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TECHNICAL REPORT ON THE EFFECTIVENESS OF THE HALTON WASTE MANAGEMENT SITE EAST STORMWATER POND TO REDUCE TSS AND ASSOCIATED CONTAMINANTS

I.G. Droppo, K. Exall, C. He, L. Grapentine and K. Spencer

WSTD Technical Note No. AEMR-TN08-005

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by

I.G. Droppo, K. Exall, C. He, L. Grapentine and K. Spencer

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Technical Report on the effectiveness of the Halton Waste Management Site East Stormwater Pond to reduce TSS and associated contaminants

Ian G. Droppo, Kirsten Exall, Cheng He, Lee Grapentine and Kate Spencer

NWRI RESEARCH SUMMARY

Plain language title

Evaluation of a stormwater pond to remove pollutants and possible best management practices to improve its operation.

What is the problem and what do scientists already know about it?

Stormwater detention ponds can be an effective best management practice for the removal of sediments and associated contaminant prior to the effluent leaving the pond. Some ponds work better than others due to their geometry and flow attenuation properties. The only way to assess how well a pond is working is to monitor it.

Why did NWRI do this study?

NWRI was asked to assess how well the East Stormwater Detention pond (Municipality of Halton – Milton, Ontario) is working to remove metal contamination. This provided a good research opportunity for NWRI to evaluate an existing pond but to also advance our knowledge around stormwater modeling and to test out some new ideas around pond operation such as polymer application and cohesive sediment tracing with rare earth elements.

What were the results?

This is a final report to the Region of Halton from a 3 year study. The final year of the study was unusual in that for the majority of the year there was no outflow. Regardless, the following was observed:

- The pond performs adequately with suspended solid and metal concentrations reduces significantly between the inlet and outlet (when outlet flow occurred).
- Currently the pond's efficiency is driven entirely by its geometry and not related to any applied BMPs.
- Macrophyte plantings at the inlet and outlet are suggested as the most cost effective measure to improving the operating efficiency of the pond.
- Holmium (rare earth element - REE) tracing was found to be an excellent method for tracing the movement of cohesive sediments and associated contaminants within the pond. Holmium, at the concentrations used, was found in an earlier study not to be toxic to aquatic life.

How will these results be used?

The results will be provided to the Halton Region as a technical report to assist them in the optimization of their stormwater pond's operation. It is expected that 2 to 3 international journal publications will be produced out of this report.

Who were our main partners in the study?

Regional Municipality of Halton and Queen Mary, University of London, UK.

Abstract

The three year project was completed on March 31, 2008 and was designed to assess the existing performance of the East Stormwater Detention Pond (Halton Waste Management Site, Regional Road 25, Milton, Ontario) with respect to sediment and associated contaminant (metals) removal. The collaboration between the Halton Region and NWRI will help in the development of improved water management strategies and treatment technologies. The first year of the project (ending March 2006) was a feasibility study for the project with the results reported in the technical publication; NWRI Technical Note No. AEMRB-TN05-007 (provided in appendix A). Following from this report the second year of the study has provided a better understanding of the flow and sediment dynamics of the pond during wet weather periods (NWRI Technical Note No. AEMRD-TN07-003 – provided in appendix B) and allowed for a more focused approach for the final year of the project. In the final year a rare earth element (REE) (holmium) was tagged to montmorillonite clay and used to trace the distribution and deposition of cohesive sediments entering the pond from the inlet. A complete toxicological study was performed on the effects of holmium on the pond biota. This report, which demonstrated no effects with the level of holmium released, is provided in Appendix C. Further, the REE results were used to validate a mathematical model that can be used in the future to investigate the benefits of best management practices (BMPs) employed to the pond and for climatic variation scenarios. Unfortunately, the pond level was extremely low for the majority of the 2007/08 sampling season and no outflow was occurring during the holmium deployment. Nonetheless, the results do provide the operators of the East Stormwater Detention Pond with an understanding of the sediment dynamics of the pond during what constitutes the majority of the year (i.e. no outflow) and a likely condition of future pond operation. It is important to realize, however, that the empirical data and model predictions will be conservative estimates due to the lack of outflow contributing to the pond circulation dynamics. This report provides the Region of Halton with information and interpretation of field data and mathematical modeling along with discussion on the potential for different BMPs to help improve the operation of the East Stormwater Pond.

Rapport technique sur l'efficacité du bassin d'orage de l'Est du site de gestion des déchets de Halton à réduire le total des solides en suspension (TSS) et les contaminants

Ian G. Droppo, Kirsten Exall, cheng He, Lee Grapentine et Kate Spencer

Sommaire des recherches de l'INRE

Titre en langage clair

Évaluation de l'efficacité d'un bassin de retenue des eaux de ruissellement à éliminer les polluants et des meilleures pratiques de gestion possible afin d'en améliorer l'exploitation.

Quel est le problème et que savent les chercheurs à ce sujet?

Les bassins d'orage peuvent être des meilleures pratiques de gestion efficaces pour l'élimination de sédiments et des contaminants qui s'y rattachent avant que l'effluent quitte le bassin. Certains bassins fonctionnent mieux que d'autres en raison de leur géométrie et de leurs propriétés d'atténuation du débit. La seule façon d'évaluer la mesure dans laquelle le bassin fonctionne bien est de le surveiller.

Pourquoi l'INRE a-t-il effectué cette étude?

On a demandé au personnel de l'Institut national de recherche sur les eaux (INRE) d'évaluer la mesure dans laquelle le bassin d'orage de l'Est (municipalité de Halton – Milton, Ontario) réussit à réduire la contamination par les métaux. Cela représentait une bonne occasion de recherche pour l'INRE non seulement pour évaluer un bassin actuel, mais aussi pour approfondir nos connaissances sur la modélisation pluviale et mettre à l'essai quelques idées nouvelles relativement à l'exploitation du bassin, telles que l'application de polymère et la reconstitution du parcours des sédiments cohésifs avec des métaux du groupe des terres rares.

Quels sont les résultats?

Il s'agit d'un rapport final pour la région de Halton à l'issue d'une étude triennale. La dernière année de l'étude était inhabituelle, en ce sens qu'il n'y a pas eu de débit sortant pendant la majorité de l'année. Malgré tout, on a remarqué ce qui suit : le bassin fonctionne adéquatement et les concentrations de matières en suspension et des métaux sont sensiblement réduites au niveau de la prise d'eau et du dégorgeoir (lorsqu'il y avait un dégorgeoir de décharge). Actuellement, l'efficacité du bassin dépend entièrement de sa géométrie et n'est pas liée à l'application des meilleures pratiques de gestion. On suggère de planter des macrophytes au niveau de la prise d'eau et du dégorgeoir comme mesure économique pour améliorer l'efficacité de l'exploitation du bassin. On a découvert que la reconstitution du parcours de l'holmium (métal du groupe des terres rares) était une excellente méthode pour reconstituer le mouvement des sédiments cohésifs et des contaminants qui s'y rapportent dans le bassin. Dans le cadre d'une étude antérieure, on a découvert que l'holmium, aux concentrations utilisées, n'était pas toxique pour la vie aquatique.

Comment ces résultats seront-ils utilisés?

Les résultats seront présentés aux responsables de la région de Halton sous forme de rapport technique en vue de l'optimisation de l'exploitation de leur bassin d'orage. On s'attend à ce que deux ou trois articles publiés dans des journaux internationaux découlent de ce rapport.

Quels étaient nos principaux partenaires dans cette étude?

La municipalité régionale de Halton et Queen Mary, University of London, Royaume-Uni.

Résumé

Le projet triennal a été terminé le 31 mars 2008 et a été conçu pour évaluer le rendement actuel du bassin d'orage de l'Est (site de gestion des déchets de Halton, route régionale 25, Milton, Ontario) relativement à l'élimination des sédiments et des contaminants (métaux) qui s'y rapportent. La collaboration entre la région de Halton et l'INRE permettra d'améliorer les stratégies de gestion des eaux et les technologies de traitement des eaux. La première année du projet (qui a pris fin en mars 2006) était une étude de faisabilité dont les résultats ont été présentés dans une publication technique, la note technique de l'INRE n° AEMRB-TN05-007 (fournie à l'annexe A). À la suite de ce rapport, la deuxième année de l'étude a permis de mieux comprendre la dynamique du débit et des sédiments du bassin pendant les temps de pluie (note technique de l'INRE n° AEMRD-TN07-003 – fournie à l'annexe B) et a permis de prévoir l'application d'une approche plus axée pour la dernière année du projet. Dans le cadre de la dernière année du projet, un métal du groupe des terres rares (holmium) a été marqué par de la montmorillonite et utilisé pour retracer la distribution et la déposition de sédiments cohésifs qui entraient dans le bassin au niveau de la prise d'eau. Une étude toxicologique complète a été réalisée sur les répercussions de l'holmium sur le biote du bassin. Ce rapport, qui a démontré que le niveau d'holmium rejeté n'avait aucune répercussion, est fourni à l'annexe C. En outre, les résultats portant sur le métal du groupe des terres rares ont été utilisés afin de valider un modèle mathématique, qui peut être utilisé à l'avenir pour mener des enquêtes sur les avantages des meilleures pratiques de gestion employées pour le bassin, et les scénarios de variation climatique. Malheureusement, le niveau du bassin était extrêmement bas pendant presque toute la saison d'échantillonnage de 2007-2008, et il n'y avait aucun débit sortant pendant le déploiement de l'holmium. Malgré tout, les résultats permettent aux opérateurs du bassin d'orage de l'Est de mieux comprendre la dynamique sédimentaire du bassin pendant presque toute l'année (c'est-à-dire qu'il n'y a aucun débit sortant) et une condition probable de l'exploitation future du bassin. Il est important de se rendre compte, cependant, que les données empiriques et les prédictions du modèle seront des estimations prudentes en raison du manque de débit sortant qui contribue à la dynamique de circulation du bassin. Ce rapport permet de fournir des renseignements aux responsables de la région de Halton, d'interpréter les données d'exploitation et la modélisation mathématique ainsi que de discuter de la possibilité d'application de meilleures pratiques de gestion différentes en vue d'améliorer l'exploitation du bassin d'orage de l'Est.

Technical Report on the effectiveness of the Halton Waste Management Site East Stormwater Pond to reduce TSS and associated contaminants

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Introduction

The three year project was completed on March 31, 2008 and was designed to assess the existing performance of the East Stormwater Detention Pond (Halton Waste Management Site, Regional Road 25, Milton, Ontario) with respect to sediment and associated contaminant (metals) removal. The collaboration between the Halton Region and NWRI will help in the development of improved water management strategies and treatment technologies.

