	0.07	63	91	500
Fluoranthene	1300	0.26	10	62	400
Pyrene	960	0.14	13	81	511
Chrysene	310	0.002	390	1160	6500
Benzo[b]- fluoranthene	160	0.001	330	960	7300

Although there are very few solubilities in the literature of organic compounds in subcritical water at elevated temperatures, the few data that have been reported demonstrate that our preliminary interpretations of the solubility enhancement shown in Table 1 are much too conservative. For example, while our preliminary extraction data indicate a minimum solubility increase of ca. 7000 for higher molecular weight PAHs, an earlier report of the solubility of benzo[e]pyrene at 350°C (and ca. 100 bar) was 10 wt% (Sanders, N.D. *Ind. Eng. Chem. Fundam.* 1986 25,171), which is 20 million times higher than its solubility of ca. 5 µg/L obtained in water at 20°C.

3.4 Removal of PCBs from Soil and Sediment at Optimal Extraction Conditions

Based on the discussions above, the optimal conditions for the extraction of PAHs for 15 min were 50 bar and 250°C. These conditions were used to determine the removal of PCBs from an industry soil and a sediment.

As shown in Table 2, the removal of all of the studied individual PCB congeners is quantitative, although the PCB concentration in the sediment is nearly a thousand times lower than that in the industry soil. The high removal efficiencies of PCBs from soil and sediment agrees very well with those obtained for PAHs from the highly contaminated soil at the same extraction conditions as discussed above. Please note that the extraction time used in Table 2 was 15 min. If the extraction time is increased, the extraction temperature and pressure could be even milder (e.g., ca. 12 bar and 200°C).

The results of this report demonstrate that water is a potentially useful extraction solvent for many organics. Subcritical water at mild conditions (≤ 50 bar and $\leq 250^\circ\text{C}$) could efficiently extract PAHs and PCBs from soils and sediments.

TABLE 2

PCB Removal from Soil and Sediment Using Water Extractions at 50 bar and 250°C for 15 min						
PCB	Soil, CRM 481			Sediment, SRM 1939		
	Cert. Conc., µg/g	Removal, % ^a	RSD, % ^b	Cert. Conc., µg/g	Removal, % ^a	RSD, % ^b
PCB-28	0.34	>99	0	2.2	>99	1
PCB-52	3.15	98	3	3.86	>99	0
PCB-101	37	98	3	0.46	>99	0
PCB-118	9.4	97	3	0.51	>99	0
PCB-149	96	98	3		>99	0
PCB-153	136	97	3		>99	0
PCB-105	1.21	98	3		>99	0
PCB-138	95.3	97	3	0.57	>99	0
PCB-128	8.72	97	3	0.1	>99	0
PCB-156	7.08	96	4		>99	0
PCB-180	123	96	6	0.16	>99	0
PCB-170	52	93	6	0.11	>99	0

^a The percentage removed by water for each PCB congener was calculated from the total quantities removed by water followed by methylene chloride sonication (16 hr) of the residues from the water extractions.

^b %RSD was based on triplicate sequential (water followed by methylene chloride) extractions.

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