VC

~~Pls review and brief me - Tks~~

3/17/98

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MAR 16 1998

March 12, 1998

Chief, NY Remediation Branch
United States Environmental Protection Agency
290 Broadway, 20th Floor
New York, New York 10007

Attn: Mr. Lorenzo Thantu
Remedial Project Manager

Re: Revised Conceptual Groundwater Flow and Transport Model
Responses to EPA Comments (dated February 20, 1998)
Continued RI/FS Activities
Liberty Industrial Finishing Site
Farmingdale, Nassau County, New York

Dear Mr. Thantu:

This letter transmits a revised Conceptual Groundwater Flow and Transport Model (CGW F&T) document, as well as, responses to general and specific comments contained in the U.S. Environmental Protection Agency (EPA) letter, dated February 20, 1998. Attached to this letter is a Sampling and Analysis Plan (SAP) for the collection of groundwater (Table 1A) and soil samples (Table 1B) to obtain the necessary parameters to calibrate the flow model and fate and transport model. A figure showing the location of wells that will be sampled for these additional parameters (i.e., parameters in addition to those obtained during the continued RI/FS groundwater sampling, according to the 1995 EPA SAP) is also attached (Figure 1).

In general, the EPA comments are addressed directly by the responses below. Substantial revisions to the CGW F&T document are limited to Section 1.0 (Introduction) and 3.1 (Flow Model), an added section regarding the calibration of the transport model (Section 3.2.3), and several adjustments to Tables 7 and 8. We believe it is not beneficial to further burden the CGW F&T document with additional specific or speculative (i.e., future conditions) scenarios that would later limit the flexibility of the modeling team. We further believe that the CGW F&T is exactly that, a conceptual paper laying out strategy and overall approach, especially in the present context of near-lacking site-specific hydrological and geochemical data for the Magothy aquifer (there is only one existing monitoring well in the Magothy aquifer; however, twenty additional wells in the Magothy aquifer are being completed by March 13, 1998).

We believes that the CGW F&T document should be accepted as final without further exchanges of formal comments and responses. The Group further believes that, with the submittal of this document, Section 41(h) of the Administrative Order of Consent has been fully met. In the interest of conducting the upcoming groundwater sampling event with the greatest efficiency, the SAP is attached to this letter (Tables 1A and 1B) detailing groundwater and soil sampling in connection with the development of the groundwater models.

RESPONSES TO EPA COMMENTS

Responses to General Comments

Response to Comment #1

Dames & Moore had previously proposed to use the MODPATH model to estimate the steady-state (dynamic) groundwater path lines, as well as, transient groundwater pathlines and capture zones resulting from the simulation of various remedial recovery/recharge scenarios (see Section 7.0, Fate and Transport Modeling Memorandum, dated March 7, 1997). During sensitivity analysis, calibrated values for horizontal and vertical hydraulic conductivity (K_x and K_y), anisotropy ratio, recharge rate, and seepage rate will be systematically changed within the range of parameters presented in Table 2 of the CGW F&T document. Sensitivity analysis will be performed by changing one parameter value at a time. The magnitude of change in heads from the calibrated solution will be reported as a sensitivity function to that particular parameter.

We agree with the EPA's recommendation to postpone the development of transport and hydrogeochemical models (using MINTEQA2 and RT3D) at least until the results of the advective analysis (using MODPATH) are presented and the model uncertainties are identified.

We would like to respond to the remaining four issues that the EPA raises, as follows:

- Issue 1 - TEAP zone delineation. We respectfully disagree that microbial analysis of soil cores and H_2 measurements are necessary to delineate TEAP zone. In addition, methods of collection and analysis of samples for these parameter are currently not well developed, and would therefore be cost prohibitive. TEAP zone delineation will be evaluated based groundwater and soil analytical parameters, as specified in Tables 7 and 8 of the CGW F&T document. Specifically, in addition to redox potential measurements, knowledge of the concentrations of dissolved gases (O_2 and CO_2), alkalinity, and electron acceptor pairs (Mn(IV)/Mn(II) as measured by total/dissolved manganese, nitrate/nitrite, Fe(III)/Fe(II) as measured by total/dissolved iron, and sulfate/sulfide) are adequate to characterize the subsurface geochemical environment and delineate TEAP zones when possible.

- Issue 2 - We agreed that complete coupling of MINTEQA2 & RT3D is, at this time, not feasible because of the computationally intensive requirements of re-running MINTEQA2 at each node. The proposed approach is, therefore, as follows:

1. Divide the site into TEAP zones or "packets of water along a flow pathway".
2. Beginning in the TEAP zone nearest the source: run MINTEQA2 using the source area groundwater concentrations of Cr(VI) and Cr(III), and determine the governing physicochemical processes for the said TEAP zone.
3. Simulate groundwater transport of Cr(VI) and Cr(III) in the said TEAP zone with RT3D using concentration data from Step 2 until the plume reaches the downgradient extent of the TEAP zone. Note: the predominant physicochemical processes identified in Step 2 will be simulated in RT3D through simplified reactions using the User-Defined Reaction Module and/or the Mass-Transfer-Limited Sorption Module available in RT3D.
4. Repeat Steps 2 and 3, using Cr(VI) and Cr(III) groundwater concentration data exiting the upgradient TEAP zone as input to the next downgradient TEAP zone until modeling criteria are met.

Finally, the use of a model capable of simulating redox zonation such as BIOMOC or BioRedox (Environmental Software Solutions, Ontario, Canada, (613) 236-0146) will be evaluated further prior to commencing fate and transport modeling.

- <u>Issue 3</u> - The EPA comment about the adequacy of our general assumptions on redox chemistry, bioremediation, and organic content of aquifer are addressed in the responses to the Specific Comments #6, #7, and #8.

- <u>Issue 4</u> - The EPA comment on the treatment of sorption in MINTEQA2 is addressed in the response to Specific comment #11.

<u>Response to Comment #2</u>

Dames & Moore did propose to simulate streams/aquifer interaction with either the Drain or River packages of MODFLOW (Section 3.1.4, Representation of Surface Water Bodies, Conceptual Groundwater Flow and Transport Models, December 22, 1997). Therefore, no revisions to the CGW F&T document are necessary.

<u>Response to Comment #3</u>

The CGW F&T document has been revised to be as specific as possible, without giving up the flexibility in the selection of modeling approach and mathematical tools.

Response to Comment #4

The model domain has been revised to include natural hydrologic boundaries to the north (regional groundwater divide) and south (South Oyster Bay). See also the response to Specific Comment #14.

Response to Comment #5

RT3D Version 1.0 (beta) is adequately tested and appropriate for use at a Superfund site. Model verification is documented by Sun and Clement (1998) in, "Verification of a reactive transport code (RT3D) against 1-, 2-, and 3-dimensional analytical solutions", which has been submitted for publication in *Ground Water*. Note: if an alternate fate and transport code (e.g., BIOMOC or BioRedox) is selected, documentation of model verification will be provided.

Responses to Specific Comments

Response to Comment #1

Dames & Moore proposed to assume a steady-state flow condition for the purpose of flow model calibration. The dynamic steady-state (not static steady-state) flow conditions will be simulated. Under dynamic average steady-state conditions, head varies spatially and flow into the system is equal to the flow out of the system. Dames & Moore proposed to simulate the existing well fields within the model domain under average pumping rates. The simulated groundwater levels will be checked against measured groundwater levels, as observed during the continued RI/FS, during the flow model calibration process. If necessary, several pumping scenarios in order to capture impacted groundwater at the Liberty site may be simulated.

Dames &Moore's response to EPA Comment 7 in Appendix A of the December 22, 1997 document referred to the sensitivity analysis under the dynamic steady-state condition, at which the flow model calibration will be performed. Dynamic steady-state condition represents the current groundwater flow equilibrium and not the pumping scenarios in order to capture impacted groundwater at the Liberty site.

Response to Comment #2

Buxton (Buxton, et. al., 1985) reported that representing the top of the Raritan confining unit as a no-flow boundary has only a minor effect on the accuracy of simulations of the groundwater system above the Raritan Confining unit. However, a small amount of water flows through this boundary into or out of the deeper Lloyd aquifer. Franke (Franke et. al., 1975), using cross-sectional analog models of Long Island, determined that this quantity is small in relation to the quantity of water in the system.

The approximate number and thickness of the model layer was proposed based on the following:

- Previous and ongoing remedial investigations indicate that the constituents of interest (COI) are distributed within the Upper Glacial aquifer and the upper 100 feet of the Magothy aquifer. The data resolution within the Upper Glacial aquifer appears to allow four model layers within the Upper Glacial aquifer. However, based on the results of the continued RI/FS groundwater sampling, this number of layers may be reduced. Similarly, two model layers with a thickness of 50 feet each were proposed for the top 100 feet of Magothy aquifer. These layers would correspond to the "C" and "D" designations of the monitoring wells that are being installed according to the December 22, 1997 well installation proposal. Therefore, the number of layers in the conceptual flow model was chosen to allow simulating COI distribution effectively. We believe that input and calibration parameters can be generated from these monitoring wells for top six layers.
- Several extraction wells installed by the South Farmingdale Water District (SFWD) and Massapequa Water District (MWD) are screened throughout the Magothy aquifer. Therefore, inclusion of total thickness of Magothy aquifer is necessary to simulate the groundwater flow. Four model layers were proposed to include the bottom 600 feet of Magothy aquifer.
- Attempts will be made to compile input and calibration parameters for each layer. However, based on the obtained parameters, the number and thickness of model layers may be adjusted.

Response to Comment #3

The purpose of a sensitivity analysis is to quantify the uncertainty in the calibrated model caused by uncertainty in the estimates of aquifer parameters, stresses, and boundary conditions. The phrase "as part of the calibration process" has been deleted from the revised CGW F&T..

Response to Comment #4

An aquifer pumping test of the Upper Glacial aquifer was proposed previously as part of pilot testing of interim groundwater remedial alternatives at the site (Dames & Moore, February 18, 1998). If this work will be carried out as proposed, the pumping test will generate modeling parameters for the upper layers of the proposed flow model (note that this proposed pumping test is being reviewed and possibly implemented separately from the activities proposed in this revised CGW F&T document). However, we wish to point out that this pumping test will not generate the necessary modeling parameters for all modeling layers, and that additional pumping tests (e.g., in the Magothy aquifer) are not planned during the continued RI/FS activities. These modeling parameters were and are being compiled from published sources.

Response to Comment #5

Laboratory testing is not deemed necessary to estimate the referenced fate and transport model variables, which will be estimated as follows:

Parameter	Method
Physical Processes	see Equations 1 & 2 of the CGW F&T document
Chemical Processes	
Sorption	see Equations 3, 4, & 5 of the CGW F&T document Freundlich constants in Equation. 5 will be estimated from published values
Precipitation/Dissolution	see the references to Table 4
Volatilization	see the references to Table 4
Diffusion	Equation 2 of the CGW F&T document
Biological Processes	
Biodegradation Pathways	will be demonstrated with groundwater analytical data (as in Table 7) and known degradation pathways (Figure 2)
Anaerobic Red. Dehalogenation	will be demonstrated with groundwater analytical data (as in Table 7) and known degradation pathways (Figure 2)
PCE and TCE Degradation	see Figure 2 of the CGW F&T document
Biodegradation Kinetics	is described on page 11 of the CGW F&T document
Microbial Inhibition	will be assessed from groundwater/soil analytical results (Table 7 and 8)
Contaminant Bioavailability	will be modeled as sorption-limited through the use of a Freundlich-type sorption isotherm
Metabolic Requirements	will be assessed from groundwater/soil analytical results (Table 7 and 8)
Electron Acceptors	will be assessed from groundwater/soil analytical results (Table 7 and 8)
Electron Donors	will be assessed from groundwater/soil analytical results (Table 7 and 8)
Toxicity and Protozoa Grazing	toxicity issues will be assessed from available and collected groundwater and soil analytical results; protozoa grazing issue has been addressed in text on page 13 of the CGW F&T document.

Response to Comment #6

We acknowledge and agree with this comment. Based on this comment, no revisions to the CGW F&T document are necessary.

Response to Comment #7

The discussion in question refers to "organic compounds" that serve as electron acceptors rather than as electron donors, and therefore is valid. The reference to electron donors in Section 3.2.2.3 of the CGW F&T document was not referring to "[halogenated] organic compounds" that could also serve as electron acceptors, but was referring to co-metabolic substrates.

Response to Comment #8

We acknowledge and agree with this comment. Lignite (organic carbon) will be included as an electron donor and a reductant. Lignite (as quantified by fractional organic carbon [f_{oc}]) has been included into Table 8 of the CGW F&T document. The range and distribution of f_{oc} in the Magothy aquifer will be determined by collecting soil samples, as summarized in the response to Comment #15 and in the Sampling and Analysis Plan (SAP) Table 1B (attached to this letter).

Response to Comment #9

Future depictions of the extent of groundwater impacts (either in cross section or plan view) will be presented in an accurate fashion and at the appropriate level of certainty, as defined by data density, data distribution and historical trends. These data presentations may or may not include contour maps wherein the level of certainty is generally expressed as solid contour lines ("observed") or dashed contour lines ("inferred"). Contouring of any discrete data (as opposed to continuous data) is likely to result in "inferred" lines only, i.e., the contours will be consistent with the data. Question marks would indicate "questionable" interpretations and, accordingly, should be used with caution or not at all. As no contoured figures are contained in the CGW F&T document, this comment does not necessitate any revisions.