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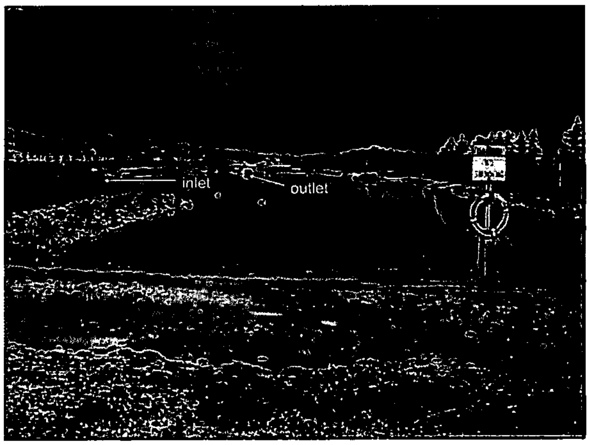
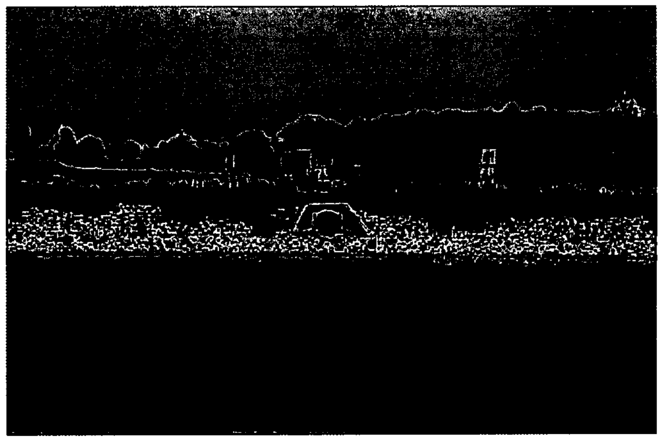
Methodology
2007 Field Station Set Up and Activity

In a typical year, the Halton East Pond is an open stormwater detention pond with the dimension of 120 m (L) x 50 m (W) and 2 m (D); there is one inlet (2 culverts) and one outlet in the pond as shown in Figure 1a. In the summer of 2007, however, the pond was very low with depths on average at 0.7m (Figure 1b). This low water level was attributed to a low rainfall year and unusually high extraction by the Region for dust control (due to the lack of access to the West pond with the construction of Cell-3).



a.



b.

Figure 1. East stormwater detention pond (a) summer 2006; (b) summer 2007; note drop in water level of greater than 1m.

Inlet and Outlet Flow Monitoring - Dog houses set up in 2006 over the inlet and outlet to house electronic and sampling equipment were maintained for the 2007 sampling period. In 2007 a flume with a calibrated V-notch weir (Figure 2) was installed in the south culvert of the inlet while a calibrated V-notch weir was installed down stream on the outlet concrete channel. These calibrated weirs along with Area Flow Velocity Meters (Sigma 950) allowed for more accurate measurements of flows.

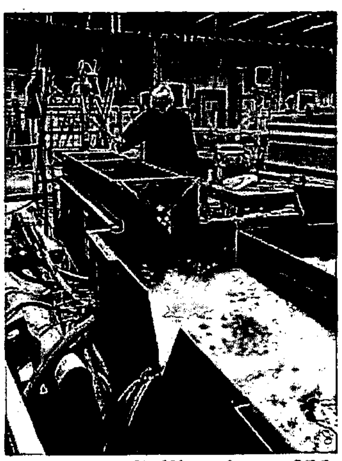


Figure 2. Calibration of V-notch weir used within the inlet culvert.

An automated sampler (Sigma 900) was also installed within the outlet pipe and south inlet culvert to collect 1 L water samples at equal time intervals. The Sigma water samplers were triggered to initiate sampling once a water level threshold was surpassed. Up to 24 1L samples can be collected for each round of sampling. These samples were analyzed discretely or in composite.

Turbulent Flow Monitoring within the Pond – Acoustic Doppler Current Profilers (ADCP) probe (Figure 3) [Sontek Hydra Ocean Probe (sn B351H)] were deployed in a downwards looking fashion off a tripod from October 10 to November 1, 2008 to assess the currents set up in the pond by both inflows and wind energy. The sensing volume on the Hydra measured velocities (128, 4 Hz samples every minute) approximately 7 cm from the bottom.

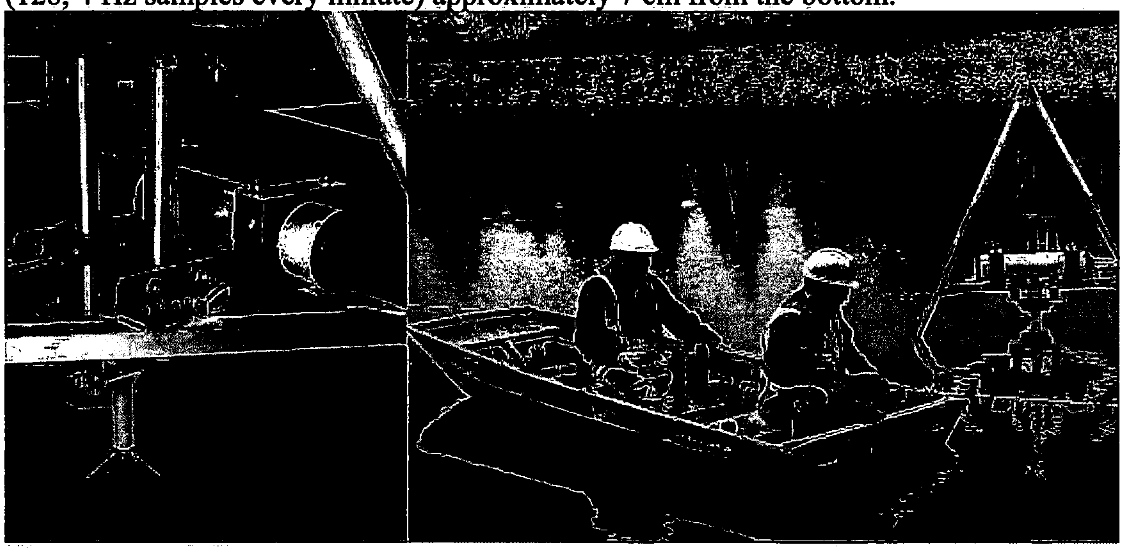


Figure 3 a) ADCP set up on tripod prior to deployment. Note the three pronged probe at the bottom is the sensor head providing X, Y and Z directional flows, b) ADCP deployed in the pond.

Meteorological Station - A CSC logger was used to record air temperature, relative humidity, wind speed and direction every 5 minutes from a portable met station as seen in Figure 4. The station was set up at the southwest corner of the pond (see Figure 8).

Figure 4. Meteorological station for recording temperature, wind speed and wind direction.

Suspended Solid Monitoring within the Pond – Two recording Optical Back Scatter (OBS) probes (Figure 5) were deployed within the pond on moorings or on the tripod of the ADCP in order to assess changes in suspended solid concentration during storm or wind events and during the REE deployment

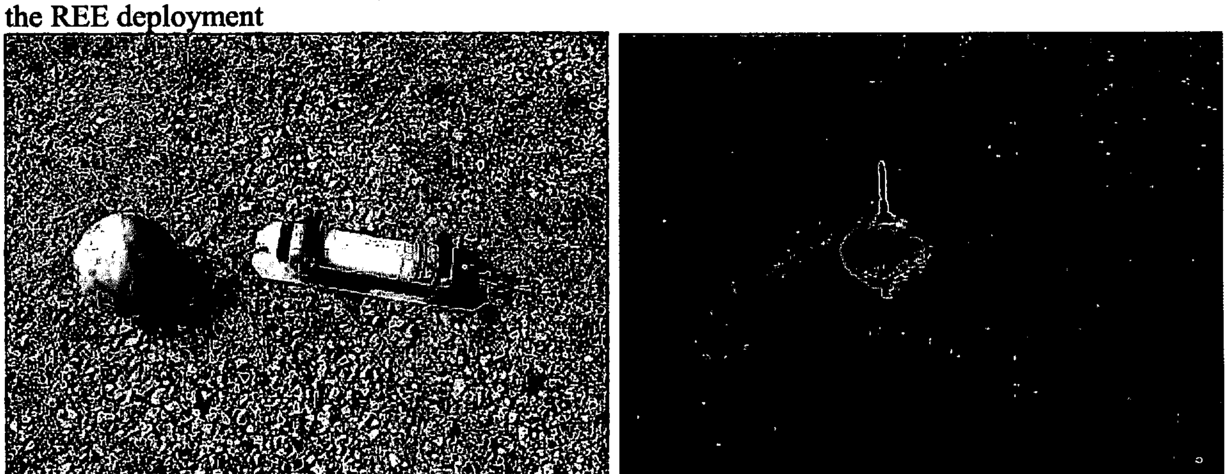


Figure 5 a) OBS probe with mooring, b) mooring with recording OBS probe suspended below during ice breakup.

Metal Chemistry Analysis – Analysis of 27 metals in both total and dissolved form were measured by ICP – MS following standard methods and QA/QC (Environment Canada, 1994). Table 1 lists these metals and their detection limits. For the purposes of this report only six metals were assessed (Cd, Cu, Fe, Mn, Pb, and Zn), and only Ho was analyzed during the REE deployment.

Table 1. Metals detection limits ($\mu g\ g^{-1}$)

Metal	MDL water	MDL sediment
Calcium	4.78	0.478
Silver	0.46	0.046
Aluminum	7.24	0.724
Arsenic	0.005	0.013
Barium	1.37	0.137
Boron	0.65	0.065
Beryllium	0.1	0.01
Bismuth	1.05	0.105
Cadmium	0.22	0.022
Cobalt	0.14	0.014
Chromium	0.15	0.015
Copper	0.5	0.05
Holmium	0.005	0.5
Iron	2.21	0.221
Potassium	7.39	0.739
Magnesium	0.31	0.031
Manganese	0.09	0.009
Molybdenum	0.26	0.026
Sodium	11.37	1.137
Nickel	0.26	0.026
Lead	0.64	0.064
Antimony	0.055	0.137
Selenium	0.009	0.022
Tin	0.5	0.05
Strontium	0.27	0.027
Titanium	0.13	0.013
Vanadium	1.96	0.196
Zinc	0.95	0.095

Total Suspended Solid TSS Concentration – TSS was determined gravimetrically by filtering a known volume of sample through a pre-weighed 0.45 μm Millipore™ cellulose acetate filter followed by drying at 100°C for 1 hour and re-weighing the filter to determine the mass of sediment per unit volume.

Rare Earth Element (REE) Study

As the majority of contaminants will be associated with fine-grained cohesive particulate matter (Horowitz, 1991), experiments using the REE Holmium (Ho) were designed to trace the movement and deposition of suspended sediment within the pond during an inflow event. This experiment allowed for the determination of which areas of the pond contributes the greatest to the removal of sediments and associated contaminants.

Toxicity Testing of Holmium - Prior to the deployment of the Ho-Clay mixture, an extensive study was carried out to investigate if there was any potential toxicological effect of Ho on the aquatic biota of the stormwater pond. Four benthic invertebrate taxa (Chironomus riparius, Hexagenia spp., Hyalella azteca, Tubifex tubifex) were exposed to Ho-clay alone and mixtures of 10, 25 and 50% Ho-clay with field-collected reference sediment for 10-28 days in standard laboratory toxicity tests. More information of the methodology for the toxicology tests can be found in Appendix C.

