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ENGINEERING DATA TRANSMITTAL

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Mary J Hartman M.J. Hartman 11 Apr 96 Signature of EDT Originator Date	Authorized Representative Date for Receiving Organization	D.G. Horton DG Horton 4/10/96 Cognizant Manager Date	Ctrl. No. ☐ Approved ☐ Approved w/comments ☐ Disapproved w/comments

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100-D Ponds Groundwater Quality Assessment

M. J. Hartman
Westinghouse Hanford Company, Richland, WA 99352
U.S. Department of Energy Contract DE-AC06-87RL10930

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Abstract:

The 100-D Ponds facility is regluated under the *Resource Conservation and Recovery Act of 1976*. The pH of groundwater in a downgradient well is statistically different than local background, triggering an assessment of groundwater contamination under 40 CFR 265.93. Results of a similar assessment, conducted in 1993, show that the elevated pH is caused by the presence of alkaline ash sediments beneath the ponds, which are not part of the RCRA unit. The 100-D Ponds should remain in indicator evaluation monitoring.

Karen H Noland 4/11/96
Release Approval Date

APR 11 1996
DATE: HANFORD
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100-D PONDS GROUNDWATER QUALITY ASSESSMENT

1.0 INTRODUCTION

The 100-D Ponds facility is regulated under the *Resource Conservation and Recovery Act of 1976* (RCRA) interim status [40 *Code of Federal Regulations* (CFR) 265]. The pH of groundwater in a downgradient well is statistically different from local background, triggering an assessment of groundwater contamination under 40 CFR 265.93. A similar assessment of 100-D Ponds groundwater was conducted for another program in 1993 (Alexander 1993). Results of that assessment show that the elevated pH is caused by the presence of alkaline ash sediments beneath the ponds, which are not part of the RCRA unit. The 100-D Ponds will remain in indicator evaluation monitoring (40 CFR 265.92).

This report presents the results of the groundwater quality assessment program for the 100-D Ponds. It is prepared in lieu of an assessment plan because the required assessment already has been completed. It is intended to meet the requirements for an assessment plan [40 CFR 265.93(d)(3)] and to report the results of the assessment program [40 CFR 265.93(d)(5)].

2.0 DESCRIPTION OF 100-D PONDS

The 100-D Ponds are located in the 100-D Area of the Hanford Site, near the Columbia River. The facility comprises a settling pond and an infiltration basin, separated by a dike (Figure 1). From 1950 through 1966, before the site was used as a RCRA unit, this location served as an ash disposal basin that received coal ash from the 184-D Powerhouse. Some of the ash was excavated before the site was converted to a RCRA disposal unit, but the 100-D Ponds are underlain by up to 20 m of ash. The ash and any dangerous waste in the ash are not part of the D-Ponds RCRA unit (DOE/RL 1993).

Effluent to the 100-D Ponds originated from two sources: the 183-D Filter Plant and the 189-D Building engineering testing laboratories. Some past discharges contained hydrochloric acid, sulfuric acid, and sodium hydroxide. Before 1986, the effluent may have had a pH greater than 12.5 or less than 2.0, which would have classified it as dangerous waste. Up to 2.3 kg (5 lb) of mercury may have been discharged to the 100-D Ponds. Effluent discharge ceased in May 1994. Between 1986 and 1994 the effluent included chlorine and flocculating agents such as aluminum sulfate.

Analyses of effluent samples in 1989-90 reveal that 100-D Ponds effluent had a mean pH of 6.97 and a mean conductivity of 147 μmho/cm (WHC 1990). No dangerous constituents were found in the effluent. No quantitative data from earlier periods are available.

3.0 HISTORY OF GROUNDWATER MONITORING AT 100-D PONDS

Interim-status RCRA groundwater monitoring wells were installed around the 100-D Ponds in 1991. Sampling began in the first quarter of 1992 (Hartman 1991). The monitoring network is illustrated in Figure 1. The facility remained in indicator evaluation monitoring through 1995. Under this program, indicator parameters (pH, conductivity, total organic carbon, and total organic halogen) at downgradient wells are compared with critical mean values (ranges, for pH) calculated from an upgradient well. A statistically significant change in downgradient concentrations indicates that the facility potentially is affecting groundwater quality.

When the 100-D Ponds were sampled in February 1996, the field pH in wells D8-4 and D8-6 were higher than the upper limit of the critical range for pH. Subsequent verification sampling showed that pH at well D8-4 was within the critical range, but D8-6 again exceeded the upper limit. The Washington State Department of Ecology was notified as required by the RCRA regulations.