Response to Comment #10

Table 7 and 8 of the CGW F&T document have been revised to reflect the substantial EPA recommendations, as contained in general comment #1, and specific comments #10 (include sulfate and TDS), #13 (include sulfate), #14 (include Fe-II/Fe-III and lignite), and #15 (include lignite). The SAP Tables 1A and 1B that are attached to this letter detail the proposed sampling and analysis program for groundwater and soil, respectively.

Response to Comment #11

We would like respond to the issues raised by this comment, as follows:

- Issue 1 - Sorption Model: The Freundlich Model will be used to simulate sorption to organic matter, and the Triple Layer Model will be used to simulate surface complexation reactions with iron oxides.

- Issue 2 - Sorptive capacity: The sorptive capacity of the Upper Glacial aquifer will be considered, and the work of Ku and others (1978) will be reviewed.

- Issue 3 - Quantification of oxyhydroxide coatings and organic matter: The nature of Fe-III oxyhydroxide coatings and organic matter content of the Magothy aquifer and the Upper Glacial sediments will be addressed by reviewing published sources and as specified in Table 8 of the CGW F&T document and in SAP Table 1B (attached to this letter). Abundance ratios of Fe-III/Fe-II will be determined (if practicable) in selected soil samples. Note, however, that Fe(III) in soils (especially in finer-grained soils) is not exclusively sequestered in iron-oxide or hydroxide coatings, but also in sheet silicates, other heavy minerals, and, to some extent, in weathered framework silicates; therefore, "knowledge" of Fe(III) concentrations is perhaps less simple to come by than implied by this comment.

Response to Comment #12

The purpose of the CGW F&T document was to lay out the conceptual approach to conducting fate and transport analysis at the site. The absence/presence of major reactive minerals (including calcite) in the upper glacial and Magothy aquifer sediments will be assessed during collection and analysis of soil samples, as specified in Table 8 of the CGW F&T document and in the attached SAP table. It is anticipated that neither metal carbonates nor sulfates will be present in any quantifiable proportions. However, lignite has been added as a reactive solid (Table 6) and considered in the geochemical modeling (Table 8).

Response to Comment #13

The mineral content of aquifer will be determined, as specified in Table 8 of the CGW F&T document and the SAP table attached to this letter. Again, the list of minerals presented in Tables 6 and 8 represents possible mineral phases that may need to be accounted for in the geochemical modeling. Whether or not to include any of the minerals listed in Table 8 (including calcite, gypsum, and dolomite) as solid phase parameters for geochemical modeling will be assessed based on the results of the geochemical/geotechnical analyses specified in Table 8.

Response to Comment #14

The northern model boundary will be extended to the groundwater divide and southern model boundary will be extended to South Oyster Bay to encompass these natural hydraulic boundaries. Figure1 has been revised accordingly.

Response to Comment #15

The areal and depth variability of f_{oc} will be characterized by collecting up to thirteen (13) soil samples from the Magothy aquifer, as specified in the SAP Table 1B (attached to this letter). These samples will be collected from two stratigraphic characterization borings, as committed to in the December 22, 1997 revised well installation proposal. One boring (SCB-1) will be located on-site, near monitoring well MW-6D, and one boring (SCB-2) will be located off-site, adjacent to well cluster MW-25B/C. The distribution of f_{oc} values will be compared to published values for the general site vicinity. The objective of this sampling effort will be to obtain defensible ranges of site-specific f_{oc} values for some, but not all stratigraphic layers that will make up the hydrogeochemical model.

If you have any questions regarding the information presented in this letter, please do not hesitate to call me.

Sincerely,
DAMES & MOORE

Matthias Ohr

Matthias Ohr
Project Manager

MO:mo
(PHL) cgw cover.doc

cc:
- Liberty Group
- EPA Regional Counsel
- NYSDEC (Mr. Cardona)
- Roy F. Weston, Inc. (Mr. Rhyner, Mr. Toskos)
- H2M Group (Mr. Loesch)
- Dvirka & Bartilucci (Mr. Maher)

TABLE 1A
On-Site and Off-Site Sampling and Analysis Plan for Fate and Transport Groundwater Model
Liberty Industrial Finishing Site, Farmingdale, New York

Well Location Information				Laboratory Parameters (Groundwater)													Field Parameters		
Well Number	Int	on-site	off-site	TCL VOCs	TAL M total	TAL M diss	Sulfate	Sulfide	Nitrate Nitrite	Chloride	Phosph.	TSS	TDS	CO_3 Alkalinity	HCO_3 Alkalinity	CO_2	D.O.	pH	Eh
Notes:				1,2	1,2	1,3	4	5	6	7	8	9	10	11	11	12	13	13	13
MW-2	A	X		1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
	B	X		1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
	C	X		1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
MW-4		X		1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
MW-6	D	X		1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
MW-9	B		X	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
	C		X	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
	D		X	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
MW-25	B		X	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
	C		X	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
MW-27	C		X	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
	D		X	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
MW-28	B		X	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
	C		X	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
MW-29	B		X	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
	C		X	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
	D			1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
MW-32	B		X	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
	C		X	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1

TABLE 1A

On-Site and Off-Site Sampling and Analysis Plan for Fate and Transport Groundwater Model
Liberty Industrial Finishing Site, Farmingdale, New York

Notes: 1. TCL VOCs = Target Compound List Volatile Organic Compounds (low-detection level); TAL M = Target Analyte List Metals

1,2 Samples for TSS, TCL, and TAL analyses are being collected from all new and selected existing monitoring wells, according to the SAP (Roy F. Weston, 1995).
Samples for the remaining parameters are being collected only for the wells listed above.

3. Samples for TAL metals (dissolved) will be field-filtered

4. Sulfate will be determined by method 375.4

5. Sulfide will be determined by method 376.1

6. Nitrate/Nitrite will be determined by method 353.2

7. Chloride will be determined by mthod 325.3

8. Total Phosphorus as phosphate will be determined by method 365.1

9. Total Suspended Solids will be determined by method 160.2

10. Total Dissolved Solids will be determined by method 160.1

11 Carbonate and Bicarbonate will determined by method 2320B (standard methods, 18th ed.)

12. Carbon Dioxide will be determined by method 4500CO2 (standard methods, 18th ed.)

13. Field parameters will be determined in flow-through cells with calibrated probes (Orion or YSI or similar).

TABLE 1B
On-Site and Off-Site Sampling and Analysis Plan for Fate and Transport Groundwater Model
Liberty Industrial Finishing Site, Farmingdale, New York

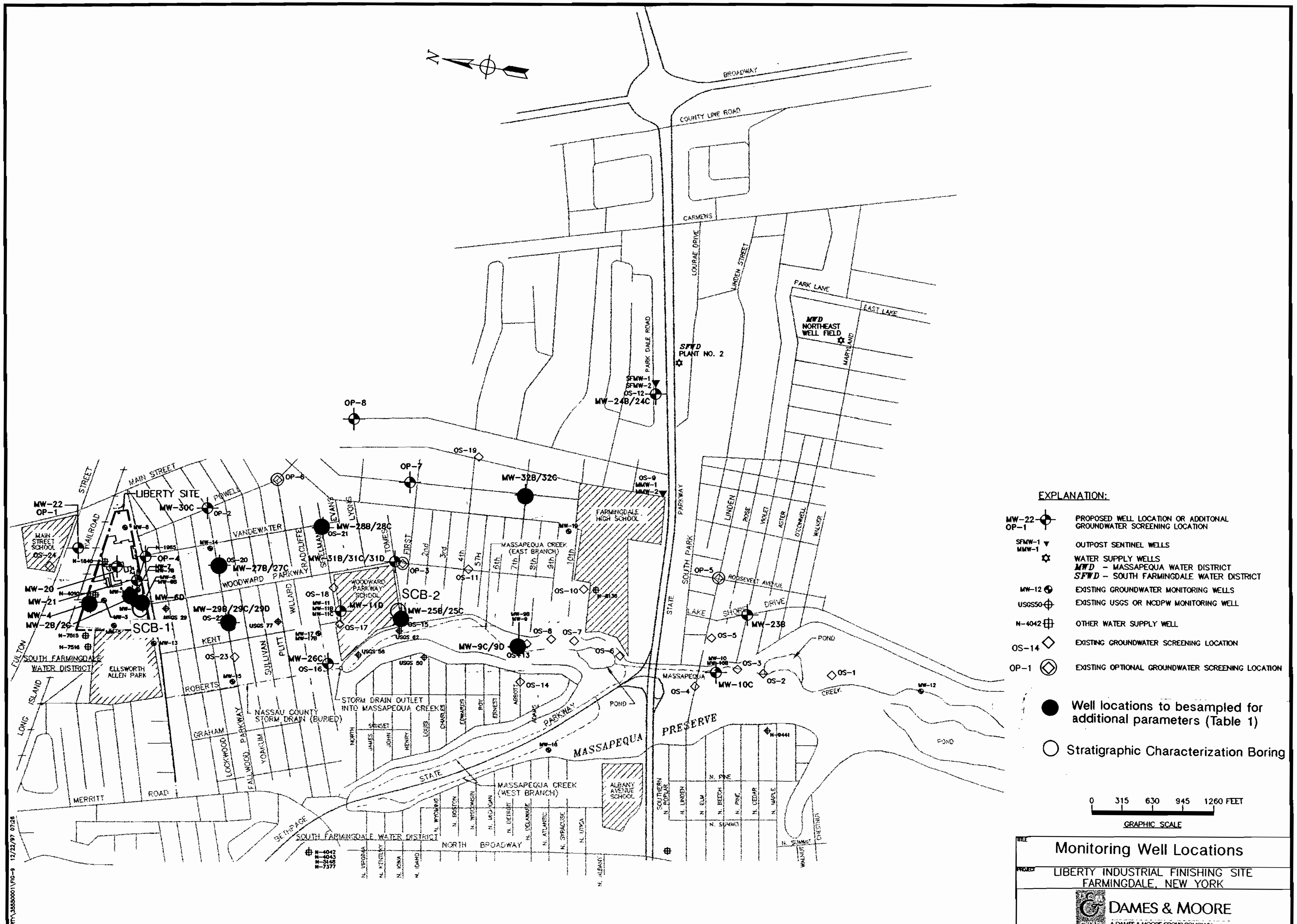
Sample Information					Laboratory Parameters (Soil)							
Boring	Location		Depth	Expected	Grain Size	CEC	XRD	f_{oc}	Fe(II)	Cd	Cr(tot)	K_v
	on-site	off-site	feet bgs	Soil Type					Fe (III)		Cr(VI)	
Notes:			1	1	2	3	4	5	6	7	8	9
SCB-1	X		60	grav. sand	1	1	1	1	1	1	1	
Location: near MW-6D			85	fine sand	1			1				1
			98	clay	1	1	1	1	1	1	1	1
			115	fine sand	1			1	1	1	1	
			135	silt/lignite	1	1	1	1	1	1	1	1
			145	sand	1			1				
SCB-2		X	60	grav. sand	1	1	1	1	1	1	1	
Location: at MW-25B/C and OS-15			70	sand/lignite	1	1	1	1	1	1	1	1
			90	fine sand	1			1				
			105	grav. sand	1			1				
			115	clay/lignite	1	1	1	1	1	1	1	1
			130	sand	1			1	1	1	1	
			145	?	1			1				1

Notes:

1. The sample depths and expected soil types for SCB-1 and SCB-2 are based on the gamma logs for MW-6D and OS-15.
2. Grain Size to be determined by hydrometer according to ASTM D-422.
3. Cation Exchange Capacity by method SW-845-9081.
4. X-ray Diffraction Analysis for mineral abundances of quartz, clays, Fe-Mn oxides and hydroxides, pyrite, carbonates, and sulfates).
5. Fractional Organic Carbon by method EPA 415.1 or method 9060.
6. Ferrous/ferric iron abundance ratio.

7,8. Cadmium and chromium (total) by method SW-846-6010, and chromium (hexavalent) by method SW-846-3060

9. Vertical permeability will be determined from Shelby Tube samples according to ASTM D-5084.



REFERENCE:
BASE MAP PROVIDED BY ROY F. WESTON
(ADAPTED FROM U.S.G.S. QUADRANGLE MAP,
AMITYVILLE, NEW YORK, 1979.)

(4) H:\LIBERTY\35550001\FIG-9 12/22/97 07:26

TITLE	Monitoring Well Locations
PROJECT	LIBERTY INDUSTRIAL FINISHING SITE FARMINGDALE, NEW YORK
	DAMES & MOORE A DAMES & MOORE GROUP COMPANY

SCALE AS SHOWN	DWN. BY R.G.B.	JOB NO. 35550-001
DATE 11/4/97	APPR. BY M.O.	FIG. NO. 1

REVISED CONCEPTUAL GROUNDWATER FLOW AND TRANSPORT MODELS
LIBERTY INDUSTRIAL FINISHING SITE
FARMINGDALE, NEW YORK

March 12, 1998

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TABLES

FIGURES

1.0 INTRODUCTION

Pursuant to Section 41(h) of the Administrative Order of Consent (Order) for Continued Remedial Investigation/Feasibility Study (CRI/FS) for Operable Unit II (Index No. II CERCLA-97-00203) at the Liberty Industrial Finishing Site (site), Dames & Moore transmitted a Fate and Transport Modeling Memorandum to the U.S. Environmental Protection Agency (EPA) on March 7, 1997. On December 22, 1997, Dames & Moore transmitted a Conceptual Groundwater Flow and Transport Model (CGW F&T) document to the EPA. Comments by the EPA to this CGW F&T document were received on February 20, 1998. This current document represents the revised CGW F&T document and is based upon the EPA comments and responses to the EPA's general and specific comments.