Deployment - A slurry of 50% pond bottom sediment and 50% holmium labeled montmorillonite clay was mixed in a 100 liter pail using a mixer shaft rotated by a high speed drill (total dry mass - 6 kg). Samples were taken prior to deployment for suspended sediment and holmium concentration, and particle structure/behaviour.

An 11,000 L tanker truck owned by the Region was used to create an artificial storm using pond water for the purposes of the simulation. Two artificial storms were created; one on October 10, 2007 with only a slurry of pond bottom sediment injected into the flow as a test run of procedures and on October 12 with the injection of the REE. Two complete flushes of the truck were used in each case to represent a bimodal storm and to allow for the complete deployment of the holmium mixture into the pond. One complete flush of the truck required approximately 30 minutes. During the initial flush of the tanker truck, and prior to the slurry injection, samples were taken at the v-notch weir for background holmium and suspended solid concentration and floc structure. The REE slurry was then injected into the flume of the inlet using a slurry pump and samples were collected for SS concentration and Ho concentration every 2 minutes beginning at 30 seconds. Floc samples were collected at the start, middle and end of the slurry injection time in duplicates using plankton chambers as per the method of Droppo et al. (1997). In addition a 4L sample was collected at the middle of the injection for floc settling characteristics following the method of Droppo (2004).

Grab samples were also collected from within the sediment plume formed within the pond during the storm events using a pole sampler and 500 ml sample bottles. The samples were analyzed for SS concentration only and served as a validation for the mathematical model described below. In addition surface floats were deployed at the outlet and a video was recorded to help delineate the extent of plume migration over the duration of the deployment. Figure 6 illustrates the physical set up during the REE deployment. Note that flow from the south culvert passed through the reed bed (which was submerged in 2005 and 2006) before reaching the water level of the pond.

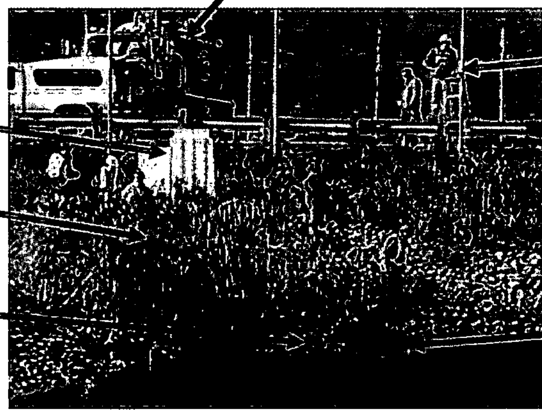


Figure 6. Operations during REE deployment experiment.

REE Sample Collection One Week after Injection - Seven days after the REE injection, bed sediment samples were collected as 1) reed bed samples, 2) pond shore samples and 3) as sediment cores taken at depth. All sampling locations were marked using GPS coordinates. Three reed bed sediment samples were collected by taking surface scrapes over approximately a 5 x 5 cm area. Samples were collected along a transect from the upper reed bed to the lower (next to water) reed bed using a stainless steel spatula which was cleaned with distilled water between uses.

Thirty pond shore samples were collected approximately every 15m along the perimeter of the pond, 30 cm from the edge and from an area of approximately 5 x 5 cm under a few cm of water. This sediment was collected using a 50 cm^3 plastic syringe with 50 cm of plastic tubing attached to the end of the syringe. Surface sediments were carefully removed by directing the tubing over the surface area while carefully extending the syringe plunger. The syringe was then flushed with pond water into the sample container. The syringe was rinsed three times with pond water between each sample.

Forty-six core samples (Figure 7a) were collected from a boat along transects (e.g. Figure 7b) marked on Figure 8. Core locations along each transect are provided in Table 2. Cores were collected with 10 cm diameter plastic tubing and extruded on site. The cores were extruded (Figure 7c) while still full of water until 4 cm of water remained above the sediment water interface. This water and any disturbed flocs were siphoned off and retained. The core was then extruded and a 5 mm sub-sample was removed from the surface using a small core ring and metal plate (Figure 7d). This sub-sample and the water sample were then composited for analysis. To avoid cross contamination between samples in the field all equipment was washed in pond water, rinsed three times in de-ionised water and then rinsed in clean pond water before use. Surface and core sediment samples were returned to the laboratory and stored at 4°C within a few hours of collection. Samples were freeze dried prior to digestion and Ho analysis.

Table 2 – location of core samples along each tag line.

Transect	Tag line location (m from inlet or west shore)	Number of cores/transect
1	2 5 10	3
2	2 3 10 15	4
3	2 3 5 10	4
4	2 5 10 15 20 25 32	7
5	3 10 15 20 25 30	6
6	5 10 15 20 25 32	6
7	3 5 10 25 40	5
8	1 5 25 40 65	5
9	3 5 10 25 40 65	6
		Total 46 cores

Figure 7. a) Core sample collection along transect, b) transect line 4 (T-4), c) core prior to extraction and d) sample collection during core extraction.

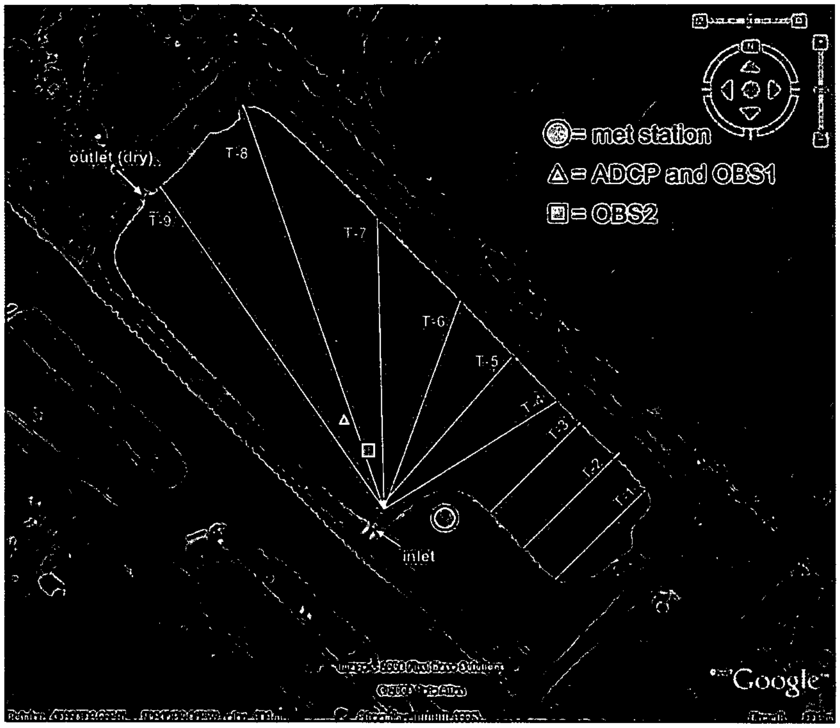


Figure 8 – Transect locations for core sampling. Pond shore samples were collected approximately every 15m along the perimeter of the pond.

Hydrodynamic Modelling

Two different three dimensional hydrodynamic numerical models (Star CD and MIKE 3) were applied in this study based on several key features: using a flexible unstructured mesh, conserving mass of all modeled components and adapting flexible coordinates in the vertical direction. Both models were verified in previous studies by comparing simulations with data measured either from a physical model or field work (He et al. 2006, He et al. 2008). Star CD was mainly used in the second year of study (2006/2007) to simulate flow conditions in the pond under various inflow rates and inlet configurations. MIKE 3 was adopted in the third year of study (2007/2008) to investigate the mud transport in the pond under measured meteorological data and given information of inflow rates and mud concentration at inlet. The simulation would provide information on flow residency times, flow pattern and the fate of sediment within the pond. In the mud transport simulations, the pond was divided as 1054 small cells in the horizontal plane and 10 evenly distributed layers in the vertical direction; the model calculated average mud concentration in each individual 3 dimensional cell at every time step.

Results and Discussion

Flows, TSS and Chemistry - Climatic issues and high water extraction rates from the East Stormwater pond resulted in there being no outflow from the pond for the majority of the year. While unusual, certainly minimizing the number of outflow events from the pond by extraction is one possible best management practice (BMP) that the Region should consider. By removing water for dust control and spraying it on the road, the Region is essentially also removing contaminants and using the buffer strips of the road edges for the bio-uptake of any pollutants present within the pond water wash. Alternatively, however, this practice may also have detrimental impacts to the downstream aquatic communities as the outlet of the pond is a feeder tributary of the Oakville, Sixteen Mile Creek. The Region would need to evaluate in conjunction with stakeholders the best options in this scenario.

Early in the sampling year, however, some inflow storm events were captured in which outflow did occur from the pond. In these cases, the pond performed as expected/designed, showing a reduction in TSS by one to three orders of magnitude (Figure 9). From these few events, it appears that for the given flows, the pond has a residency time of approximately 6 hours as is evident by the time differences between the peak TSS of the inflow and the outflow. Given the significant loss in TSS, and the modeling results (see below), it is evident that this time is sufficient for the settling out of sediment, although as discussed below, other BMPs could be employed by the Region to improve residency time and sediment/contaminant removal.