When one indicator parameter at a downgradient well exceeds the critical mean value, the following actions are required by the regulations:

(1) *"... the owner or operator must provide written notice to the Regional Administrator--within seven days of the date of such confirmation ... that the facility may be affecting ground-water quality" [40 CFR 265.93(d)(1)].*

(2) *"Within 15 days after the notification under paragraph (d)(1) of this section, the owner or operator must develop and submit to the Regional Administrator a specific plan ... for a ground-water quality assessment program at the facility" [40 CFR 26.593(d)(2)].*

The following requirement applies under an assessment program:

(3) *" ... submit to the Regional Administrator a written report containing an assessment of the ground-water quality" [40 CFR 265.93(d)(5)].*

The first requirement, for notification of the regulators, has been met. This report is intended to fulfill the second and third requirements.

4.0 EVALUATION OF DATA

4.1 DILUTION EFFECTS

The low-conductivity effluent discharged to the 100-D Ponds has diluted groundwater in the area. Conductivity of groundwater in wells D8-4 and D8-6 is lower than ambient groundwater (Figure 2). This low-conductivity groundwater cannot be attributed to proximity to the Columbia River because other wells nearer the river (e.g., D8-5) have higher conductivity.

Tritium, chromium, and nitrate are elevated in 100-D Area groundwater from waste sites located upgradient of the 100-D Ponds. These constituents are not present in the diluted pocket of groundwater surrounding the ponds. They have increased in upgradient well D5-13 after discharge to the ponds ceased in 1994. This trend is also reflected in an increase in conductivity in the upgradient well (see Figure 2).

4.2 ELEVATED pH

The pH of groundwater from wells D8-4 and D8-6 has been higher than in surrounding wells since monitoring began (Figure 3). Effluent discharges in the past tended to be slightly acidic (low pH) (Alexander 1993). Hanford sediments would tend to buffer the solution and make it slightly alkaline. More significantly, the presence of coal ash beneath the ponds would raise pH. Coal ash is very alkaline and tends to increase the pH of groundwater in contact with it.

A hydrochemical conceptual model was developed by Alexander (1993) to explain the groundwater monitoring results in the vicinity of 100-D Ponds (Figure 4). The effluent entering the 100-D Ponds had low specific conductance, was slightly acidic, and contained a lower concentration of most ions than ambient groundwater. The sediments beneath the ponds consist of coal ash up to 20 m thick. Coal ash has the following characteristics:

- Rich in heavy metals
- Has an alkaline pH (9.5)
- Is composed of unburned coal (carbon), periclase (MgO), lime (CaO), iron oxides (magnetite, etc.), minor sulfates, and alpha-quartz (McCarthy and Groenwold 1983).

When the pond effluent came in contact with the fresh ash, the major initial reactions were as follows (Alexander 1993):

A. Formation of hydroxides

$$CaO + H_2O \rightarrow Ca(OH)_2 \text{ (portlandite)} \quad (1)$$

$$MgO + H_2O \rightarrow Mg(OH)_2 \text{ (brucite)} \quad (2)$$

B. Formation of mobile metal oxyanions

$$SeO_4^{2-},\ CrO_4^{2-},\ HAsO_4^{2-},\ SbO_4^{2-},\ MoO_4^{2-},\ \text{etc.} \quad (3)$$

The mobile metal oxyanions are removed from the system by groundwater. Over time, the portlandite and brucite flush down through the ash layer and into the sediments of the Ringold Formation that underlie the ash. Here the portlandite and brucite undergo dissociation:

C. Dissociation of hydroxides

$$Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^- \quad (4)$$

$$Mg(OH)_2 \rightarrow Mg^{2+} + 2OH^- \quad (5)$$

The dissociation process supplies OH^- ion to elevate the pH of the groundwater beneath the ponds. In addition, the natural sediments contain sources of HCO_3^- and CO_3^{2-} that contribute to alkaline conditions.

Other continuing reactions within the system involve the formation of calcite ($CaCO_3$), calcium bicarbonate [$Ca(HCO_3)_2$], and numerous Al-, Mg-, Mn-, and Fe-hydroxy compounds. Less mobile metals like zinc, lead, copper, mercury, and cadmium are trapped in the zone beneath the backfill. The alkaline carbonate zone creates, in effect, a "geochemical trap" for cationic heavy metals.