The numerical modeling study at the site will consist of the setup and calibration of a three-dimensional groundwater flow model and particle-tracking analysis. Based on the results of particle-tracking analysis, a contaminant transport and geochemical model may be used to simulate higher-order processes and to predict the fate and transport of the constituents of interest (COI) under existing natural conditions and, if necessary, various remedial alternatives. The scope of the modeling study encompasses the following:

- Review of background information and identify data gaps;
- Formulation of a conceptual model of groundwater flow and COI transport at the site;
- Model setup and preparation of input data;
- Flow model calibration and sensitivity analysis for existing groundwater flow conditions;
- Particle-tracking analysis
- Model calibration for existing COI distribution and COI transport mechanisms at the site (if justified);
- Modeling using hydrogeochemical equilibrium model (if justified);
- Transport model calibration and sensitivity analysis for existing COI distribution and COI transport mechanisms at the site (if justified); and
- COI fate and transport modeling for various remedial alternatives (if justified).

A preliminary CGW F&T was previously presented in the Memorandum, dated March 7, 1997, and a groundwater flow model (MODFLOW) and contaminant transport model (MT3D), together with an equilibrium hydrogeochemical model (MINTEQA2), were proposed. In the December 22, 1997 CGW F&T document, Dames & Moore proposed to replace MT3D by a new transport model RT3D (Three-dimensional Multi-species Reactive Transport in Porous Media, developed by the U.S. Department of Energy, Clement et al., 1997). Based on the comments received from the EPA, the development of the MINTEQA2 and RT3D model will be postponed until the results of an advective analysis are presented and the uncertainties in the simulation of advective pathways can be evaluated.

This document presents conceptual descriptions of the groundwater flow model (Section 3.1), the COI transport model (Section 3.2), and the hydrogeochemical model (Section 3.3).

2.0 REVISED TRANSPORT MODEL

A recently released contaminant fate and transport model, RT3D, developed by the Pacific Northwest National Laboratory will be used in place of MT3D. RT3D is a new reactive transport simulator that has all the capabilities of MT3D, but can also be used for simulating reactive multispecies transport in three-dimensional saturated porous media. RT3D is a public domain FORTRAN-90 based software package. The current version of RT3D uses the basic input/output driver, advection, and dispersion routines from the version DOD_1.5 of the MT3D simulator. As with MT3D, RT3D requires that the USGS groundwater flow model MODFLOW be used to compute groundwater transport velocities.

RT3D is sufficiently flexible for simulating all of the relevant constituent reactions, microbial metabolisms, and microbial transport kinetics discussed below. As a research tool, RT3D has been used for modeling several laboratory and pilot-scale experiments; in addition, it is currently being used to model several sets of field-scale natural attenuation data. RT3D Version 1.0 (beta) is adequately tested and appropriate for use at the site. Model verification is documented by Sun and Clement (1998) in, *"Verification of a reactive transport code (RT3D) against 1-, 2-, and 3-dimensional analytical solutions"*, which has been submitted for publication in the journal *Ground Water.*

3.0 CONCEPTUAL MODELS

This section presents descriptions of the conceptual flow model (Section 3.1) and the conceptual organic and inorganic constituent transport and hydrogeochemical models (Sections 3.2 and 3.3).

3.1 FLOW MODEL

A detailed three-dimensional conceptual groundwater flow model was developed for the study area. The hydrogeological setting, groundwater flow, basic model assumptions, and model domain, model grid, and boundary conditions are described below.

3.1.1 Hydrogeological Setting

The Liberty site is directly underlain by the Upper Glacial deposits of Pleistocene age. The Upper Glacial aquifer is composed of fine to coarse sands and gravel and is approximately 85 feet thick. The water table at the site is currently approximately 17 to 19 feet below ground surface (bgs). The Magothy Formation is underlying the Upper Glacial aquifer. The predominant grain size of the Magothy Formation is fine sand with thin beds and lenses of silt and clay. The anticipated thickness of the Magothy Formation is 700 feet in the vicinity of the Liberty site. The Magothy Formation is underlain by the Raritan Clay, a regionally important confining unit that separates the Magothy aquifer above from the Lloyd aquifer below.

3.1.2 Groundwater Flow

Groundwater of concern at the site occurs within two aquifers - the Upper Glacial and Magothy aquifers. A surface water body, Massapequa Creek, is located downgradient of the site. The Massapequa Creek originates approximately 1,000 feet south of the site, travels south-to-southwest through several ponds along Massapequa Preserve to Massapequa Lake. The groundwater flow from the Upper Glacial aquifer continues downgradient within the aquifer with some portion discharging to Massapequa Creek. The Magothy aquifer discharges primarily to the south shore bays.

Groundwater elevation data generated during the remedial investigation (Roy F. Weston, January 1994) indicate that groundwater within the Upper Glacial aquifer moves predominantly in a south-southwesterly direction towards Massapequa Creek. The average hydraulic gradient is reported to be 0.0022. The average effective porosity and horizontal hydraulic conductivity are reported to be 0.3 and 270 ft/day, respectively (Franke, et. al., 1972). The vertical and horizontal hydraulic conductivity ratio is reported to be 1:10 (Franke, et. al., 1972). The specific yield of the Upper Glacial aquifer is reported to be 0.2 (Warren et. al., 1968). These hydraulic parameters for the Upper Glacial aquifer will be further evaluated and verified during a proposed on-site pumping test, as described in the *"Field- and Bench-Scale Testing Program and Conceptual Design Work Plan, Interim Remedial Groundwater Action"* (Dames & Moore, dated February 18, 1998).

Groundwater in the Magothy aquifer is reported to migrate in a south-southeasterly direction (Roy F. Weston, January 1994). The hydraulic characteristics of the Magothy aquifer at and downgradient of the site will be further investigated during the continued RI/FS activities (these activities do not include any aquifer pumping tests). Horizontal hydraulic conductivity (K_x) and the anisotropic ratio of horizontal to vertical hydraulic conductivity (K_y) are reported as 50 ft/day and approximately 1:36, respectively (Franke, et. al., 1972). The effective porosity of Magothy aquifer material is reported to be 0.25 (Warren et. al., 1968). The specific storage of Magothy aquifer is reported to be 6×10^{-7} ft^{-1} (Buxton, et. al., 1985).

3.1.3 Basic Model Assumptions

The following assumptions were made in the development of the conceptual groundwater flow model for the Liberty site:

- Dynamic steady-state flow conditions prevail in the aquifers;
- The Magothy aquifer is underlain by a confining layer, which dips in the general direction of groundwater flow;
- Groundwater recharge is uniform throughout the study area;
- The well fields are withdrawing water at constant pumping rates from the Magothy aquifer;
- The branches of Massapequa Creek in the study area are shallow and in hydraulic contact with the groundwater table.

3.1.4 Model Domain, Grid, and Boundary Conditions

The model grid will cover an area of approximately 50,000 feet by 23,000 feet (Figure 1). As shown in Figure 1, the southern boundary of the model domain will follow South Oyster Bay, and the northern boundary of the model domain will extend to the regional groundwater divide, which is located approximately 4 miles north of the site. Therefore, the northern and southern domain boundaries encompass natural hydraulic boundaries, thus minimizing any adverse effects of artificially imposed boundary conditions. The western boundary of the model domain will be defined by Hicksville Road in the northwest of the model domain and the Oyster Bay - Seaford Expressway in the southwest portion of the model domain. The eastern boundary of the model domain will extend to approximately 10,000 feet east of the site. The Massapequa Water District and South Farmingdale Water District supply wells that are within the model domain are also shown in Figure 1.

Model Layers

The model may consist of a grid of ten layers. The first four layers will represent the Upper Glacial Aquifer, which has a saturated thickness of approximately 75 feet in the site area. The remaining layers represent the Magothy aquifer, which is approximately 700 feet thick, such that the depth of the model domain may extend to Raritan Clay. The domain is subdivided into ten model layers in order to allow an appropriate representation of vertical velocity variations and vertical variations in COI concentrations in the aquifers (note that the actual number of layers may be reduced if the observed vertical variations of the hydraulic parameters and COI concentrations will provide insufficient layer resolution). Vertical velocity components are induced by the partially penetrating pumping wells and other three-dimensional hydrogeological features such as the various creeks and lakes.

The tops and bottoms of the model layers will be chosen such that they follow approximately the topographical surface and the water table. This may result in relatively complex model geometry within each layer. The approximate layer thicknesses are presented in Table 1. Within each layer, all cells will be of equal thickness. Thus, the shape of each layer top and bottom will be identical, but the absolute elevation of the layers may differ by the layer thickness.

Three-Dimensional Model Grid

A grid of rectangular cells with side lengths varying from a minimum of 200 feet by 200 feet to an average of approximately 500 feet by 500 feet will used to discretize the domain in plan view. In areas where groundwater impacts or steep concentration gradients will be observed, the grid will be refined. Considering the model domain of 50,000 feet long and 23,000 feet wide, average rectangular cell dimensions of approximately 500 feet by 500 feet, and ten model layers, the model may consist of a total of 46,000 cells (i.e. 100 x 46 cells per layer).

Boundary Conditions

A groundwater divide, along which no-flow conditions are imposed, is present approximately 4 miles north of the site. The major surface water feature is the South Oyster Bay, located approximately 5 miles south of the site. There are no significant hydraulic boundaries (specified head, no-flow, or specified flow boundaries) within 5 miles east or west of Liberty site.

Representation of Surface Water Bodies

The interactions between the aquifers and the Massapequa Creek, ponds, and Massapequa Lake within the Massapequa Preserve will be in incorporated in the model. Additional surface water bodies in the model will include Seaford Creek within the Tackapausha Preserve, Jones Creek, Carman Creek, Amityville Creek, and Woods Creek. The surface water bodies will be represented as features that either supply water or act as drains, depending on the local flow conditions in the aquifer.

The water levels in the surface water bodies will be set in accordance with ground surface data obtained from the corresponding USGS topographic maps (Amityville, N.Y.). A limited amount of data on water levels within the model domain will be collected during the continued RI/FS activities. Where available, these data will be used to confirm or adjust the water levels specified in the model.

Recharge

The two natural sources that provide most of the recharge are precipitation and subsurface inflow. Annual precipitation in the study area averages about 45 inches, fifty percent of that is lost mainly by surface and near-surface evapotranspiration and by direct runoff. Direct runoff is reported to be approximately 5 to 15 percent of the total precipitation of the drainage basin (Perlmutter et. al., 1979). The remainder of the precipitation, which averages 22 inches annually, seeps down to the water table. Recharge from precipitation will be set 22 inches/year throughout the study area. Additional recharge, including cesspool, waterline leakage, and recharge basin effects may betaken directly from the existing regional groundwater flow model.

Discharge

Groundwater is discharged from the aquifers by subsurface outflow, withdrawal by pumping wells, seepage into Massapequa Creek, and evapotranspiration. Two public water supply well fields, operated by the Massapequa and South Farmingdale Water Districts, are located approximately 8,000 feet south/southeast of the site. These well fields withdraw groundwater from the Magothy aquifer. The pumping wells within the model domain will be incorporated in the model. The discharge into Massapequa Creek may be taken directly from the regional model.

3.1.5 Groundwater Flow Modeling Using MODFLOW

A detailed three-dimensional groundwater flow model will be constructed for the study area, and the numerical simulation of the groundwater flow system will be conducted with the USGS MODFLOW model. The model will be calibrated against observed head data in order to allow the subsequent prediction of COI migration under various remedial alternatives.

The USGS model MODFLOW (MacDonald and Harbaugh, 1988) is currently the most widely used groundwater flow model. It simulates groundwater flow in three dimensions by using a block-centered finite-difference approach. The subsurface can be described as a sequence of layers, each of which may contain cells of spatially varying properties. The model can handle unconfined, confined, leaky, or a combination of such conditions in any one of its model layers. Flow associated with wells, areal recharge, evapotranspiration, drains, and streams can also be simulated.

3.1.6 Flow Model Calibration

The flow model will be calibrated against the current groundwater conditions, as observed during the continued RI/FS activities. Monitoring wells are being installed at various vertical intervals in Upper Glacial and Magothy Aquifers well clusters, according to the revised monitoring well installation proposal, dated December 22, 1997. It is anticipated that installation of these proposed monitoring wells will be completed by March 13, 1998. Measured water levels in each model layer will be checked against the simulated water levels during the calibration process.

The quality of a model calibration is expressed by plotting the observed versus calculated hydraulic head values. For a perfect calibration, the resulting data points fall onto a correlation line; for practical hydrogeological model applications, however, the observed versus calculated data points will scatter about this line. The model calibration will be further checked by computing the residual mean error. In addition, the residual mean will be normalized against the observed range of values (i.e. difference between maximum and minimum observed head value), in order to determine the quality of the model in the context of the site. The calibration statistics will be presented in the final report.