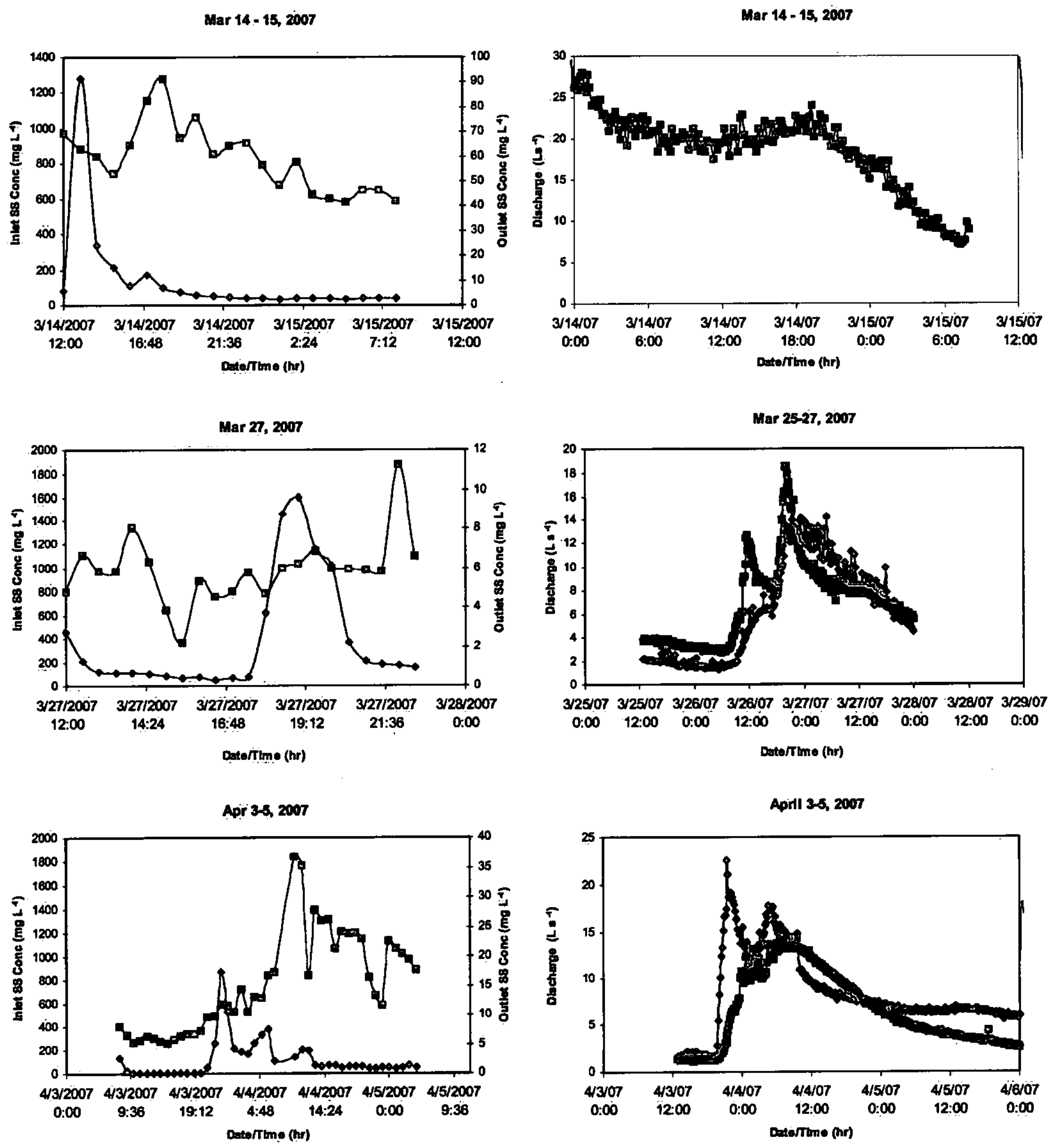


Figure 9 – Changes in TSS between the inlet (Red) and outlet (Green) of the pond for three different storms. Note that there is a lag time of approximately 6 hours between the peak TSS concentrations. No inlet data for March 14-16 storm due to ice in pipe.

Although there were only two events with chemical analysis on the outflow, it is evident that the pond also functioned well on these few storm events in terms of total metal concentration reduction (Table 3a). With the removal of suspended sediment there is a concomitant reduction in the total metals concentration leaving the pond. Note also that all inlet total metal concentrations (Table 3a) were above the Canadian Water Quality Guidelines for the Protection of Aquatic Life (CCME, 2007), however the outlet samples have concentrations below the guidelines for Pb and Zn. Once again, our confidence in these values is low given that they are based only on 2 samples. In addition, the sample taken on April 3, 2007 had high values relative to the sample on March 29th even though the storms generated flows of similar magnitude (Figure 9). It is evident that more sampling would need to be done to obtain a statistically significant data base. The poor reduction in dissolved metals (Table 3b) for the two storms is not surprising as its concentration is independent of the sediment fraction and as such settling of sediment will have little influence on the dissolved fraction concentration [note, with the exception of an anomaly for Cu, the total (whole water sample with dissolved and particulate matter) concentration is higher than the dissolved analysis].

Table 3a. Total (whole water sample) metals from composite samples at inlet (In – n=8) and outlet (Out – n=2). Note Canadian Water Quality Guidelines for the Protection of Aquatic Life - Cd 0.017 μg L^{-1}, Cu 2-4 μg L^{-1}, Fe 300 μg L^{-1}, Mn no guidelines, Pb 1-7 μg L^{-1} and Zn 30 μg L^{-1}.

	Cd In	Cd Out	Cu In	Cu Out	Fe In	Fe Out	Mn In	Mn Out	Pb In	Pb Out	Zn In	Zn Out
Mar29/07	0.577	ND	33.1	4.17	16400	340	496	194	13.2	2.93	132	13.0
Apr3/07	0.291	0.103	71.0	60.0	12300	990	400	257	9.04	3.60	87.2	43.2
May16/07	0.379	-	24.7	-	4410	-	176	-	ND	-	90.8	-
May27/07	0.637	-	71.5	-	6100	-	391	-	3.64	-	81.0	-
Jun5/07	1.71	-	54.3	-	34000	-	923	-	20.6	-	210	-
Jun12/07	0.648	-	38.6	-	20700	-	518	-	8.16	-	154	-
Jun19/07	1.01	-	83.3	-	54900	-	1130	-	24.9	-	224	-
Aug7/07	0.621	-	35.6	-	15700	-	320	-	9.38	-	116	-
Mean	**0.734**	**0.051**	**51.5**	**32.1**	**20564**	**665**	**544**	**226**	**11.1**	**3.27**	**137**	**28.1**
SD +/-	**0.45**	**0.07**	**21.6**	**39.5**	**16643**	**460**	**321**	**44.5**	**8.28**	**0.47**	**55.2**	**21.4**

Table 3b. Dissolved phase of metals from composite samples at inlet (In – n=8) and outlet (Out – n=2). Note no guidelines available for dissolved phase.

	Cd In	Cd Out	Cu In	Cu Out	Fe In	Fe Out	Mn In	Mn Out	Pb In	Pb Out	Zn In	Zn Out
Mar29/07	ND	0	21.3	7.77	1.37	0	70.7	178	2.62	3.12	26.2	12.0
Apr3/07	ND	ND	32.3	31.3	19.7	29.7	43.5	161	2.51	1.89	17.0	38.3
May16/07	ND	-	18.9	-	69.0	-	55.8	-	ND	-	44.1	-
May27/07	0.254	-	19.2	-	38.4	-	138	-	0.716	-	53.7	-
Jun5/07	ND	-	11.8	-	44.3	-	178	-	1.95	-	38.6	-
Jun12/07	ND	-	29.3	-	40.2	-	91.7	-	1.58	-	115	-
Jun19/07	0.033	-	10.5	-	7.70	-	95.4	-	1.92	-	12.0	-
Aug7/07	ND	-	17.7	-	ND	-	77.7	-	3.10	-	28.4	-

Mean	0.036	0	20.5	19.5	27.6	14.9	93.9	170	1.80	2.51	41.9	25.2
SD +/-	0.089		8.14	16.6	24.4	21.0	44.4	12.0	1.03	0.870	32.6	18.6

Although sample numbers were low, loads of metals (g day^{-1}) were calculated to provide some insight into the levels of metals entering and leaving the pond. For the two events in which inlet and outlet samples were obtained, the pond was successful in reducing the loading of metals to the down stream creek often by an order of magnitude (Table 4). No inlet sample was obtained for the March 13-16 flow event as the flow sensors were iced up in the culvert. The loadings for this initial event of the spring melt had the highest loadings (with the exception of Cu). This is not surprising given that this will be the "first flush" of the year for surface wash off and as such, suspended solids concentrations were at a high level (Figure 9).

Table 4. Mean discharge and loading values for the duration of the storm events for both the inlet and outlet. Note that outlet volumes and loadings are based on the flow duration of the inlet.

	Outlet Loading Mar. 13-16 (g day^{-1})	Inlet Loading Mar. 26-29 (g day^{-1})	Outlet Loading Mar. 26-29 (g day^{-1})	% reduction	Inlet Loading Apr. 3-6 (g day^{-1})	Outlet Loading Apr. 3-6 (g day^{-1})	% reduction
Cd	0.03	0.32	0.02	93.8	0.39	0.02	94.9
Cu	20.0	22.2	13.9	37.4	27.2	13.2	51.5
Fe	415.2	8884	287	96.8	10878	274	97.5
Mn	141.1	235.0	97.6	58.5	287.8	93.2	67.6
Pb	2.0	4.8	1.4	70.8	5.9	1.3	78.0
Zn	17.5	59.2	12.1	79.6	72.5	11.6	84.0

On two occasions, there was enough suspended sediment within the inflow samples to do direct metal analysis on the sediment fraction entering the pond. Table 5 shows that in both cases all metals with the exception of Pb associated directly with the suspended sediment were below the severe effects level for the protection of aquatic sediment quality (MOEE, 1993). This is the level at which the use of sediments by benthic organisms will be significantly affected. This is a slightly worse case than from the 2006/2007 results (Appendix B), however, such results will be seasonally and storm dependent. Further, unfortunately with the lack of storm flow and therefore samples for the 2007/2008 sampling season, it is evident that more work would need to be done to fully characterize the chemical dynamics of the East Stormwater Pond. Nonetheless, it is clear that trends point to the pond functioning in an appropriate manner.

Table 5. Mean total metals concentrations compared to MOEE guidelines (n=3).

Metal	LEL (µg g^{-1})	SEL (µg g^{-1})	Total Concentration June 5, 2007 (µg g^{-1})	Total Concentration June 19, 2007 (µg g^{-1})	Mean Total Concentration (n=2) (µg g^{-1})	Stand. Deviation (µg g^{-1})
Cd	0.6	10	2.11	2.00	**2.06**	± 0.078
Cu	16	110	61.1			
Fe	20000	40000	38700	37800	**38250**	± 636
Mn	460	1100	715	618	**667**	± 68.6
Pb	31	250	19.1	13.8	**16.5**	± 3.75
Zn	120	820	213	147	**180**	± 46.7

Sediment dynamics

The primary focus for the 2007/2008 research year was on the REE experiments. These experiments were used to assess the efficiency of the pond and to determine those areas of the pond which are most and least effective in the removal of sediments. The results were also used to validate a mathematical model of the pond circulation and sediment removal spatial distribution.

Toxicity Testing – The results of the toxicity tests provided confidence that Ho could be released at the experimental concentrations without any harmful effects on the pond or downstream biota. Overall, only the 100% Ho-clay treatment resulted in significantly higher toxicity than the reference sediment. Mean survival at the end of the exposures to 100% Ho-clay was 7, 53, 2 and 100% for Chironomus, Hexagenia, Hyalella and Tubifex, respectively. Exposure to a negative control treatment of 100% clay resulted in minor reductions in growth, but no lethal responses. Highest concentrations of Ho at which no toxicity was observed were 1400 µg/g for sediment and 11 µg/L for water. Potential impacts of Ho-clay released into natural waters would be expected only where Ho-clay persists in sediment at proportions >50% for at least several days. As such, given the level of Ho-clay introduced into the pond was substantially less than 50%, no toxicological effects were anticipated from this experiment. More information and discussion on the toxicology study can be found in Appendix C.