The pH of groundwater samples from wells D8-4 and D8-6 collected after 1994 has increased (see Figure 3). This increase in pH followed the cessation of discharge to the ponds. When the ponds were in use, infiltrating water stayed in the vadose zone and aquifer beneath the ponds for only a short time. Since discharge ceased, the water stays in contact with hydroxide minerals in the vadose zone and in the aquifer beneath the pond for a much longer period. Reactions 4 and 5 have more time to approach chemical equilibrium, which in turn increases the pH of pore fluid in contact with the hydroxide mineral phases. During the longer residence time, higher concentrations of OH^- accumulate in residual soil moisture and drainage, and/or in aquifer pore fluid.

5.0 CONCLUSIONS AND RECOMMENDATIONS

Elevated pH in wells D8-4 and D8-6 is caused by reaction of water and coal ash. The coal ash is not part of the 100-D Ponds RCRA unit and is not subject to 40 CFR 265, Subpart F. Groundwater monitoring at the 100-D Ponds should remain under an indicator evaluation program as allowed by 40 CFR 265.93(d)(6):

> *"If the owner or operator determines that no hazardous waste or hazardous waste constituents from the facility have entered the ground water, then he may reinstate the indicator evaluation program..."*

The monitoring program calls for semiannual sampling of the four wells in the network, as described in the monitoring plan (Hartman 1991).

pH is expected to continue exceeding the upper limit of its critical range at well D8-6 and perhaps at D8-4. If such exceedances occur, Ecology will be notified within 7 days of the finding, as required by 40 CFR 265.93(d)(1). Unless other conditions have changed significantly, the notification letter will refer to this report to fulfill the requirement for an assessment plan and report [40 CFR 265.93(d)(2) and (d)(5)].

6.0 REFERENCES

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Figure 1. Groundwater Monitoring Wells Located Near the 100-D Ponds.