3.1.7 Sensitivity Analysis

Subsurface conditions can never be accurately defined, and any analysis based on assumed, estimated, or interpolated input parameters will always result in some uncertainty. The major uncertainties involved with the prediction of the advective migration of COI at the site will be identified during model development. Thus, thorough sensitivity analyses of the flow model's input parameters, which will include horizontal hydraulic conductivity, anisotropic ratio, recharge rate, and seepage rate, will be conducted.

During sensitivity analysis, calibrated values for K_x and K_y, anisotropic ratio, recharge rate, and seepage rate will be systematically changed within the range of parameters presented in Table 2. Sensitivity analysis will be performed by changing one parameter value at a time, so that the magnitude of change in heads from the calibrated solution will be reported as a sensitivity function to that particular parameter.

3.1.8 Input Parameters

Aquifer properties were collected from published sources and are presented in Table 2. Uniform aquifer properties will be assumed for each aquifer for the initial simulation. If necessary and available, these properties will be adjusted for each model layer during the calibration process.

An aquifer pumping test of the Upper Glacial aquifer was proposed previously as part of pilot testing of interim groundwater remedial alternatives at the site (Dames & Moore, February 18, 1998). If this work will be carried out as proposed, the pumping test will generate modeling parameters for the upper layers of the proposed flow model (note that this proposed pumping test is being reviewed and possibly implemented separately from the activities proposed in this revised CGW F&T document). However, we wish to point out that this pumping test will not generate the necessary modeling parameters for all modeling layers, and that additional pumping tests (e.g., in the Magothy aquifer) will not planned during the continued RI/FS activities. Therefore, these modeling parameters, including those listed in Table 2, will be compiled using reliable and consistent values from published sources.

The hydraulic properties of the Upper Glacial and Magothy aquifers on Long Island have been extensively studied, which allows a reliable estimation of aquifer properties in the study area. Horizontal hydraulic conductivity, K_x, in the Upper Glacial Aquifer were verified during the RI (Roy F. Weston, January 1994) by performing slug tests in selected on-site and off-site monitoring wells. The reported K_x ranged from 122 to 629 ft/day, which correspond well with established regional and local K_x of 270 ft/day (Franke, et. al., 1972).

The tabulated values (Table 2) of aquifer properties will be used as input parameters for the initial simulation. Model calibration will be performed through a trial and error procedure in which aquifer properties are adjusted until a reasonable match between simulated water elevations and measured water elevations are obtained. The calibrated aquifer properties will be used for subsequent simulations.

3.1.9 Particle Tracking Analysis Using MODPATH

Dames & Moore will use MODPATH model to estimate the steady-state (dynamic) groundwater path lines, as well as, transient groundwater path lines and capture zones resulting from the simulation of various remedial recovery/recharge scenarios (if necessary). The computer program MODPATH was developed by the USGS (Pollock, 1989) to calculate three dimensional particle tracking from output of steady-state flow simulations obtained using MODFLOW. MODPATH can be used to compute three-dimensional path lines and the position of particles at specified points in time.

3.2 TRANSPORT MODEL

3.2.1 Distribution of Constituents of Interest

The results of on-site and off-site groundwater screening were submitted to the EPA in the December 22, 1997 revised monitoring well installation proposal. The December 22, 1997 proposal contained plan view maps showing the concentrations of specific COI within the Upper Glacial and Magothy Aquifers, and cross section maps showing the vertical concentration distribution of specific COI. Note that, in general, the groundwater quality information needed to complete the conceptual models of inorganic and organic constituent source location(s), mass, and distribution will be based upon groundwater sampling of the new and selected existing monitoring wells, according to the Sampling and Analysis Plan (SAP) for continued RI/FS activities (Roy F. Weston, February 1995). The collection of any groundwater parameters that are beyond the February 1995 SAP, but are necessary to complete the transport modeling proposed here, is specified in Tables 7 and 8 and in the tables attached to the cover letter to this revised CGW F&T document.

3.2.2 Fate and Transport Processes

The processes that generally govern the fate of the primary organic COI (PCE and TCE) are summarized in Table 3, and discussed below.

3.2.2.1 Physical Processes

Contaminants are transported in groundwater by advection (i.e., the movement of a solute at the speed of the average linear velocity of groundwater), as given by:

$$v = \frac{K x i}{n_e} \qquad \text{(Eqn.1)}$$

where, K = hydraulic conductivity in the direction of groundwater flow
i = hydraulic gradient in the direction of groundwater flow
n_e = effective porosity

Another major physical process that affects contaminant movement in groundwater is dispersion. Dispersion refers to spreading of contaminants caused by the fact that not all of the contaminant actually moves at the same speed as the average linear velocity. Contaminant movement is strongly influenced by the presence of local heterogeneity that causes deviations from the average linear velocity. Typically, it is assumed that these deviations are represented by a relation similar to Fick's law of diffusion. The dispersion term, D, is usually calculated from

$$D = \alpha \, x \, v + D^* \qquad \text{(Eqn.2)}$$

where, α = Dispersivity
D^* = Coefficient of molecular diffusion

3.2.2.2 Chemical Processes

Sorption

Sorption and desorption describe the chemical solid-aqueous solution exchange potential and are often estimated by an equilibrium partition coefficient, K_d, and assumed to be linear. Under these assumptions, mass transfer is symmetrical with respect to the forward and backward direction. Estimates of K_d are typically used to determine a retardation factor for the COI, which is used in solute transport models and expressed as:

$$R = 1 + \frac{\rho K_d}{\omega} \qquad \text{(Eqn.3)}$$

where, R = retardation factor
ρ = soil bulk density
ω = soil moisture content.

K_d can be approximated by the following expression:

$$K_d = f_{oc}K_{oc} \approx f_{oc}0.63K_{ow} \qquad \text{(Eqn.4)}$$

$f_{oc} \equiv$ fraction organic carbon
$K_{oc} \equiv$ chemical organic carbon to water partition coefficient
$K_{ow} \equiv$ chemical octanol to water partition coefficient

Typical K_{ow} values for of the primary organic COI and their daughter-products (1,1-DCE, 1,2-DCE, and VC) are summarized in Table 4.

At many sites, however, a significant "tailing effect" in constituent concentrations has been observed during remediation. One potential explanation of this phenomena is the apparent slow desorption of constituents from soil matrices. Under these assumptions, sorption is non-linear (the forward rate of sorption differs from desorption) and can be approximated with a Freundlich-type expression. The rate of retardation due to sorption non-linearity is then inversely related to the constituent concentration (i.e., sorption increases as concentration decreases) and can be expressed as:

$$R = 1 + \frac{\rho K_d N}{\omega} C^{N-1} \qquad \text{(Eqn.5)}$$

where, R = retardation factor
ρ = soil bulk density
ω = soil moisture content
N is the Freundlich constant ($N<1$).

Precipitation / Dissolution

Precipitation and dissolution describe chemical aqueous solution-organic exchange potential and are characterized by the solubility of a compound. The solubility of the primary organic COI and their daughter-products are summarized in Table 4.

Volatilization

Volatilization describes how compounds behave at a gas-liquid surface such as the partitioning between air-water and air-organic systems. In dilute systems, the volatilization potential can be estimated from Henry's law constant and vapor pressure of a particular compound. In concentrated systems or when non-aqueous phase liquids (NAPL) exist, volatilization potential can be estimated using Raoult's law and the activity coefficient, mole fraction, and vapor pressure of a particular compound. Values of Henry's law constant, and vapor pressure for of the primary organic COI and their daughter-products are summarized in Table 4.

Diffusion

Molecular diffusion is the process that brings reactants into contact with each other and enables the physicochemical processes described above to occur. In addition, molecular diffusion transports chemicals across boundaries, for example, into a living cell, onto a particle surface, or across the air-water interface. Combined, these physicochemical processes govern chemical equilibria and distribution between the four phases: aqueous, solid (including colloids), gas, and organic (NAPL). The thermodynamics and kinetics of these physicochemical processes will ultimately decide a compound's fate in a subsurface environment. For example, if a compound is sorbed to organic matter in the subsurface then it may not be readily available for microbial degradation or volatilization. The kinetics and thermodynamics of desorption, dissolution, and diffusion will then determine how quickly, if at all, a compound becomes available for these actions. Subsurface environmental conditions that affect physicochemical processes include pressure, temperature, pH, redox condition, and aqueous solution composition (organic solute and solvent, and inorganic salt concentrations).

3.2.2.3 Biological Processes

Potential Biodegradation Pathways

Biodegradation potential is dependent upon two factors: (1) the compound must be biodegradable, and (2) microorganisms capable of degrading the compound must be present and evenly distributed in the impacted area. If these factors are not satisfied, then appreciable *in situ* biodegradation will not occur. Intrinsic (naturally occurring) biodegradation of chlorinated solvents, such as PCE and TCE, typically occurs under anaerobic conditions. One of the predominant mechanisms for transformation of chlorinated solvents is reductive dehalogenation. A brief review of anaerobic reductive dehalogenation and the specific anaerobic degradation pathway of PCE and TCE by this mechanism is presented below.

Anaerobic Reductive Dehalogenation

Anaerobic reductive dehalogenation results in the replacement of a halogen by hydrogenolysis or dihalo-elimination. The process proceeds sequentially until all halogens have been removed. The reductive process is usually supported through co-metabolism. Under this scenario, the halogenated organic compound acts as an alternative electron acceptor for either sulfate reducing or methanogenic bacteria. The reductive dehalogenation is carried out by electrons from the oxidation of the primary substrate (electron donor). The success of the process relies on a proper balance between appropriate electron acceptors and electron donors.

PCE and TCE Degradation Pathway

The microbially mediated degradation pathway of PCE and TCE is illustrated in Figure 2. As shown in Figure 2, PCE degrades sequentially to TCE, then to *cis*-DCE, and then to VC, and finally to ethane or ethene via reductive dehalogenation.

Biodegradation Kinetics

The kinetics of biodegradation must allow for the remediation to be completed in a reasonable time frame. The rate of *in situ* biodegradation is a complex function of intrinsic biokinetic parameters, mobile and immobile microorganism concentration, electron acceptor and contaminant physicochemical properties, and soil moisture content.

Currently there is no systematic methodology to quantitatively determine biodegradation kinetics *in situ*. Most often, an overall rate of *in situ* biodegradation is quantified by measuring the rate of consumption (disappearance) or production of indicator compounds. This method will be used to determine site-specific biodegradation rates for PCE, TCE, *cis*-DCE, and VC based on site-specific groundwater concentration data, and then compared to published values.

Another technique that may used to derive the site-specific biodegradation rates is an exponential regression analysis of contaminant concentration versus time data, measured at individual wells. Alternatively, a method developed by Bushcheck and Alcantar (1995) could be used to separate the contributions of advection, dispersion, sorption, and biological decay to the total observed decay rate. This technique uses constituent concentrations observed at multiple wells along a transect coincident with the predominant groundwater flow in an analytical solution to one-dimensional contaminant transport with first-order decay.

In either case, the site-specific biodegradation rate for each COI will then be used in the contaminant fate and transport model RT3D.

Microbial Inhibition Potential

Several factors may inhibit *in situ* biodegradation; these include: (1) low constituent bioavailability; (2) microbial metabolic requirements; and (3) the presence of toxins and grazing protozoa.

Contaminant Bioavailability

In the subsurface, biodegradation generally occurs in the pore and (soil) bound water phase, primarily by microorganisms that exist in biofilms immobilized on soil particle surfaces and suspended in pore water. In order for biodegradation to occur, the target constituent must therefore be in an aqueous phase, within the microenvironment of the acting microorganisms (Alexander, 1994). Inhibition of *in situ* biodegradation will occur when constituents are bound to soil matter through sorption processes, or are contained in an organic phase, or otherwise resist dissolution into an aqueous phase and are not bioavailable.

Microbial Metabolic Requirements

Microorganism metabolic requirements (or factors) can be divided into two groups: chemical and physical (Gaudy and Gaudy 1988). Of the chemical requirements, a carbon and energy source (electron donor), an electron acceptor, and proper nutrients are among the most important. Important physical factors are pH, temperature, and salinity. Physical factors, in general, act as selective agents by determining the types of organisms that can grow, and by influencing the growth rates of those organisms that can grow under the prevailing conditions. Inhibition of *in situ* biodegradation will occur when microorganism metabolic requirements are not met, and result in less than optimal microorganism growth conditions. The role of electron acceptors and electron donors in this process are discussed below.

Electron Acceptors

The availability of electron acceptors in anaerobic systems affects reductive dehalogenation by competing with the halogenated compounds for reducing potential. The influence of electron acceptors is explained by thermodynamic principles. Recalling that microorganisms will couple redox half reactions that yield the greatest free energy provides the basis for understanding these principles. In the absence of molecular oxygen, the electron acceptor successive levels are Mn(IV), NO_3, Fe(III), organic compounds, SO_4, and CO_2. In the case of reductive dehalogenation, "organic compounds" are analogous to chlorinated solvents. The specific influence of electron acceptors, however, can not be generalized. Different microbial systems and different soil-water chemical conditions undoubtedly cause shifts in the thermodynamic equilibrium, and therefore, multiple electron-accepting processes are ongoing simultaneously.