<u>REE Experiment</u>: *Floc Characteristics and Behaviour* – For the REE experiments to be meaningful, it was critical that the Ho infused clay/pond sediment particles behave in every way like natural pond sediment. To determine if this was the case, floc size and structure, settling velocity, density and porosity were compared between natural pond sediment and the Ho infused clay/pond sediment. While the sediment containing Ho visually appeared the same, it generally had a smaller size distribution with fewer larger flocs formed (Figure 11 a and b). Regardless, the behaviour (settling) of the flocs was very similar with no significant difference between the slopes of the regression line (t-test, p=0.05) and greater than 80% of the variance explained. The Ho flocs were slightly denser (Figure 11d) than the control flocs (no Ho) (Figure 11c) but were uncharacteristically slightly more porous (Figure 11e and f). Regardless, the fact that the particles were transported in a similar fashion suggests that we can be confident that they behave similar to the natural sediments entering the pond. The smaller particles of the Ho clay are likely, however, to travel farther which would suggest that our experiment and modeling is representative of a worst case scenario for the pond operation.

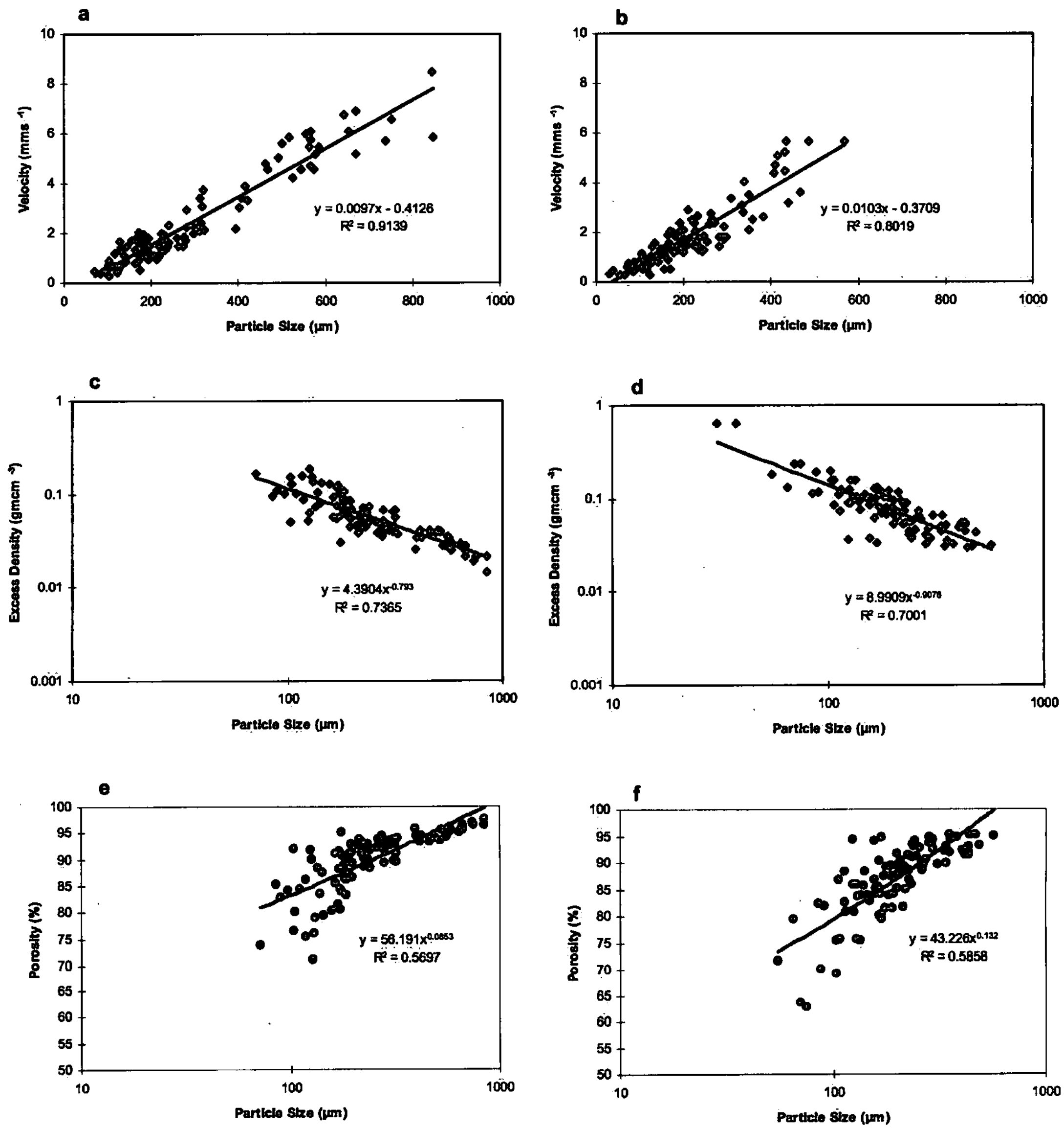


Figure 11. Example settling velocity, excess density (density – density of water) and porosity for runs done with no REE (a, c and e - October 10 – only pond bottom sediment deployed into pond) and with REE (b, d and f - October 12).

REE Experiment: *REE Injection observations* - Figure 12 shows the Ho-clay and pond sediment plume during its deployment on October 12. The plume, as delineated by the brown sediment colour and surface floats, initially had a northeast directional flow followed by a due east flow. Once the plume reached point A on Figure 12, it was observed to move around the shore in a southerly direction. During the REE injection, water samples were collected to assess the change in Ho samples with changes in suspended solid concentration. Figure 13 shows that although the tanker truck flush was approximately 30 minutes the sediment slurry was injected over a 10 minute interval. During this time the TSS reached 1300 mg L^{-1}. As sediment loading increased, so too did the Ho concentrations, reaching a maximum of approximately 2200 µg L^{-1}. As concentrations declined, so too did the Ho concentration. The plume was allowed to disperse/settle for 7 full days following the injection.

Figure 12. Image of the Ho-clay and pond sediment plume, October 12, 2008. Arrows show plume dispersion directions during and after the time of photo. Image also shows the ADCP (OBS is located on the leg of the tripod closes to the plume).

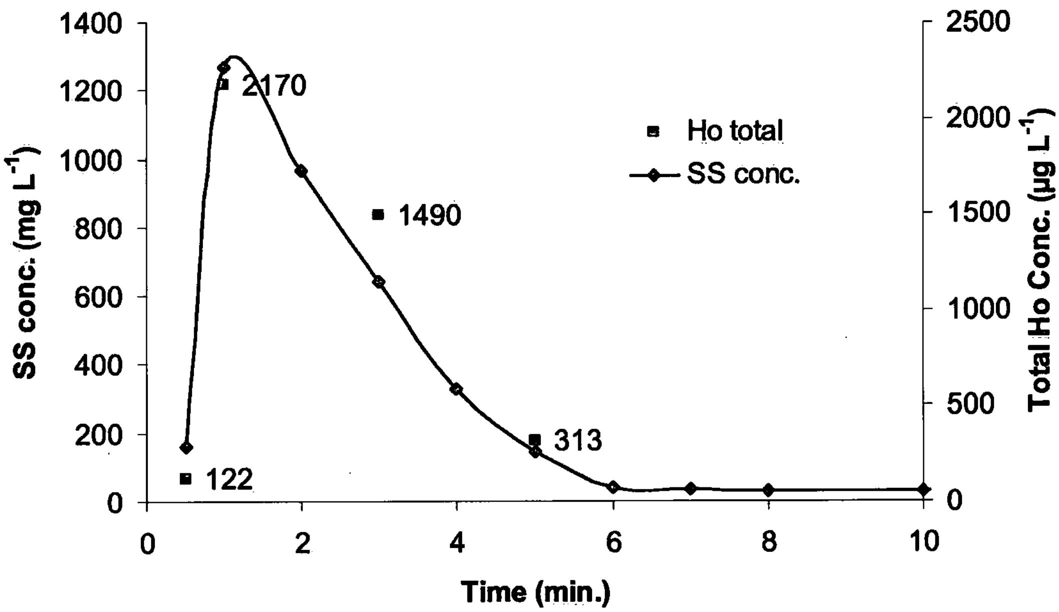


Figure 13. Pollutograph of suspended solid and total Ho concentrations (whole water samples) with time during injection of slurry into flume at the pond inlet.

REE concentrations - Following the 7 days, sampling commenced with the collection of close to 80 sediment samples (reed bed, shore line and bed sediment). Note that Ho concentrations were very low or not detected in sediment samples taken before REE injection (see Appendix C, Toxicity report on Holmium).

Reed Bed Holmium - While Ho was found in the reed bed (Table 6), the effectiveness of the reeds is marginal to negligible in terms of improving sediment removal during low water periods such as in the summer of 2007. This is primarily related to the reed bed being entirely out of the water providing only limited trapping capacity during the overland flow generated by the tanker truck. There is, however, an increase in concentration from the culvert to the pond suggesting a cumulative trapping in the terrestrial reed bed. Reed beds can be an effective BMP as they slow the water flow down and thus allow for sediment deposition, removing associated contaminants from the water column. In addition the reed will provide for some dissolved contaminant removal through the uptake of the plants and root systems themselves (e.g., see Cardwell et al., 2002). An expansion of the reed bed at the inlet would therefore provide some benefit in the effective operation of the pond. Further, reed bed plantings at the outfall of the pond would also provide further "filtering" of the sediments prior to discharge to the downstream creek.

Table 6. Ho concentrations from 3 reed bed samples collected after the artificial storm flow finished.

	Ho Concentration $\mu g\ g^{-1}$
Reed Bed – Close to Culvert	1.10
Reed Bed –Middle	1.72
Reed Bed – Close to Pond Water	3.71

Every sediment sample taken in the pond (shore and surface core samples) contained Ho above detection limit (See Appendix D). Figure 14 provides the spatial interpolation of the Ho concentrations and, as expected, the concentrations were highest close to the inlet and extended out in the direction that the plume was visually observed. While concentrations are low (<1 $\mu g\ g^{-1}$) in the majority of the pond, the fact that Holmium was found throughout suggests that, with the flow and climactic conditions over the 7 day period, that the entire pond did contribute to the removal of sediments. In this regard then, the pond is behaving as it should with the majority of sediments and contaminants removed quickly near the inlet and only small amounts (likely finer sediments) are dissipating into the pond where further deposition occurs as facilitated by the process of flocculation (Droppo 2004).