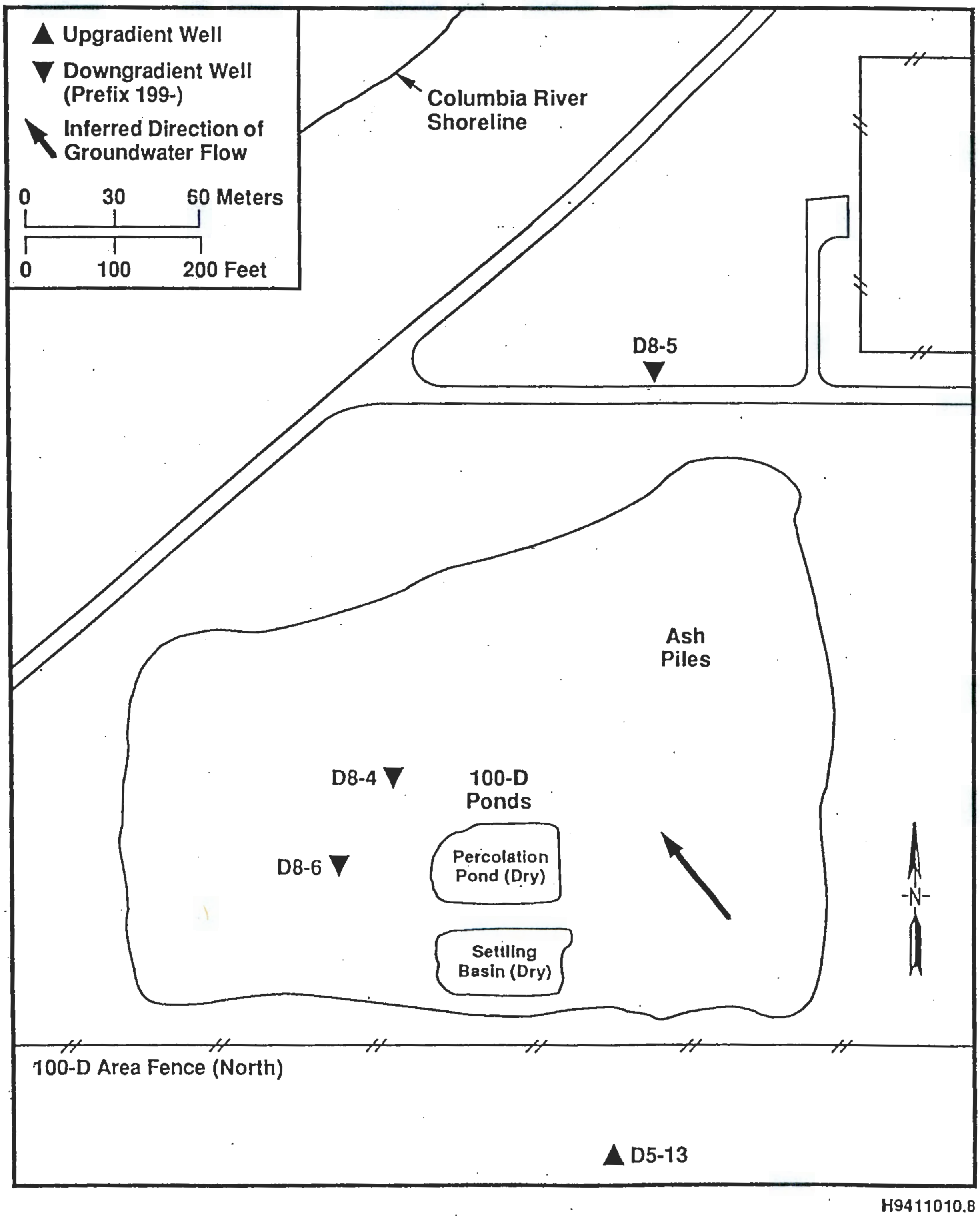

Figure 2. Field Conductivity in 100-D Ponds Wells.