Electron Donors

In general, almost any substrate that can be degraded anaerobically to either acetate or hydrogen will serve as an electron donor. Hydrogen and acetate are used by sulfate reducing microbes and/or methanogenic bacteria that use the chlorinated solvents as electron acceptors. If substrate is limited, ethanol or benzoate may be added as a supplemental substrate to further stimulate biological activity. Ethanol is rapidly degraded anaerobically resulting in the rapid production of hydrogen. Benzoate is more slowly degraded anaerobically resulting in a slower production of hydrogen.

Toxicity and Protozoa Grazing

The presence of toxins such as certain heavy metals and metabolic intermediates (e.g., daughter products and "suicidal enzymes") can also inhibit *in situ* biodegradation. In addition, protozoa grazing on indigenous bacteria can inhibit *in situ* biodegradation. This effect, however, is averaged out as the population of indigenous protozoa and bacteria rise and fall in response to each other.

3.2.3 Calibration of Transport Model

The transport model will be calibrated by varying input parameters over the approximate range of values specified in the table below, until predicted constituent plume concentrations closely match the observed concentrations.

Transport Model Input Parameters

Control Parameters	*Range*	*Notes*
time step, dt	$C_o < 1$	Courant number (C_o) will be maintained at less than one, $C_o \equiv v\,(dt / dx)$
maximum grid size, dx	$P_e < 2$	Peclet number will be maintained at less than two, $P_e \equiv dx / \alpha_L$

Aquifer Properties	*Range*	*Notes*
soil porosity, *n*	0.20 - 0.40	
soil bulk density, ρ_b	1.5 - 2.0 g/cm^3	
soil moisture content, ω	5 - 25 %	
soil fraction organic carbon, f_{oc}	0.01 - 15 %	and as determined from soil f_{oc} data
longitudinal dispersivity, α_L	50 - 150	ratio of α_L to α_T between 5:1 and 2:1
transverse dispersivity, α_T	10 - 50	ratio of α_L to α_T between 5:1 and 2:1

Chemical Properties	*Notes*
retardation factor, R	will be calculated for individual constituents in accordance with Eqn. (1) and Eqn. (2) of the Organic Contaminant Conceptual Model
biodegradation rate, k	will be calculated for individual constituents as specified in Section 3.2.2.3 (Biodegradation Kinetics)

3.3 HYDROGEOCHEMICAL MODEL

3.3.1 Distribution of Constituents of Interest

The results of on-site and off-site groundwater screening were submitted to the EPA in the December 22, 1997 revised monitoring well installation proposal. The December 22, 1997 proposal contained plan view maps showing the concentrations of specific COI within the Upper Glacial and Magothy Aquifers, and cross section maps showing the vertical concentration distribution of specific COI. Note that, in general, the groundwater quality information needed to complete the conceptual models of inorganic and organic constituent source location(s), mass, and distribution will be based upon groundwater sampling of the proposed and existing monitoring wells, according to the SAP for continued RI/FS activities (Roy F. Weston, February 1995). The collection of any groundwater parameters that are beyond the February 1995 SAP, but are necessary to complete the hydrogeochemical modeling proposed here, is specified in Tables 7 and 8 and in the tables attached to the cover letter to this revised CGW F&T document.

3.3.2 Physicochemical Processes

Multiple physical and chemical processes affect the interaction of groundwater and soil and determine the fate of inorganic COI in the subsurface. Some of these processes are listed in Table 5, along with example chemical reactions, and are discussed further below in the context of chromium and cadmium fate and transport in the subsurface. In contrast to chromium, cadmium [Cd(II)] is a simple metal that is not redox sensitive, although other components of minerals containing Cd(II) may be affected by the redox potential of the subsurface.

3.3.2.1 Speciation

The dominant chromium species in groundwater are shown in Figure 3, along with the stability field for the chromium solid $Cr(OH)_3$. In the range of natural groundwater pH and under reducing to slightly oxidizing redox potential, cationic and neutral species of Cr(III) ($CrOH^{2+}$, $Cr[OH]_2^+$, and $Cr[OH]_3^0$) dominate with the solid $Cr(OH)_3$ and are stable over a large portion of the pH/Eh region. Under more oxidizing conditions, the Cr(VI) anionic species $Cr_2O_7^{2-}$ (dichromate), $HCrO_4^-$ (bichromate) and CrO_4^{2-} (chromate) are dominant (Nikolaidis *et al.*, 1994; Rai *et al.*, 1984). The groundwater pH at the Liberty site appears to be depth dependent, with higher pH values in the upper aquifer (6.0 to 6.8), and the lower pH values in the Magothy Aquifer (4.7 to 5.5).

The dominant cadmium species in groundwater are shown in Figure 4, along with the stability field for the cadmium solid CdS. In the range of natural groundwater pH and redox conditions, the cationic species of Cd(II) predominates. Under more reducing conditions, the neutral species CdS is stable, and at groundwater pH in excess of 9, the hydrolyzed cationic, neutral and anionic species of $CdOH^+$, $Cd(OH)_2^0$ and $Cd(OH)_3^-$ become dominant.

3.3.2.2 Complexation

In addition to hydroxyl and other inorganic species, Cr(III) may form complexes with organic acids and water-soluble organic matter, thereby enhancing the mobility of chromium (James and Bartlett, 1983). Cd(II) may undergo stepwise formation of complexes involving ligand species, such as chloride, hydroxides, and water soluble organic matter. In subsurface environments with pH values less than about 9, the formation of the complex $CdOH^+$ is unlikely, and cadmium-chlorine complexes will dominate.

3.3.2.3 Sorption

Cr(III) and Cd(II) exhibit typical cationic sorption behavior (Deutsch, 1997). Adsorption increases with pH as the adsorbent surface sites become more negatively charged and attractive to cations. Specific adsorption of Cr(III) onto iron and manganese oxides likely occurs under oxidizing conditions (Korte *et al.*, 1976). Solid organic matter (e.g., lignite, which is abundant in the upper Magothy aquifer) may also be an important sorbent, although complexation with dissolved organic ligands may reduce adsorption. Because of the low solubility of the reactive Cr(III) solid $Cr(OH)_3$, the effect of the Cr(III) sorption on chromium mobility is generally not considered an important factor (Deutsch, 1997).

The dominant Cr(VI) species, chromate, exhibits typical anionic sorption behavior. Adsorption decreases with increasing pH as the sorbent surfaces become more negatively charged. Adsorption also decreases when competing dissolved anions are present (Deutsch, 1997): adsorption onto iron oxides and hydroxides has been shown to be suppressed by 50 to 80 percent in the presence of typical groundwater concentrations of dissolved HCO_3^- and SO_4^2 (Zachara *et al.*, 1987). Orthophosphate (PO_4^{3-}) also competes for adsorption sites with chromate (Barlett and Kimble, 1976). Adsorption of chromate is not affected by the presence of cations.

The adsorption edge (i.e., the pH at which 50 percent of the total species of interest is sorbed) for Cd(II) sorption onto iron oxyhydroxides and aluminous oxides (i.e., clays) is located at pH values of about 5.5 to 6.5, and complete sorption will occur at a pH value of about 8. Adsorption of Cd(II) is suppressed by the presence of chloride and sulfate and other sorption inhibitors (i.e., compounds that are competitively sorbed and, therefore, limit the sorption capacity for Cd).

These surface reactions can be modeled in MINTEQA2 in several ways; for the purpose of this modeling effort, the Freundlich Model will be used to simulate sorption to organic matter, and the Triple Layer Model will be used to simulate surface complexation reactions with iron oxides.

3.3.2.4 Dissolution / Precipitation

Mineral solubility is another geochemical process that affects the fate of inorganic constituents in the subsurface environment. The challenge in modeling mineral equilibrium is in selecting reactive minerals that might form in the subsurface. The solubility of a mineral can vary over many orders of magnitude and is dependent on such factors as the pH, Eh, ionic strength, and dissolved concentrations of ligands for each particular system. Because of the variability of mineral solubility, the concentration of chromium in groundwater, as limited by the solid concentrations, will be site-specific. The reactive minerals that are typically present in most subsurface environments are listed in Table 6, along with specific chromium and cadmium minerals.

3.3.2.5 Oxidation / Reduction

Oxidation-reduction processes play a major role in affecting the mobility of chromium because it is relatively mobile as Cr(VI) and immobile as Cr(III). It has been shown that where abundant reactive organic matter is present, Cr(VI) can be reduced to Cr(III) (Barlett and Kimble, 1976). Under somewhat acidic conditions, it has been found that Cr(VI) reduction by Fe(II) may occur. In that case, the reduction of chromium may be followed by the precipitation of the low-solubility solid $(Fe,Cr)(OH)_3$ (amorphous), depending on the prevailing pH (Eary and Rai, 1991). The natural sources of ferrous iron in the environment that may reduce chromate include residual amounts of reduced iron in minerals such as hematite and biotite. Other naturally occurring reductants such as dissolved sulfides have also been shown to be capable of reducing Cr(VI) (Schroeder and Lee, 1975).

The rate of reduction of Cr(VI) to Cr(III) increases with decreasing pH (Henderson, 1994). At pH values near 5, the half-life of Cr(VI) is ca. one month, whereas at a pH of 7 the half-life may be several years (Deutsch, 1997). In the case where ferrous iron is the reductant, the pH effect may be due to the greater solubility of iron minerals under low-pH conditions and the resulting higher dissolved concentration of Fe^{2+}. In general, the redox condition of most subsurface environments favors the reduction of Cr(VI) to Cr(III); however, it has been shown that oxidized manganese in the form of MnOOH and MnO_2 can oxidize Cr(III) to Cr(VI) (Barlett and James, 1979). This oxidation is fairly slow under slightly acid to basic conditions and is probably limited by the solubility of $Cr(OH)_3$ (Eary and Rai, 1987). Cr(III) does not appear to be significantly oxidized by the presence of dissolved oxygen in natural water (Eary and Rai, 1987).

3.3.3 Mathematical Modeling Approach

The coupling of a complete geochemical modeling code such as MINTEQA2 (Allison *et al.* 1991) with a finite difference or finite element transport code (MODFLOW/RT3D) is not considered a feasible approach to mass transport modeling with extensive geochemical reactions because of the computationally intensive requirements of modeling the geochemistry at each node of the grid. Instead, the proposed approach is as follows: 1) Divide the site area into separate redox domains (TEAP zones) or "packets of water along a flow pathway; 2) Beginning in the TEAP zone nearest the source, run MINTEQA2 using the source area groundwater concentrations of COI and determine the governing physicochemical processes for this TEAP zone; 3) Simulate groundwater transport of COI in this TEAP zone with RT3D using concentrations data from Step 2 until the "water packet" reaches the downgradient extent of the TEAP zone. The predominant physicochemical processes identified in Step 2 will be simulated in RT3D through simplified reactions using the User-Defined Reaction Module and/or the Mass-Transfer-Limited Sorption Module available in RT3D; 4) Repeat Steps 2 and 3, using the groundwater concentration data exiting the upgradient TEAP zone as input to the next downgradient TEAP zone until modeling criteria are met.

The groundwater and soil parameters that may be evaluated for the organic and inorganic COI fate and transport modeling are listed in Table 7 and Table 8, respectively. It may not be necessary to evaluate all of the parameters that are listed (e.g., an easily measurable parameter such as chloride may be used a proxy for other halogen sorption inhibitors, using accepted abundance ratios). The groundwater parameters (unless otherwise specified in the CRI/FS work plan) will be evaluated from the Upper Glacial and Magothy aquifer wells listed in the SAP Table 1A that is attached to the cover letter to this revised CGW F&T document. Similarly, the soil parameters will be evaluated from the on-site and off-site stratigraphic characterization boring, as specified in the SAP Table 1B.

4.0 REFERENCES

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TABLE 1
MODEL LAYER GEOMETRY

Layer No.	Thickness (feet)	Aquifer
1	not specified	Upper Glacial
2	25	Upper Glacial
3	25	Upper Glacial
4	25	Upper Glacial
5	50	Magothy
6	50	Magothy
7	100	Magothy
8	100	Magothy
9	200	Magothy
10	200	Magothy

Note: Layer 1 will contain the water table; the water table position will be calculated iteratively by the model and therefore the thickness for layer 1 is not specified.