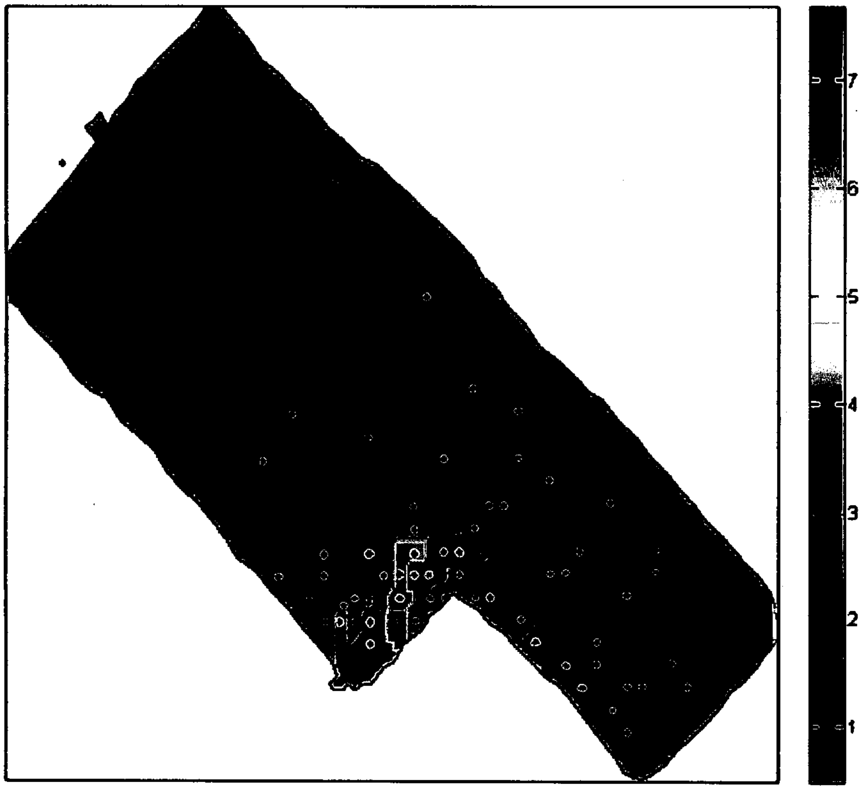
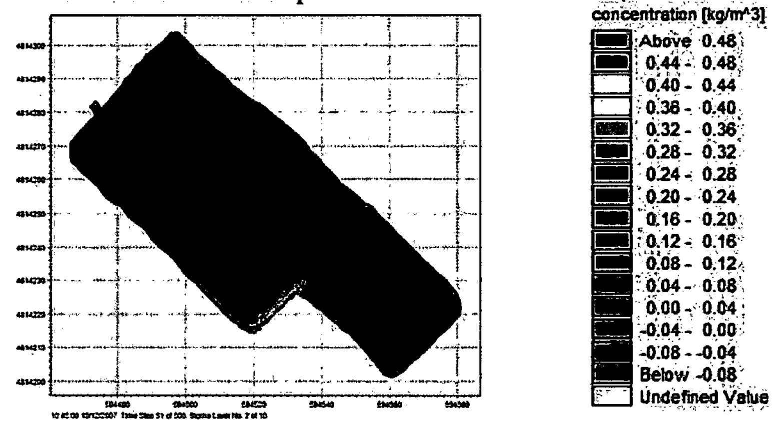


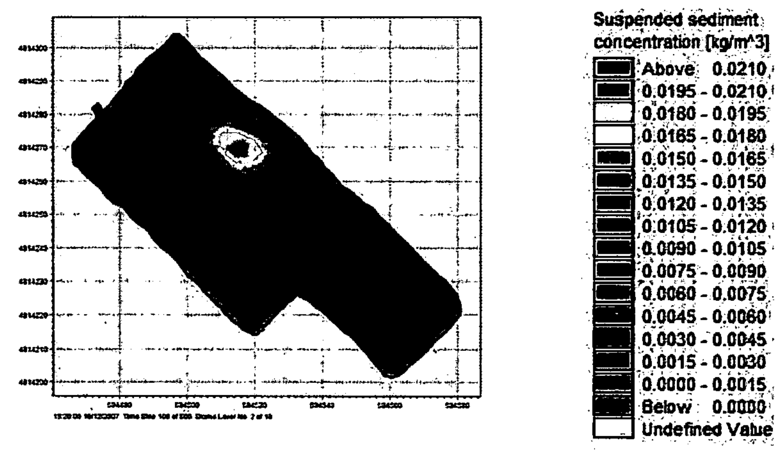
Figure 14. Spatial interpolation of Ho distribution within the pond based on measured core samples taken 7 days following injection (scale in $\mu g\ g^{-1}$).

Model Predictions of REE Sediment Distribution - Figure 15 provides three selected time steps from the model for the bottom most layer (average 10 cm off the bottom). This layer is assumed to represent proportional depositional areas within the pond. As with the actual data (Figure 14), Figure 15 illustrates that the entire pond did contribute to the removal of the REE. This agreement serves as an important validation of the model. Unlike Figure 14, the model result figures allow for a temporal evolution/interpretation of the transport and deposition of the REE sediment. In this regard the model shows that the greatest proportion of sediment removed from the pond water column took place close to the inlet during the initial phases of the simulation (Figure 15a). The ever decreasing peak level of suspended solid concentration (note progressive reduction in sediment concentration values with figures) with time and transport duration, migrate out towards the outlet (Figure 15b and c). The final time step (Figure 15c), although with very low concentrations of sediment, shows a secondary "hot spot" near the inlet again possibly due to the recirculating nature of the pond with no outlet flow. Also the simulated flow lines of Figure 16 (although this is representative of a flow rate 10 times higher than during the REE deployment – from Appendix B report) show that there is a recirculation within the zone of the inlet that may result in a "trapping" of sediments within a vortex of sorts at this location (this effect is likely to be more prominent at lower flows such as that in the simulations). Regardless, the figures show the effective migration of REE sediments throughout the pond at depth.

a 10:45 10/12/07– Time step #51



b 15:20 10/12/07 – Time step #106



c 0:10 10/14/07 – Time step #500

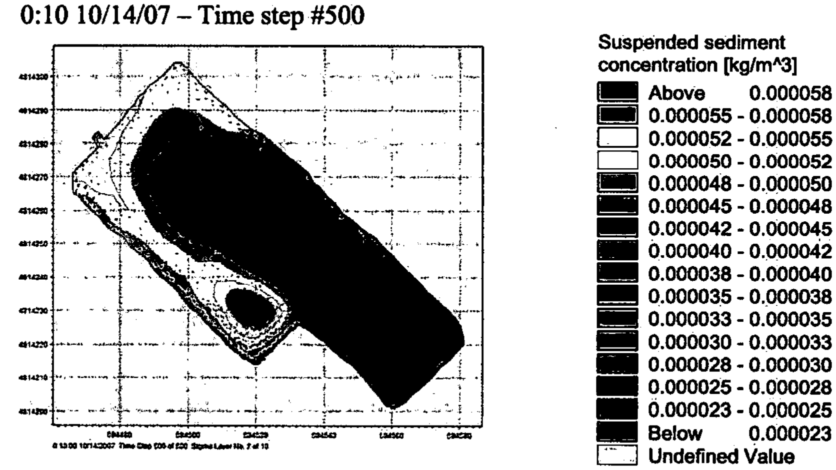


Figure 15. Selected model outputs for 3 time steps over a 2 day period for the bottom most simulation layer (10cm from bottom of pond).

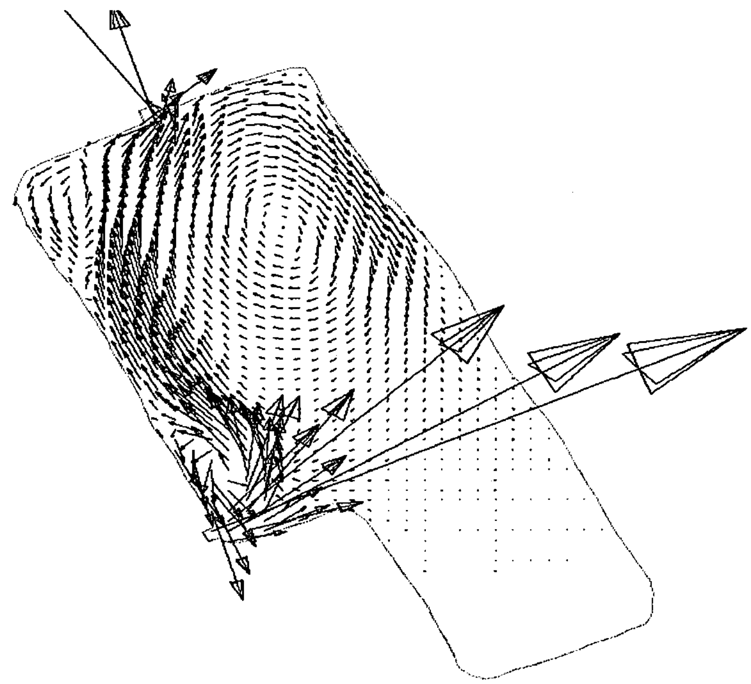
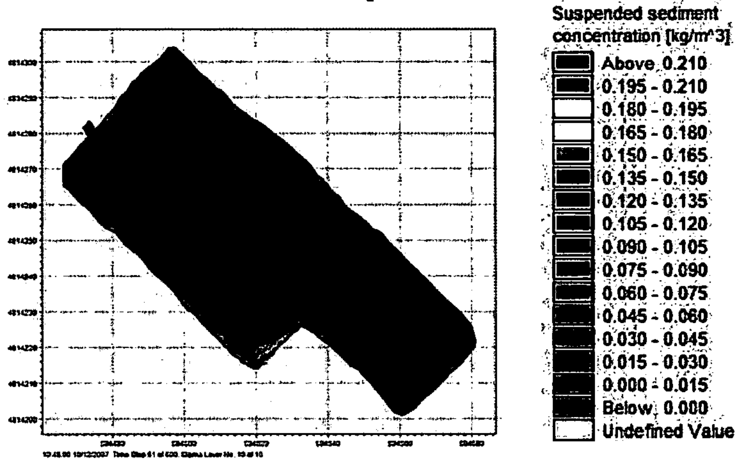


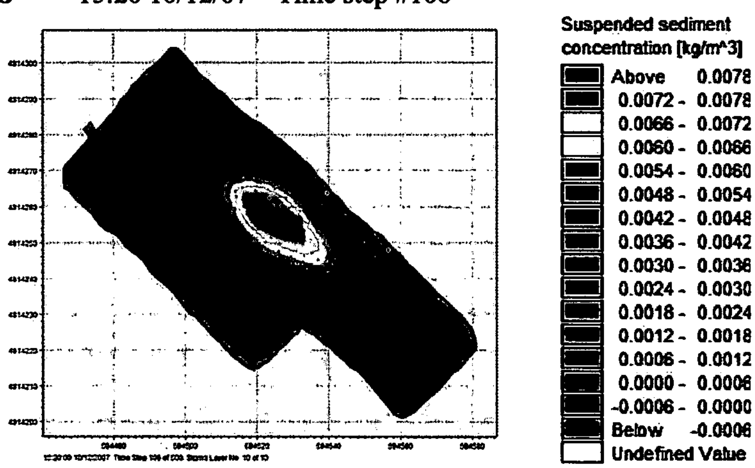
Figure 16. The simulated velocity field in the Halton East Pond with plants right in front of the inlet pipe (flow velocity = 1 $m\ s^{-1}$; flow rate = 1.2 $m^3\ s^{-1}$).