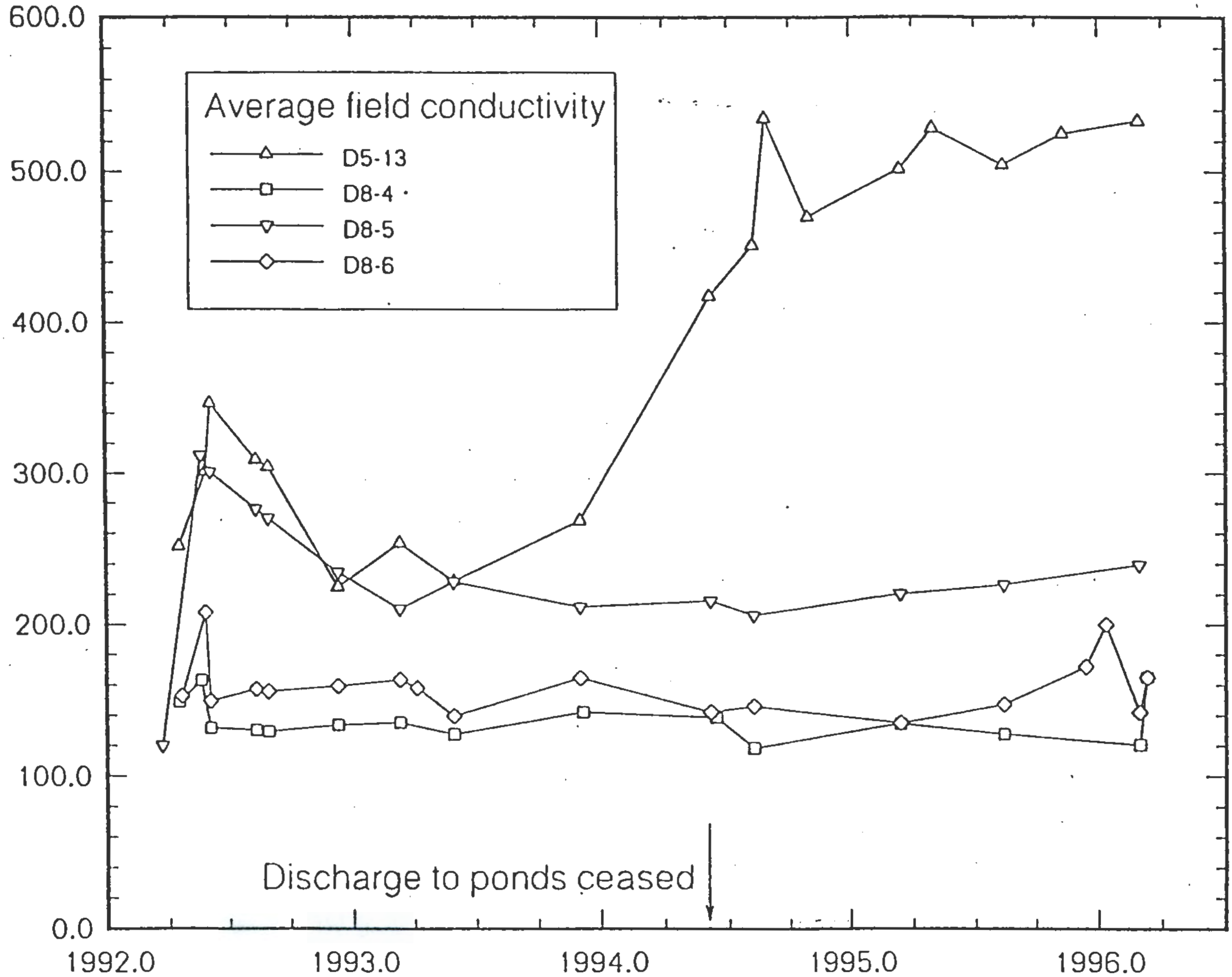

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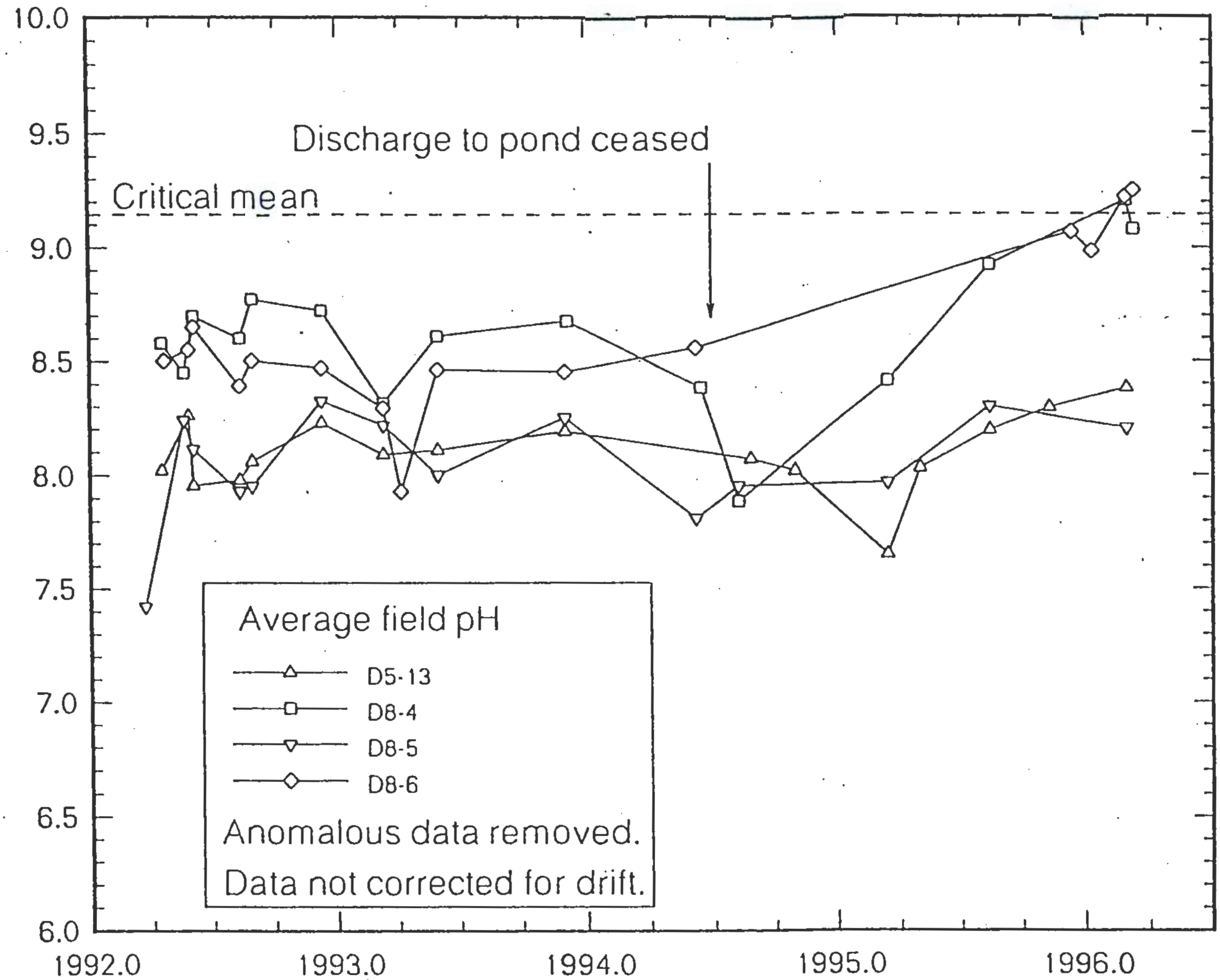
Figure 3. Field pH in 100-D Ponds Wells.