TABLE 2
FLOW MODEL INPUT PARAMETERS FOR INITIAL SIMULATION

Input Parameters	**Start-up Value**	**Source**	**Ranges of Parameters for Sensitivity Analysis**
Longitudinal Horizontal Hydraulic Conductivity, K_x ft/day	Upper Glacial = 270 Magothy Formation = 50	Franke, et. al., 1972	+50%, +25%, 0%, -25%, -50% of calibrated K_x
Transverse Horizontal Hydraulic Conductivity, K_y, ft/day	Upper Glacial = 270 Magothy Formation = 50	Franke, et. al., 1972	+50%, +25%, 0%, -25%, -50% of calibrated K_y
Vertical Hydraulic Conductivity, K_z, ft/day	Upper Glacial = 27 Magothy Formation = 1.4	Franke, et. al., 1972	+50%, +25%, 0%, -25%, -50% of calibrated anisotropic ratio
Specific Yield, S_y	Upper Glacial = 0.24	Warren et. al., 1968	Not calibrated for steady-state simulation
Specific Storage, S_s, /ft	Magothy Formation = 6×10^{-7}	Buxton, et. al., 1985	Not calibrated for steady-state simulation
Porosity, n	Upper Glacial = 0.30 Magothy Formation = 0.25	Franke, et. al., 1972 Warren et. al., 1968	Not used for MODFLOW simulation, used by MODPATH for particle tracking
Recharge, inches/year	Upper Glacial = 22	Warren et. al., 1968	+50%, +25%, 0%, -25%, -50% of calibrated recharge
Evapotranspiration, inches/yr	Upper Glacial ~ 0	Wexler, et. al., 1988	
Seepage Rates		Regional Model	+50%, +25%, 0%, -25%, -50% of calibrated seepage rates
Well Fields		Well location, screen interval, and pumping rate of all pumping wells within the model domain will be collected and included in the model	

TABLE 3
PROCESSES GOVERNING THE FATE OF ORGANIC CONSTITUENTS

Physical	*Chemical*	*Biological*
Advection	Sorption	Potential Biodegradation Pathways
Dispersion	Precipitation / Dissolution	Biodegradation Kinetics
	Volatilization	Microbial Inhibition Potential - Contaminant Bioavailability - Metabolic Requirements - Toxins
	Diffusion	

TABLE 4
PHYSICAL / CHEMICAL PROPERTIES OF ORGANIC CONSTITUENTS

Compound	**Specific Gravity** [a]	**K_{ow}** [b]	**Solubility** [b] **(20°c) (mg/L)**	**Vapor Pressure** [c] **(mm Hg)**	**Henry's Constant** [c] **(atm-m^3/mol)**
PCE	1.63	398	150	17.8	0.0259
TCE	1.47	240	1,100	57.9	0.0091
1,1-DCE	1.25	69.2	400 - 2,500	600	0.034
1,2-DCE	1.27	3.02 - 5.01	600 - 6,300	208 - 324	0.00656 - 0.00758
VC	0.91	2.4	1.1 - 60	2660	0.0819

Sources:

a Deutsch, W.J. 1997. *Groundwater Geochemistry: Fundamentals and Applications to Contamination.* Lewis Publishers. New York, NY.

b USEPA. 1990. Basics of Pump-and-Treat Ground-Water Remediation Technology. EPA-600-8-90/0003. March.

c Schwarzenbach, R.P., P.M. Gschwend, D.M. Imboden. 1993. Environmental Organic Chemistry. John Wiley & Sons, Inc. New York, NY.

TABLE 5
PROCESSES GOVERNING THE FATE OF INORGANIC CONSTITUENTS

Process	*Example Chemical Reaction*
Ion Speciation	$\mathrm{Cr(OH)_2^+ + H^+ \leftrightarrow Cr(OH)^{2+} + H_2O}$ $\mathrm{Cd(OH)^+ + H^+ \leftrightarrow Cd^{2+} + H_2O}$
Ion Complexation	$\mathrm{Cr(OH)_2^+ + Cl^- + 2H^+ \leftrightarrow CrCl^{2+} + 2H_2O}$ $\mathrm{Cd(OH)^+ + Cl^- + H^+ \leftrightarrow CdCl^+ + H_2O}$
Mineral Dissolution/Precipitation	$\mathrm{Cr(OH)_2^+ + H_2O \leftrightarrow Cr(OH)_3\,(a) + H^+}$ $\mathrm{Cd(OH)^+ + H_2O \leftrightarrow Cd(OH)_2\,(a) + H^+}$
Oxidation/Reduction	$\mathrm{Cr(OH)_2^+ + O_2 \leftrightarrow CrO_4^{2-} + 2H^+}$
Adsorption/Desorption	$\mathrm{CrO_4^{2-} + Fe(OH)^{2+} \leftrightarrow FeOH \cdot CrO_4}$ $\mathrm{Cd^{2+} + Fe(OH)^{2+} \leftrightarrow FeOH \cdot Cd}$

TABLE 6
TYPICAL REACTIVE MINERALS IN THE SUBSURFACE ENVIRONMENT

Carbonates	***Oxides / Hydroxides***
Calcite [$CaCO_3$]	Ferrihydrite [$Fe(OH)_3$]
Dolomite [$CaMg(CO_3)_2$]	Goethite [$FeOOH$]
Siderite [$FeCO_3$]	Gibbsite [$Al(OH)_3$]
Rhodochrosite [$MnCO_3$]	Pyrolusite [MnO_2]
Magnesian Calcite [$(Ca,Mg)CO_3$]	
Sulfates	***Sulfides***
Gypsum [$CaSO_4 \bullet 2H_2O$]	Pyrite [FeS_2]
Alunite [$KAl_3(SO_4)_2(OH)_6$]	Mackinawite [Fe/S]
Jarosite [$KFe_3(SO_4)_2(OH)_6$]	Orpiment
Jurbanite [$AlSO_4(OH)_6$]	
Silicates	***Organic Matter***
Clay	Lignite
Zeolites	
Amorphous Silica [SiO_2 am]	
Chromium Specific Minerals	
Oxidizing Conditions	***Reducing Conditions***
Chromite Cr_2O_3	$Cr(OH)_3$ amorphous
Chromatite ($CaCrO_4$)	$(Fe,Cr)(OH)_3$
Hashemite ($BaCrO_4$)	$FeCr_2O_4$
Crocoite ($PbCrO_4$)	Cr_2O_3
Iranite ($PbCrO_4 \bullet H_2O$)	
Cadmium Specific Minerals	
Oxidizing Conditions	***Reducing Conditions***
Otavite ($CdCO_3$)	Greenockite (CdS)
$Cd_3(PO_4)_2$	$Cd(OH)_2$, amorphous

Source: Adapted from Deutsch (1997)

TABLE 7
GROUNDWATER PARAMETERS FOR GEOCHEMICAL MODELING

Data	Use
Major Ions Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, HCO_3^-, CO_3^{2-}, Cl^-, SO_4^{2-}, S^{2-}, NO_2^-, NO_3^-, TDS	Calculation of solution complexes; calculation of ionic strength and solute activity; saturation indices for minerals with these components
pH	Ion speciation / complexation and mineral solubility
E_h and Redox Potential	Ion speciation / complexation and mineral solubility of redox-sensitive elements
Dissolved Gases O_2, CO_2	Qualitative measure of redox potential Stability of groundwater pH
Minor / Trace Elements Fe, Mn, Al	Clay and oxyhydroxide mineral equilibria
Trace Metals Ba, Cr, Pb, Cu, Zn Hg, Cd	Mineral equilibria, competitive adsorption
Trace Semi-Metals As, Se	Mineral equilibria, competitive adsorption
Trace Non-Metals F, Br, P	Complexation, mineral equilibria, competitive adsorption
Organic Compounds VOCs	Complexation, oxygen consumption, sorption and redox reactions

Source: Adapted from Deutsch, 1997.

VOCs and major and trace metals contained in TAL inorganics will be collected from selected existing and new monitoring wells, according to the February 1995 SAP. Field measurements, using flow-through-cells will include pH, redox potential and dissolved oxygen. Samples for analyses for TDS, major anions, alkalinity, dissolved carbon dioxide will be collected from the monitoring wells listed in Table 1A of the cover letter to this CGW F&T document. Chlorine concentrations will be used as proxies for fluorine and bromine concentrations (if necessary), using accepted abundance ratios.

TABLE 8
SOLID PHASE PARAMETERS FOR GEOCHEMICAL MODELING

Constituent of Solid Phase	**Potential Impact on System**
Calcite	Mineral solubility control on solution concentration, partial measure of neutralization capacity
Gypsum	Mineral solubility control on solution concentration
Dolomite	Source of constituents to solution, partial measure of neutralization capacity
Clay mineral identification, quantification & cation exchange capacity	Exchange sites for major cations, mineral solubility control on solution concentration
Ferric and Manganese oxyhydroxides	Mineral solubility control on solution concentration, adsorption substrates for minor/trace elements
Pyrite	Mineral solubility control on solution concentration, source of acidity under oxidizing condition
Silicate Minerals	Sources of many dissolved constituents
Fractional Organic Carbon (Lignite)	Adsorbent medium for organic and inorganic compounds, reducing agent, source of dissolved carbon

Source: Adapted from Deutsch, 1997

Two stratigraphic characterization borings will be completed prior to the compilation of the transport and hydrogeochemical models, according to the well installation proposal, dated December 22, 1997. Soil samples from the depths listed in Table 1B of the cover letter to this CGW F&T document will be analyzed for grain size, cation exchange capacity, mineral abundance by x-ray diffraction (major silicates, Fe-Mn oxides and hydroxides, pyrite, carbonates, sulfates), fractional organic carbon, cadmium, chromium (total and hexavalent), and ferric and ferrous iron (if practicable), and vertical permeability.

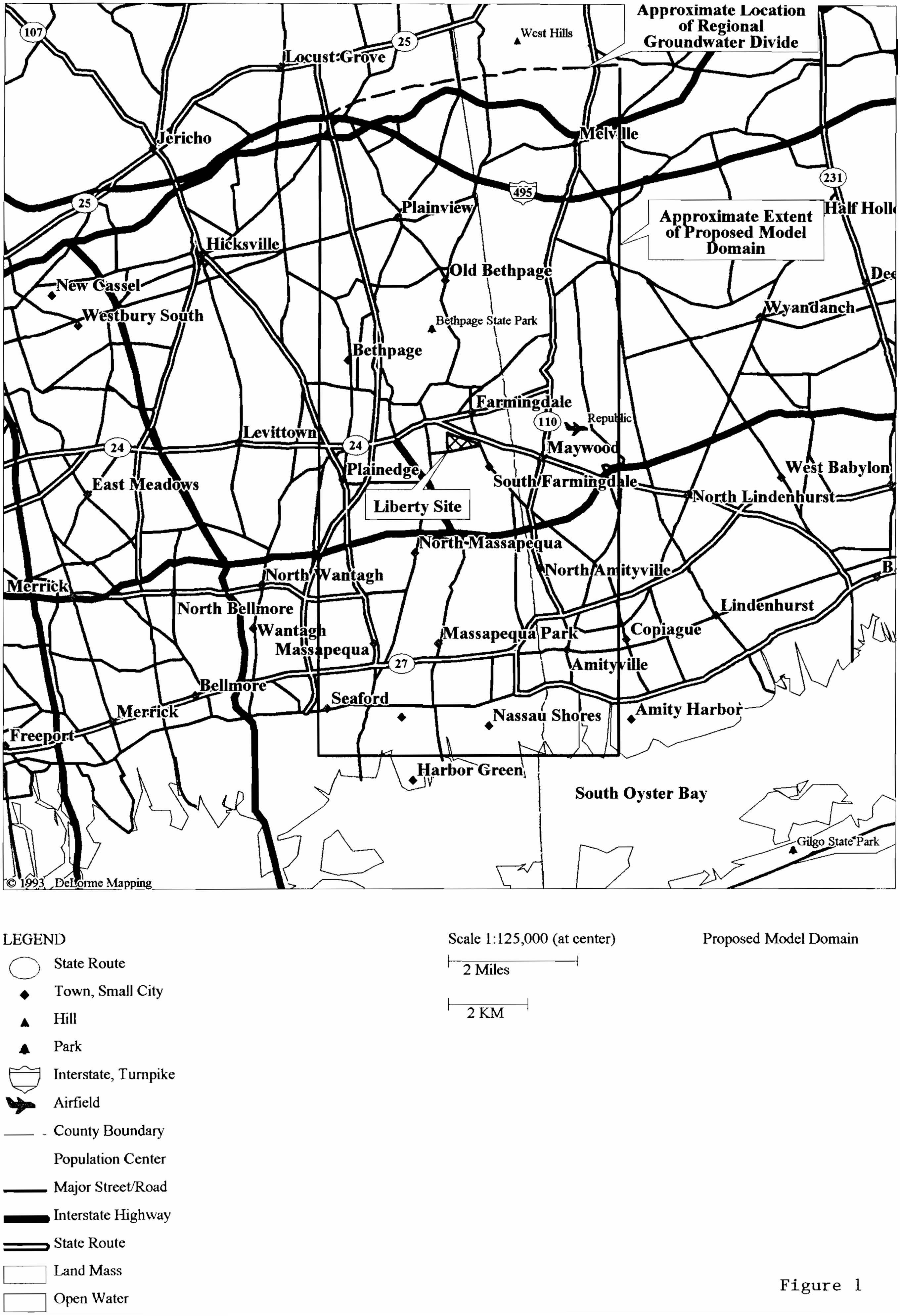
Approximate Location of Regional Groundwater Divide
Approximate Extent of Proposed Model Domain
Liberty Site
107
25
24
27
110
231
495
West Hills
Locust Grove
Jericho
Melville
Plainview
Half Holl
Hicksville
Old Bethpage
New Cassel
Dee
Westbury South
Wyandanch
Bethpage State Park
Bethpage
Farmingdale
Republic
Levittown
Maywood
Plainedge
West Babylon
East Meadows
South Farmingdale
North Lindenhurst
North Massapequa
North Amityville
North Wantagh
Merrick
B
North Bellmore
Lindenhurst
Wantagh
Copiague
Massapequa Park
Massapequa
Amityville
Bellmore
Seaford
Amity Harbor
Merrick
Nassau Shores
Freeport
Harbor Green
South Oyster Bay
Gilgo State Park
© 1993 DeLorme Mapping
LEGEND
State Route
Town, Small City
Hill
Park
Interstate, Turnpike
Airfield
County Boundary
Population Center
Major Street/Road
Interstate Highway
State Route
Land Mass
Open Water
Scale 1:125,000 (at center)
2 Miles
2 KM
Proposed Model Domain