While Figure 15 illustrates the simulated results for the bottom layer, Figure 17 provides the results for the surface layer (10cm below the surface). Here we see the influence of the wind on the surface sediment concentration as the highest sediment concentrations are always further ahead than those at the corresponding time step in the bottom simulation layer (Figure 15). This is particularly evident in Figure 17b, where a "tail" trailing southward from the higher concentration zone has migrated to the north in the pond. This "tail" of the plume was visually observed and validated with the float markers. Notice that for the same time step the highest concentration for the lower layer (Figure 15b) is slightly more north with no tail such as that in Figure 17. This shows the dynamic nature of the sediment transport due to different flow conditions in the surface and bottom layers in this three dimensional model. Had there been an outflow at the time of the simulation, this "drawing" flow would have no doubt had some impact on the distribution of the sediment.

a 10:45 10/12/07– Time step #51



b 15:20 10/12/07 – Time step #106



c 00:10 10/14/07 – Time step #500

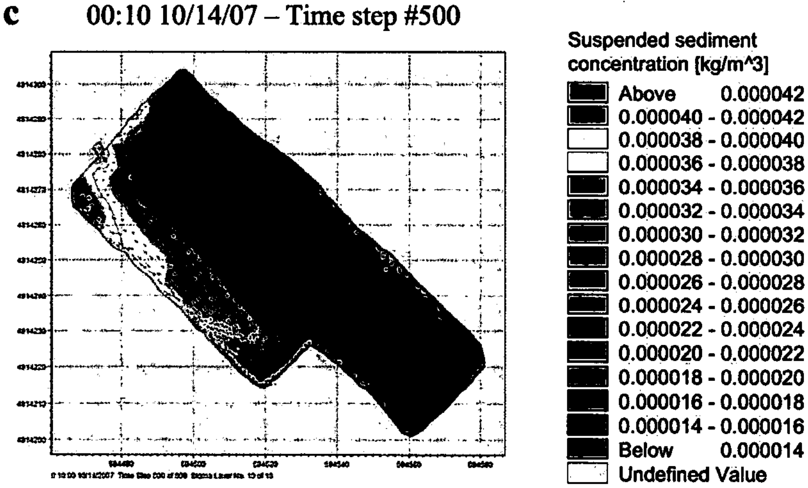


Figure 17. Selected model outputs for 3 time steps over a 2 day period 10 cm below the surface of the pond.

Possible BMPs for the East Stormwater Pond

The following discussion of possible BMPs for the pond is presented for information only; the Region may wish to pursue these ideas further with a follow-up engineering feasibility study.

Over this three year study, it can be concluded that the East stormwater pond is providing a level of reduced suspended solids concentrations and associated contaminants and that all areas of the pond are contributing to its operation, although not equally (as seen in Figures 15 and 16). It is evident, however, that this reduction in contaminants is strictly related to the geometry of the pond and not due to other applied BMPs.

Pond geometrical features that affect pollutant removal performance and effluent water quality are well documented (US DOT, 2002) and include: residence time (length-to-width ratio), the depth of the permanent pool, the total depth and the presence and design of a sediment forebay. The residence time in a stormwater pond influences the overall pollutant removal performance. To achieve an adequate residence time, it is generally supported that the length-to-width ratio should be maximized (minimum 3:1, although 4 or 5:1 preferred), while short-circuiting should be avoided (OMOE, 2003). From the sediment transport modeling as related to the REE deployment (Figures 15 and 17) it is evident that the entire pond does have some sediment carrying flow capacity even though the pond depth at the time of experimentation was well below optimal (a mean depth of 1-2 m is suggested – OMOE, 2003). It is worth noting again, that the depth at the time of experimentation (0.7m) was unusual and that the east stormwater pond does generally meet the above suggested depths. By maintaining an optimal depth of 1-2m, resuspension and outlet blockage is minimized, while an extended settling depth and time is provided. This optimal depth should be heeded by the Region for the next time the pond is dredged as very high depths can lead to anoxic conditions which can result in the release of metals and organics from the sediment into the dissolved phases (OMOE, 2003).

While the pond geometry seems adequate based on the results presented in this report, there are some options that the Region may wish to consider to improve the overall performance of the East stormwater pond. A common method for the increase of detention time is the use of berms (OMOE, 2003), which redirect flow and effectively lengthen the flow path between inlet and outlet Berms can be "hard" installations (retaining walls, earth embankments) or as simple as polyethylene sheeting tied off on stakes driven into the pond bottom to channel the flow back and forth to the outlet. Earthen berms may also be vegetated to allow some filtration of the stormwater. The drawback of such an installation is the potential high cost (depending on design), increased land consumption (or reduced pond volume when retrofitting an existing pond), maintenance requirements and aesthetic impacts. Such issues would need to be taken into account by the operator and stakeholders.

An additional common tool to improve solids removal in a stormwater pond is to install a sediment forebay which serves as a pre-treatment zone, improving pollutant removal by trapping larger solids near the inlet of the pond and facilitating maintenance by providing easy access to a smaller area for maintenance equipment. A sediment forebay consists of a smaller, fairly deep, discrete cell, which is separated from the rest of the pond by an appropriate barrier, such as an earthen berm or concrete wall (Centre for Watershed Protection, 2003) Given the small size of the East stormwater pond, this may not be an appropriate addition to the pond. Alternative solids removal methods already in use at the site, such as filtration through hay bales and geotextile or fabric filter cloth in the ditch leading into the pond, may also make such a forebay unnecessary, as coarse solids are likely removed through such processes. These filtration processes do, however, require regular maintenance to avoid clogging.

While increasing the trapping efficiency of the pond perimeter with additional grasses and plantings (e.g., grassed swale) can be an effective way of reducing sediment loading (OMOE, 2003), in the case of the East stormwater pond, this is unlikely to be a cost effective measure given the dominance of the inlet for sediment supply and minimal direct overland flow observed. However, it is suggested that increasing the growth of aquatic vegetation within the pond will enhance filtration (by reducing flow velocities) and will increase metals and nutrient uptake. The OMOE Stormwater Management Planning and Design Manual (OMOE, 2003) provides a list of species of trees, shrubs, vines and herbaceous materials which are appropriate for use at various depths in stormwater ponds and wetlands. Additional plantings, particularly at the inlet and outlet ends of the pond, may further improve sediment, metals and nutrient removal in the East stormwater pond. This proves itself to be a relatively inexpensive option with the only drawbacks being the possible increased maintenance time due to the need to remove wind blown debris from within the vegetated area (which is minimized by the fencing surrounding the pond), and some impact on the ease of dredging the pond.

Conclusion

Over the three year study, a significant amount of monitoring, modeling and experimentation has taken place which all suggests that the pond does result in a substantial reduction in the suspended sediment and metal loading to the downstream environment. Work with a rare earth element (Holmium) provided broad agreement with the modeling results as pertaining to the pond's ability to remove fine cohesive sediments and associated contaminants (it should be noted that the holmium did not exhibit any significant toxicity at the concentrations used in this study). Results showed that the entire pond did contribute (although disproportionately) to the removal of sediment entering the pond at the inlet. The reed bed, as it stands, provides minimal assistance in removing sediments. It is suggested that further macrophyte plantings within the pond at the inlet and outlet would be the most suitable and cost effective BMP to improve pond performance and effluent water quality. Geotextile covers/filters over the inlet pipes and hay bales on the ditch side of the road should be maintained as a "first order" of defense against sediment entering the pond. A depth of between 1 and 2 m should always be maintained by the Region and should be accounted for during any future dredging operations in the pond. The current regime of water extraction for dust control is also indirectly a useful management operation. If the pond can be maintained within the above optimal depth but with no outflow then an added storage capacity is utilized with only outflow occurring when this is exceeded. No flow to the receiving stream could, however, have detrimental wildlife effects that must be considered. Other BMP options are provided and could prove useful should sufficient funding be available.

Acknowledgements

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Appendix B

1st Year Technical Report (AEMRB-TN05-007)

Halton Waste Management Site East Stormwater Pond
Particle characterization and flocculant addition results update

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Preamble

The East Pond surface water (stormwater) pond at the Halton Waste Management Site collects surface runoff from roads and a capped section of the landfill. Samples from the East Pond are occasionally high in concentrations of certain metals. It has been suggested that this relates to poorly settled suspended solids in the pond, and that addition of a flocculant to the pond could improve solids settleability, thereby improving removal of associated metals. A flocculant of unknown composition, United 228 Flocculant Concentrate, has been supplied to municipality staff. The efficiency of this flocculant, in terms of improving solids aggregation and settling, could depend on the method of addition. In particular, the efficiency of flocculants is often dependent on the mixing provided during addition. No such mixing mechanism is available for the stormwater pond at this point and according to site staff, surface application is the intended method of distribution. Jar tests were conducted at NWRI using pond water to evaluate the effect of mixing on flocculation with United 228 or another polymer. Characteristics of the primary particles and flocs in the pond, such as size, settling velocity, and porosity, were also studied. The results of these tests will assist the site operators in determining further courses of action.

Bassin Est de rétention des eaux pluviales – site de gestion des déchets de Halton Caractérisation des particules et ajout de floculant – mise à jour des résultats

Ian G. Droppo et Kirsten Exall

Préambule

Le bassin Est de rétention des eaux de surface (eaux pluviales) au site de gestion des déchets de Halton recueille le ruissellement des routes et d'une section recouverte du site d'enfouissement. Des échantillons provenant du bassin Est présentent parfois des concentrations élevées de certains métaux. Il a été avancé que cet état de choses est lié à la présence dans le bassin de solides en suspension mal décantés, et que l'ajout d'un floculant pourrait y améliorer la décantabilité des solides, ce qui aiderait à en enlever les métaux associés. Un floculant de composition inconnue, appelé *United 228 Flocculant Concentrate*, a été fourni au personnel de la municipalité. L'efficacité de ce floculant, pour ce qui d'améliorer l'agrégation et la décantation des solides, pourrait dépendre de la méthode d'ajout. En particulier, l'efficacité des floculants est souvent fonction du degré de mélange assuré pendant l'ajout. On ne dispose pas actuellement de mécanisme de mélange pour le bassin de rétention et, selon le personne du site, c'est l'application en surface qui est la méthode de distribution prévue. Des essais de floculation ont donc été menés à l'INRE sur l'eau du bassin, pour évaluer les effets du mélange sur la floculation, pour le produit United 228 ou un autre polymère. On a également examiné les caractéristiques des particules primaires et des flocs dans le bassin, comme la taille, la vitesse de décantation et la porosité. Les résultats de ces tests aideront les exploitants de site à déterminer les approches à adopter.