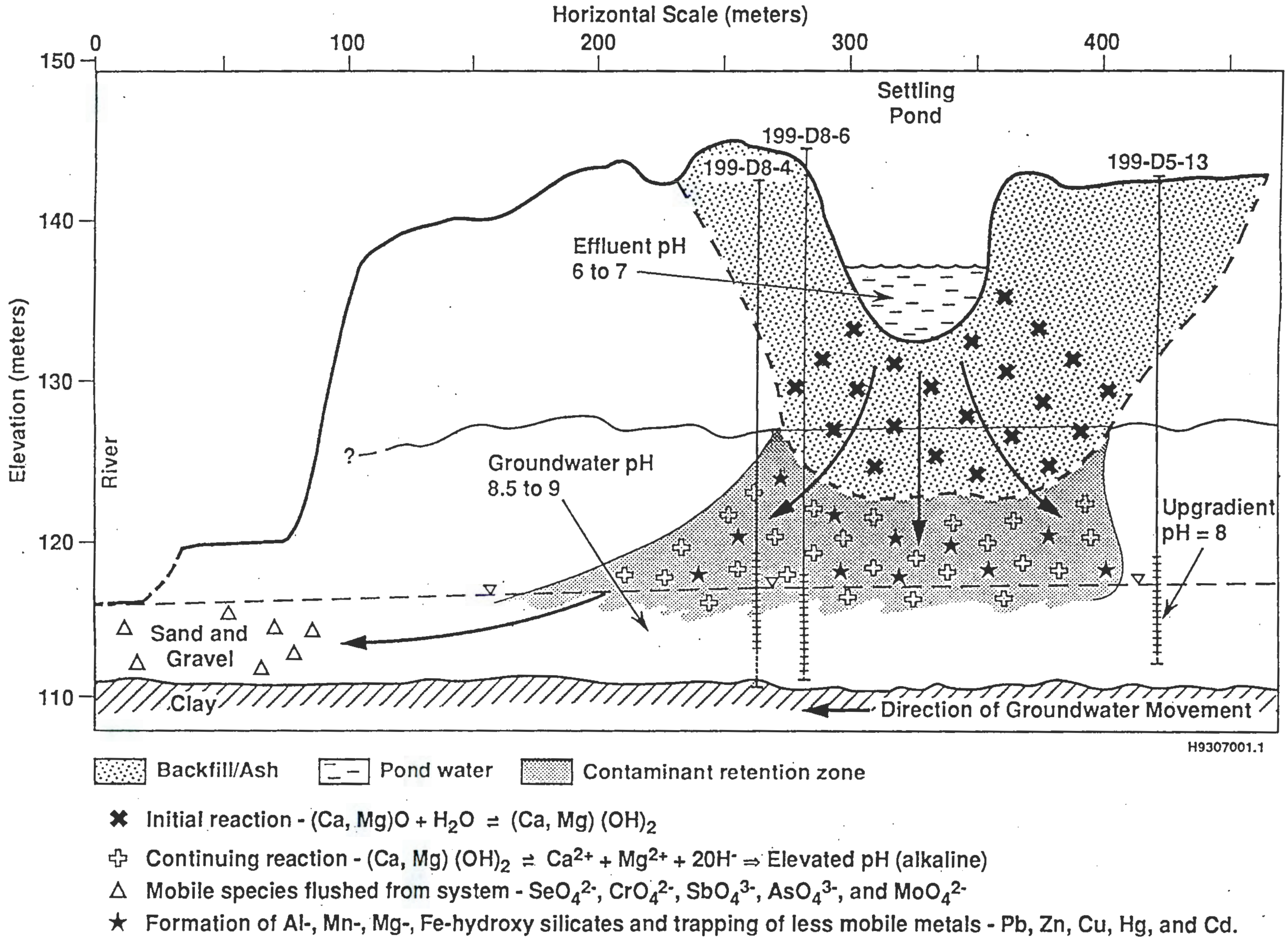


Figure 4. Conceptual Model for the 100-D Ponds (Alexander 1993).

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