Figure 1

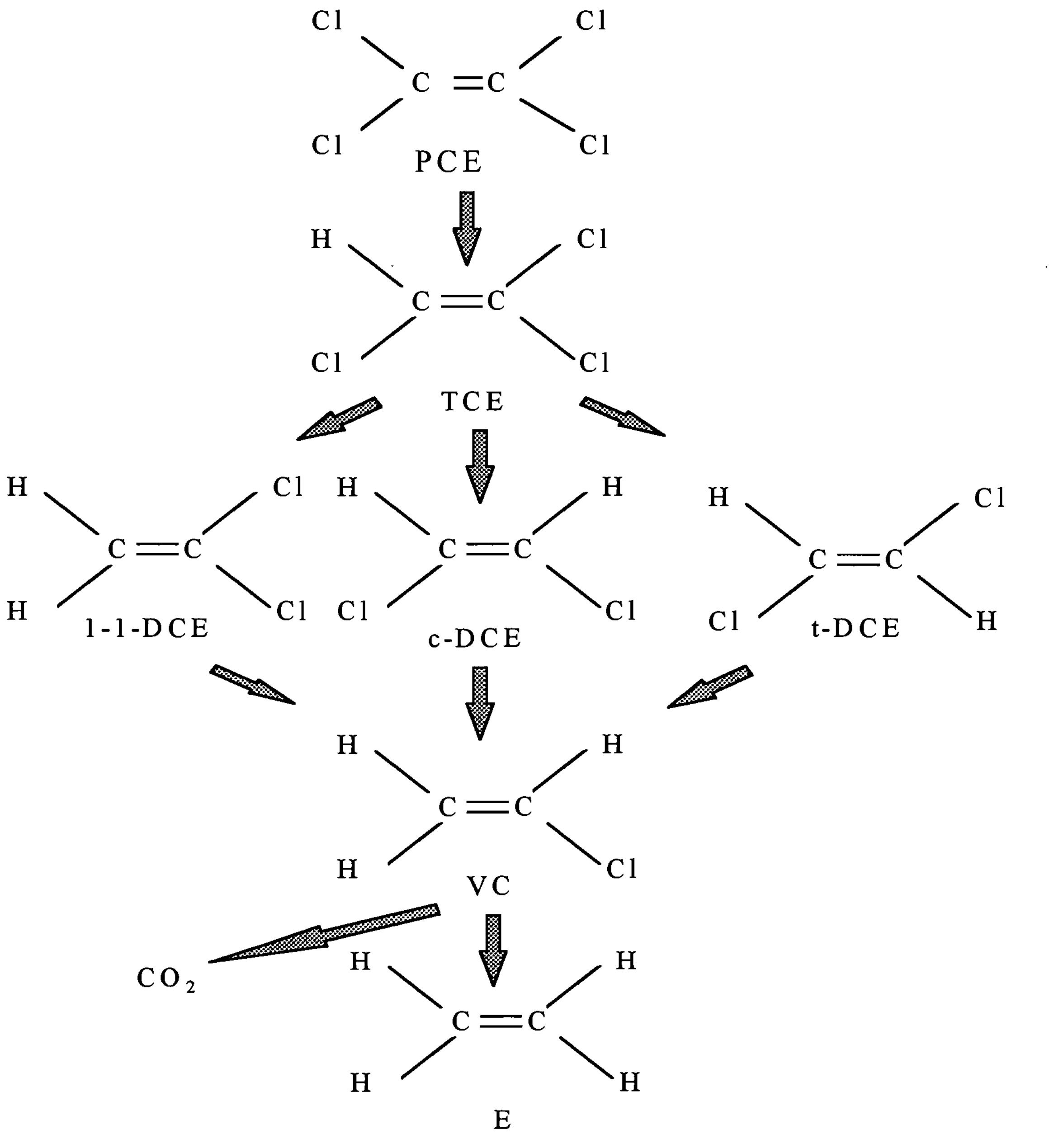

FIGURE 2 ANAEROBIC DEGRADATION PATHWAY OF PCE, TCE, DCE, and VC

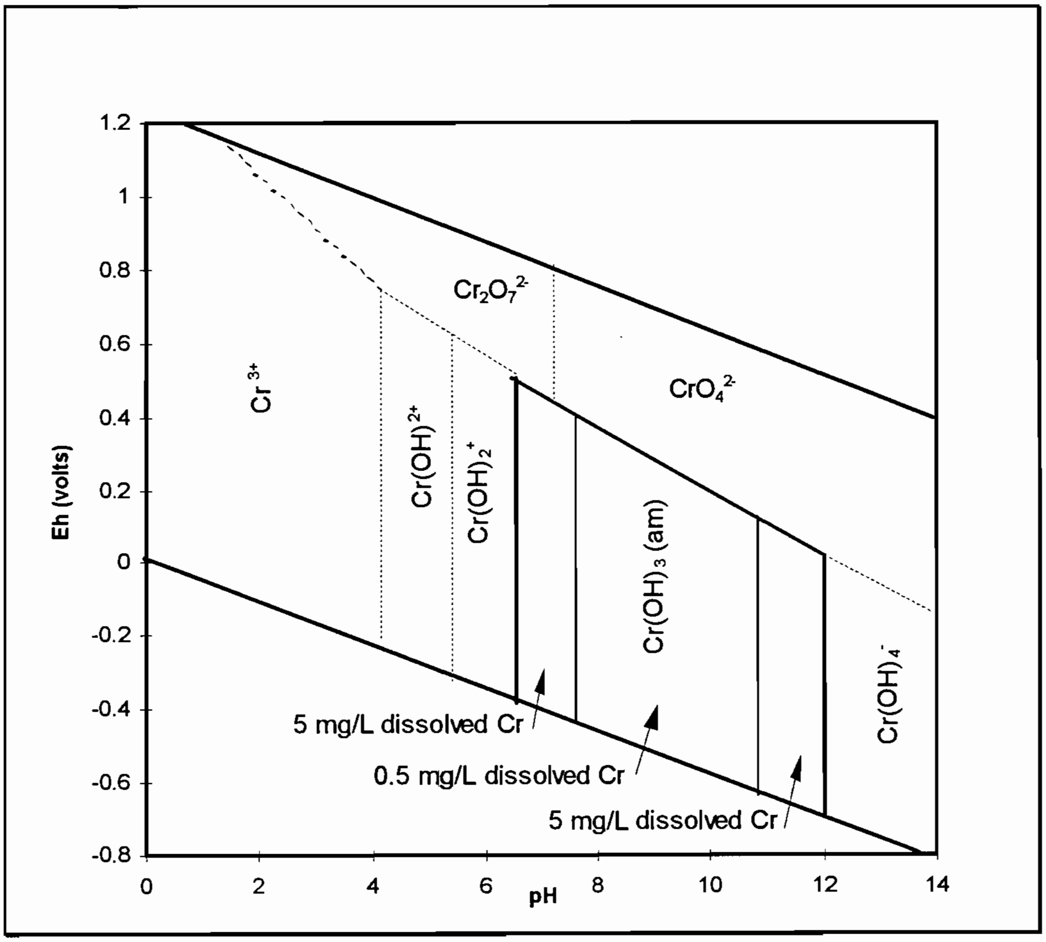

FIGURE 3 CHROMIUM SPECIATION AND MINERAL EQUILIBRIUM

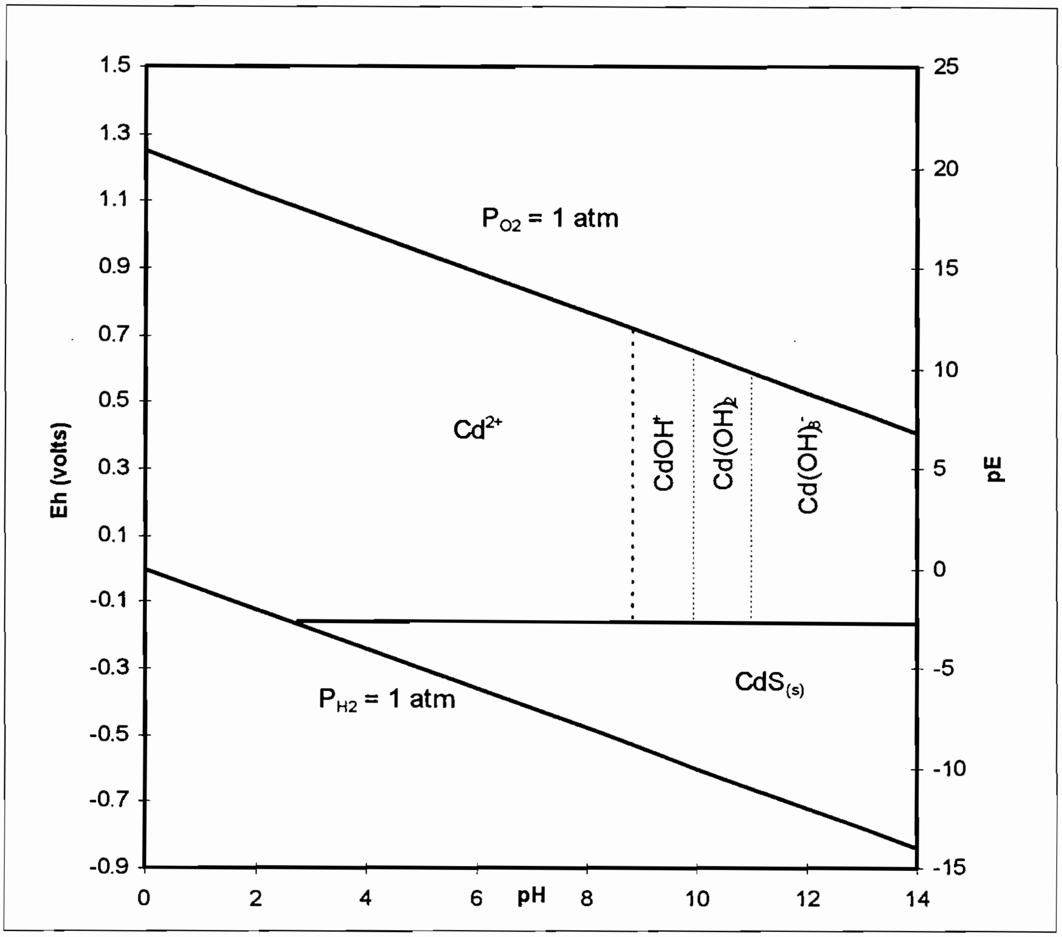

FIGURE 4 CADMIUM SPECIATION AND MINERAL EQUILIBRIUM

FEB 20 1998

R 3/12/98 VC

Ralph Golia, P.G.
Manager of Philadelphia Operations
Dames & Moore
2325 Maryland Road
Willow Grove, PA 19090

Ref: Liberty Industrial Finishing Superfund Site - Continued Remedial Investigation/Feasibility Study (CRI/FS): Dames & Moore's (D&M's) December 22, 1997 Conceptual Groundwater Flow and Transport Models Document

Dear Mr. Golia:

The U.S. Environmental Protection Agency (EPA) is in receipt of Dames & Moore's December 22, 1997 Conceptual Groundwater Flow and Transport Models document which provides details on a conceptual groundwater flow model, a conceptual transport model, and conceptual hydrogeochemical models to be performed for various organic and inorganic constituents at the Liberty site. We have reviewed your December 22, 1997 submittal and provide comments in an enclosure to this letter.

Realizing the need to commence the modeling effort in the near future, we request that you submit a revised Conceptual Groundwater Flow and Transport Models document by March 11, 1998.

If you have any questions regarding the enclosed comments, please contact Lorenzo Thantu of my staff at (212) 637-4240.

Sincerely yours,

Doug Garbarini, Chief
Eastern New York Remediation Section

Enclosure

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SYMBOL ---->		ENYRS						
SURNAME -->		DG Garbarini						
DATE -------->		2/20/98						

cc: Victor Cardona, NYSDEC
Henry Ku, USGS
Gary Loesch, H2M
Rich Baldwin, H2M
Tom Maher, Dvirka and Bartilucci
Theodore Toskos, Roy F. Weston, Inc.
John Williams, USGS

bcc: Michael Mintzer, ORC
Linda Ross, ERRD
Lorenzo Thantu, ERRD

ENCLOSURE

EPA'S COMMENTS ON DAMES & MOORE'S DECEMBER 22, 1997 CONCEPTUAL GROUNDWATER FLOW AND TRANSPORT MODELS DOCUMENT

GENERAL COMMENTS

1. The success or failure of attempts to couple geochemical reactions with transport models very directly depends upon the accuracy of the ground-water-flow model in simulating advection. Advection is visualized with particle-tracking analysis. MODPATH is the U.S. Geological Survey (USGS) particle tracker for use with MODFLOW. A presentation of the results of particle tracking, in conjunction with sensitivity analysis, should be the precursor to a study that attempts to simulate higher-order processes affecting the fate of COI's. This application of particle tracking to MODFLOW ground-water flow output, in conjunction with a sensitivity analysis (where the dependent variable of the analysis would be advective flow velocities) prior to attempting solute transport modeling, would provide a much better sense of the accuracy of solute transport model results.

   The determination of the NCDPW model that public wells are potentially at risk should also be subject to a particle-tracking analysis (if it has not been done so already) and compared with any ground-water flow model developed by D&M. It is recommended that the development of an RT3D model be postponed until the results of an advective analysis are presented. Furthermore, D&M should give some indication of how they will proceed with the sensitivity analysis prior to this presentation. A column can be added to Table 2 (pg. 23) that indicates test ranges of parameters, and there should be a discussion of the criteria for evaluating the results of varying parameters, parameter zonation, and sensitivity of additional items such as model discretization. Following the particle-tracking analysis, the following questions can then be posed: (1) once the effect of uncertainties in hydraulic parameters on simulation of advective pathways is apparent, how can these uncertainties be minimized? and (2) can an effort to simulate higher-order processes with RT3D be justified, given the current level of uncertainty in the ground-water flow model?

   Overall, the compilation of geochemical parameters and reactions for solute transport modeling provided in the D&M report is thorough. MINTEQA2 is generally a good model for calculating ion exchange, and a reasonable model for ionic speciation and redox reactions of inorganic constituents. There are serious limitations with most solute-transport models available in that rates of biodegradation of organic compounds and sorption of contaminants will vary significantly depending on redox conditions (terminal electron-accepting processes) that occur in zones, and can't be spatially simulated. D&M's approach in considering physical and geochemical processes with MINTEQA2 at separate "packets" of water along a flow path, and coupling these reactions with flow in RT3D seems very complex and probably would not be feasible for more than a few cells. There are a few models, such as BIOMOC (Essaid and Bekins, in press), that do consider redox zonation and the corresponding variation in biodegradation rates. The use of such a model assumes, however, that these redox or TEAP zones have been adequately characterized at and around the Site, either by microbial analysis of core samples or by H2 measurements in wells (Lovley and Goodwin, 1988), and the data collected for the Site seems limited to redox potential, which is qualitative at best. Some of the general assumptions made on redox chemistry, bioremediation, and organic content of the aquifers in the report are vague and sometimes incorrect. Much of the discussion of sorption is general, and does not discuss details of how MINTEQ2A will be used. Several specific examples are listed, below, in **SPECIFIC COMMENTS** section, for consideration in solute-transport modeling simulations, and in future remedial activities. In addition, some very useful references are also provided below.

2. Details regarding how streams will be simulated is lacking. Consideration should be given to simulating streams/aquifer interaction with either the Drain or the River packages of MODFLOW (not by specified heads or fluxes), thereby allowing a convenient way of determining sensitivity of stream discharges and flow velocities to streambed hydraulic properties.

3. D&M's December 22, 1997 Conceptual Groundwater Flow and Transport Models Document is often vague about what aspects of the modeling effort will actually be done, and does not propose to base the hydrologic model on site-specific data. Although it is understood that when dealing with a complex system, the modelers must be given flexibility in the selection of approach and mathematical tools, the extensive use of words, "may" and "could", as presently used in the document, hampers the Agency's constructive review of the document. Therefore, specific conditions under which a particular approach may be utilized should be outlined.

4. Provide the projected distances, from the Site, for the artificial boundaries which will be used for the Site grid.

5. The fate and transport model provides flexibility by incorporating a variety of geochemical processes. Provide documentation that the Version 1.0 (beta) which may be used is adequately tested for use at a Superfund site.

SPECIFIC COMMENTS

1. Section 3.1.3, "Steady-state flow conditions prevail", p. 6 - There are a number of potential problems with projecting steady-state flow conditions into the future: (1) augmentation of stream flow by NCDPW, (2) changes in public supply pumping -- as a result of the Liberty site or for other reasons, (3) changes in industrial pumping -- including implementation of a pump-and-treat system, and (4) drought. These factors can invalidate the use of a steady-state flow field as input to RT3D. Furthermore, migration of a plume can not be represented in steady state, and it is unlikely the source loading was continuous. On a different note, D&M's proposed steady-state model would be representative of current conditions and presumably would include simulation of pumping wells in the area. D&M's

response to EPA Comment 7 in appendix A (p.38), however, refers to a calibrated model of non-pumping conditions. This apparent contradiction needs to be explained.

2. Section 3.1.4, p. 7 - The use of the Raritan as an impermeable boundary must be cautioned. On a regional basis, about 5% of water table recharge ultimately moves across this layer. In addition, the rationale for selecting the number and thickness of layers must be specified. Although not stated in the proposal, it is assumed that the properties of each model cell will be edited to reflect the hydraulic properties of the corresponding part of the geologic column.

3. Section 3.1.8, p. 10 - Sensitivity analysis is not part of the calibration process. In the calibration process, parameters are "tweaked" to generate the best fit of simulated to observed heads and flows. After completion of this process, a thorough set of sensitivity tests can be conducted -- these results are not to be used to improve model calibration. One reason that this order is important is because the calibrated model does not represent a "unique" solution.

4. Section 3.1.9 - Although D&M acknowledges that a slug-test will characterize only a small area immediately adjacent to the well, and that a slug test will not provide all the hydraulic parameters necessary for the modeling effort, D&M proposes to utilize slug-test data as input parameters. D&M also proposes to use regional values for the aquifer parameters and then modify those until the simulated water elevations match the observed ones.

   It is a known fact that hydraulic conductivity values obtained from slug-tests are, at best, order-of-magnitude indicators of aquifer conditions, and not a true measurement of this property. Given all the other uncertainties stemming from the translation of the geologic map into model cells, the use of order-of-magnitude data only compounds the uncertainty. Given the complex, multivariate equations used in the model, a large combination of reasonable values of aquifer properties exist that when entered into the model can yield a match between the observed and the simulated values, without representing the actual aquifer conditions. The use of hydraulic conductivity estimates from slug tests, further undermines the reliability of the parameter calibration. For these reasons, aquifer pumping tests should be conducted to establish the necessary parameters. As such aquifer pumping tests are already being planned as part of an interim groundwater action implementation at the Liberty site, the purpose of which is to minimize, through installation of a groundwater containment system, the migration of contaminated groundwater in the Upper Glacial (shallow) aquifer away from the Site, D&M's efforts to establish the necessary modeling parameters should not be burdensome. (Alternatively, if there are good, reliable and consistent values, published in the literature, for the Site vicinity, and if D&M uses them to start-off the model runs, D&M should propose to do confirming tests for parameters which the sensitivity analysis shows to be critical, or for parameters that have to be adjusted substantially, in order to make the model fit.)

5. Section 3.2.2 - This section presents a very thorough discussion of the variables that control

contaminant transport. However, this section does not explain how these variables will be estimated. An explanation needs to be provided on how these parameters will be estimated. Any laboratory testing necessary should also be proposed.

6. Section 3.2.2.3, p. 14, Anaerobic Reductive Dehalogenation Relating to the Statement that Reductive Dehalogenation Proceeds Sequentially Until All Halogens Have Been Removed - The tendency of chlorinated ethenes to undergo reduction (under reducing conditions) decreases with fewer chlorine substituents. Furthermore, the tendency of chlorinated ethenes to undergo oxidation (under aerobic conditions) increases with a decreasing number of chlorines. Vinyl chloride, which is a daughter product that is relatively reduced, proceeds only at a very slow rate under highly reducing conditions, but can undergo anaerobic oxidation by microbial Fe(III)-reduction Bradley and Chapelle (1996).

7. Section 3.2.2.3, p. 15, Electron Acceptors - Successive levels of free energy yield of electron acceptors are listed, and include "organic compounds," which is ordered after Fe(III) and before sulfate. This may be valid for some organic compounds, but is not valid for those that behave as electron donors, as this has also been alluded to in Specific Comment 6, above.

8. Section 3.2.2.3, p. 16, Electron Donors - Lignite (organic carbon) is an important electron donor, and a reductant, naturally present in the Magothy aquifer that should be considered. Lignite is abundant (see Specific Comment 15, below), and typically associated with sulfate-reducing bacteria under natural conditions (Brown and others, 1997). The sulfate-reducing conditions associated with lignitic zones may be important to consider for redox reactions (i.e., reductive dehalogenation of polychlorinated compounds, and biodegradation of vinyl chloride under Fe(III)-reducing conditions).

9. Section 3.3.1, p. 16 - The distribution of COI (particularly the chlorinated compounds) that are shown in cross section maps from D&M's November 7, 1997 ground-water screening report is somewhat misleading, as the spatial extent of the plumes appear well defined, but are often supported by only one or two data points. Many of these plumes probably run together, and although dash lines are used, question marks should be added in future depictions to fully demonstrate the uncertainty of their extent. There is significant heterogeneity in Magothy sediment texture and organic carbon content.

10. Section 3.3.2 - The proposal presents a good synopsis of the physicochemical processes that may control contaminant fate and transport. Table 7 indicates that D&M will collect a variety of data necessary to conduct this modeling. A technical memorandum, in the form of a standard correspondence, that details the proposed sampling and analysis program should be submitted to EPA. Table 7 should also include sulfate and TDS. Please also indicate if the species of iron (ferric, ferrous) and manganese will be determined.

11. Section 3.3.2.3, p. 17, Sorption - Please state which sorption model(s) D&M plan to use? There are several options to model surface reactions in MINTEQA2, and generally the user

must provide thermodynamic database files of surface reactions. The sorption model used is very important. For example, several models neglect electrostatic influences, while others (e.g., Langmuir) assume a specified number of surface sites available for adsorption. The sorptive capacity of the aquifers should be considered --- Ku and others (1978) suggested that the sorptive capacity for Cr and Cd in the upper glacial aquifer, near the source, has probably been reached. Knowledge of Fe(III) oxyhydroxide coatings is also very important for sorption (Ku and others, 1978; David and others, 1991; Kent and others, 1995). Magothy aquifer sediments generally have much lower Fe(III) concentrations (<1 to 87 mg/g) (Brown and others, 1997) compared to upper glacial sediments. Also, the high organic matter content of the Magothy aquifer must be considered to determine the sorption of metals and other contaminants.

12. Table 6, p. 27 - Calcite is essentially absent in upper glacial and Magothy aquifer sediments. See a paper that may be useful on heavy minerals occurrences and distribution in western Suffolk County (Brown, 1996). Lignite should be included as a reactive solid in the geochemical modeling (Table 6).

13. Table 7 (p. 28) and Table 8 (p. 29) Relating to Geochemical Modeling - Calcite is essentially absent in the upper glacial and Magothy aquifer sediments, and the same is probably true for gypsum and dolomite. These three minerals, however, are listed in Table 8 (p. 29) as solid phase parameters for geochemical modeling. Inclusion in the model of relatively soluble or reactive phases such as these, which may not be present in the aquifer material, could lead to misleading and incorrect results. It is important, therefore, that the mineral content of the aquifers be accurately characterized prior to development of the geochemical model. Also, sulfate is not listed in Table 7 (p. 28) among the major ions to be included in the geochemical model. This is probably an oversight.

14. Figure 1 (Oversize), Proposed Model Domain Groundwater Modeling Studies - Based on published maps of the Long Island water table and the Magothy potentiometric surface, the regional ground water divide is about 3 miles north of the proposed northern model boundary shown in this figure, and South Oyster Bay is only about one mile south of the proposed southern boundary. The northern model boundary should be extended to the ground-water divide and the southern model boundary should be extended to south of the coast to encompass these natural hydraulic boundaries. By doing this, boundary conditions from the Nassau County regional model would not be needed in these areas, thus minimizing the adverse effects of artificial boundaries.

15. Table A-1, p. 43, The Range in Foc Listed Under Aquifer Properties, in Response to EPA Comment 12 - The organic carbon fractions reported (0.01-0.5%) may be acceptable for Pleistocene deposits, but they are much too low for much of the Magothy aquifer. Based on cores that the USGS has sampled from four bore holes in middle Magothy sediments of southwestern and south central Suffolk County, organic carbon content can range from less than 0.05% to 13.9%. Organic matter in the form of lignite often is associated with poorly

permeable sediments (2-13.9%) in the Magothy but can also be distributed throughout sandier sediments (0.1-0.7)%. These data are reported in a paper currently in review (Brown and others, 1998). Sirois and others (1986) found similar results in a single bore hole at Tanner Park, in western Suffolk County. Organic carbon in sands ranged from .01-1.7%, and organic carbon in silt/clay- dominant sediments ranged from 1.2-13.7%. Since the retardation factor, and the Kd, are very much dependent on the soil fraction organic carbon content, higher organic carbon contents obviously will have a large effect on model results for sorption/desorption and contaminant migration in parts of the shallow Magothy aquifer contaminated with metals and chlorinated compounds. Because D&M has indicated that the groundwater parameters will be evaluated from selected upper glacial and Magothy aquifer wells, it needs to be emphasized that D&M obtain several samples from the Magothy aquifer to sufficiently characterize foc.

16. References

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