Update on results of June 24 sampling

Water samples were collected from near surface and 60 cm depths at locations near the inlet, centre and outlet of the pond on June 24, 2005. According to data from monitoring stations in Toronto, Hamilton, and Oakville, there had not been a significant rainfall (e.g., over 3 mm in a single day) in over a week as of that date. Total suspended solids (TSS) concentrations were measured in duplicate with filters of two pore sizes, 1.2 microns and 0.45 microns; results are shown in Table 1, below. The TSS concentrations were relatively low (averaging ~32 mg/L), varying little at the three locations in the pond and increasing slightly with depth. The higher measured concentrations with the finer pore size filter (0.45 μm) indicate that the suspended solids are quite fine, a fact which is supported by particle size analysis (Table 2). Primary particle sizes (the individual particles) are consistent between sampling sites with d_{50} values around the clay fraction. Effective floc size (aggregate particles suspended within the pond) (Figure 1) were similar at the centre and outlet sampling sites but showed a larger size at the inlet. As there was no influent to the pond, such a difference is possible due to wind generated bed resuspension (prevailing wind was from the outlet to the inlet resulting in a possible accumulation of resuspended sediment close to the inlet and adequate mixing to allow for particle particle interaction and flocculation). The slightly higher concentrations at depth (Table 1) and the reasonable quiescent settling velocities (on average around 1 mm s^{-1}) (Figure 2) may support the possibility of wind resuspension. The flocs suspended within the pond were of a low density and high porosity suggesting high water content. It should, however, be realized that this preliminary analysis is based only on single samples and further work would be required to confirm such a hypothesis.

Table 1: TSS concentrations (in mg/L) at various locations in the East Pond, June 24. 2005

	Surface		60 cm depth	
	1.2 μm filter	0.45 μm filter	1.2 μm filter	0.45 μm filter
Inlet	26	32	32.5	39.5
Centre	27	32	31.5	30
Outlet	27	36	28.5	36

Table 2: Particle size (by volume) of the natural suspended floc (composite particle) and individual primary particles following sonication.

	Median particle size (floc) (μm)	Median particle size (primary particles) (μm)
Inlet	41.2	5.85
Centre	21.0	5.39
Outlet	24.8	5.35

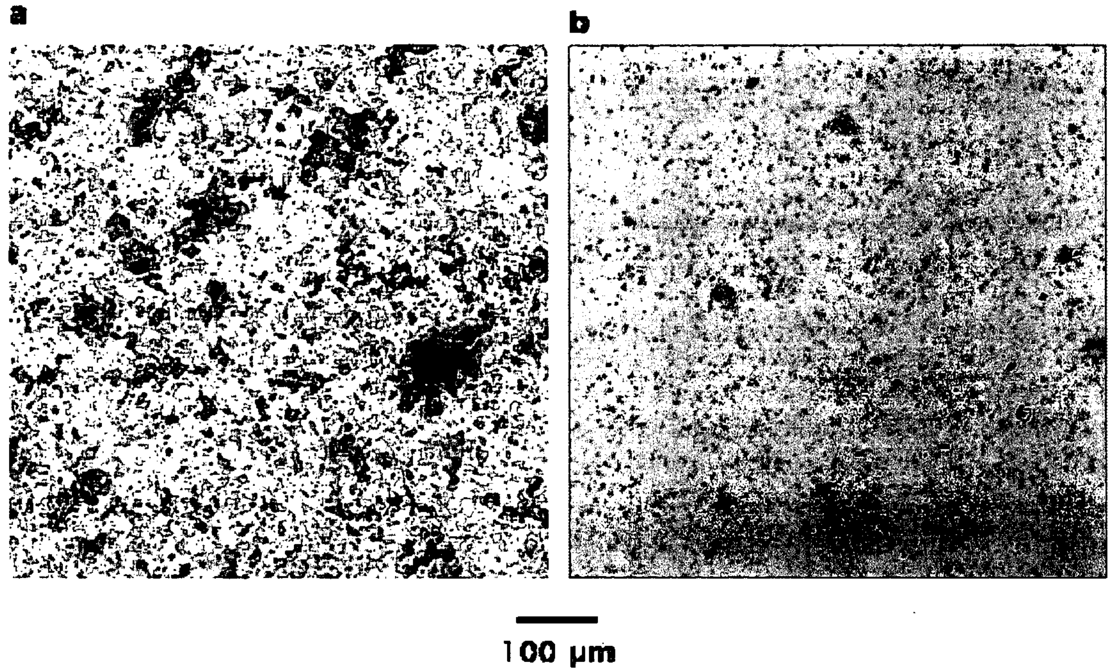


Figure 1: Representative micrographs of a) the effective floc particles, and b) the sonicated primary particles which make up the flocculated particles.

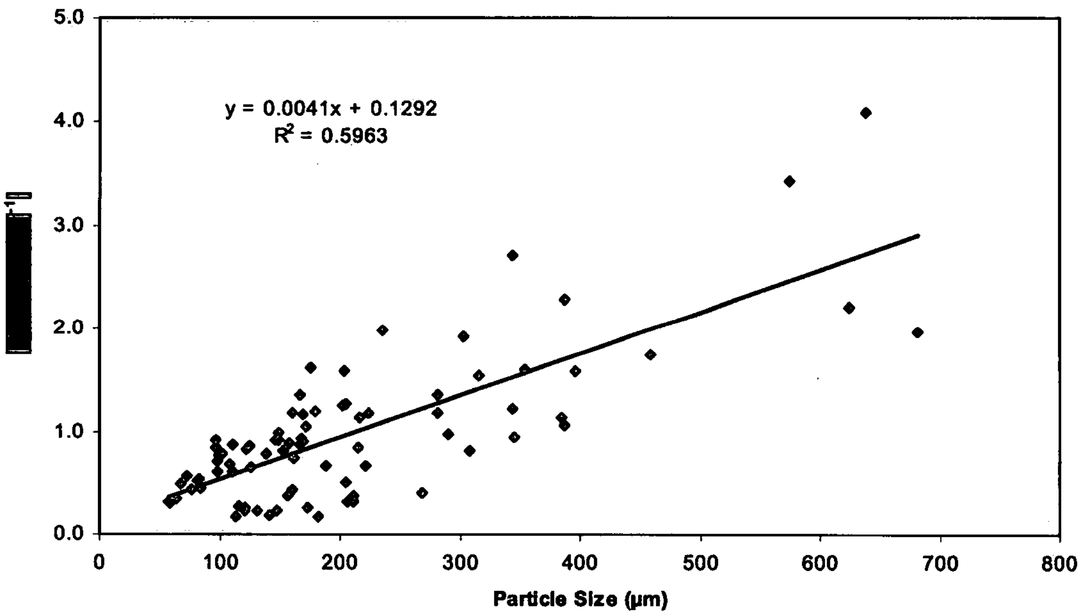
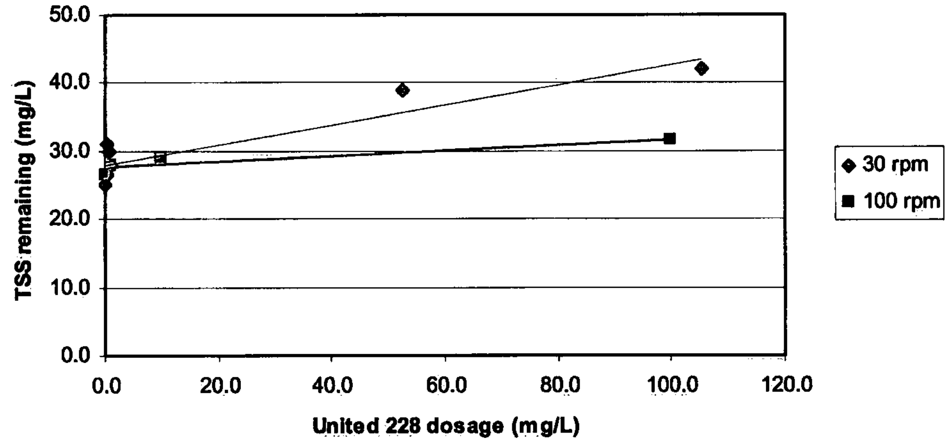


Figure 2: Settling velocity of suspended flocculated sediment collected at all 3 sites (samples combined to provide enough sediment for statistically significant analysis).

Laboratory jar tests with pond water were conducted with United 228 (United Laboratories) and a polyacrylamide flocculant from CIBA Specialty Chemicals, using various conditions of flocculant dosage and mixing. Supplier instructions on the United 228 label suggested a working dosage of approximately 100 mg/L for sewage treatment. In these studies, United 228 was added to a beaker at dosages of 0.1 to ~100 mg/L, mixed with a paddle at 30 rpm or 100 rpm, then left to settle for 20-30 minutes. No dosage of polymer or mixing speed resulted in TSS reductions; in fact, high polymer concentrations resulted in slightly increased TSS concentrations. Similar results were observed with the polyacrylamide at dosages that have been previously applied in treatment of stormwater, 0.2-1 mg/L. At the very low initial TSS levels seen in water of the East Pond, the addition of flocculant has little beneficial effect on suspended solids in the pond, as can be seen in Figure 3 below, regardless of mixing rate. As mixing during polymer addition is generally considered to be the optimal method of application, it can be expected that polymer addition without mixing would be similarly ineffective.



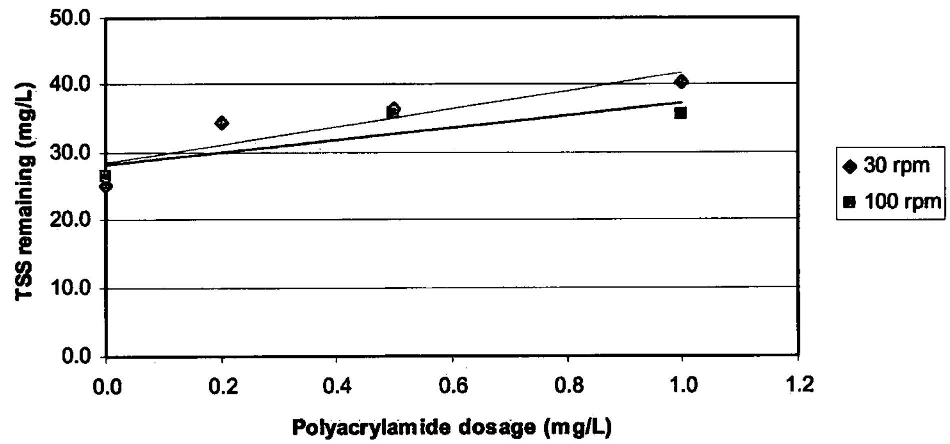


Figure 3. Residual TSS after jar tests with United 228 and polyacrylamide at two mixing speeds.

The addition of polymer may enhance the settling of incoming solids during a storm event when concentrations are higher, or improve the stability of the sediment bed in the pond; however, the hydraulics of the system will need to be better understood to optimize addition of polymer for these purposes. More in-depth analysis of residence time, circulation and turbulence in the pond would be needed. This would entail a more extensive temporal and spatial sampling program in collaboration with the Halton Region. It is important to note that completion of further work would depend on the availability of both NWRI staff time and funds.

Appendix B

2nd year Technical Report (No. AEMRD-TN07-003)

Technical Report on the effectiveness of the Halton Waste Management Site East Stormwater Pond to reduce TSS and associated contaminants

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Introduction

The three year project is designed to assess the existing performance of the East Stormwater Detention Pond (Halton Waste Management Site, Regional Road 25, Milton, Ontario) with respect to sediment and associated contaminant (metals) removal. The collaboration between the Halton Region and NWRI will help in the development of improved water management strategies and treatment technologies.

The first year of the project (2005) was a feasibility study for the project with the results reported in the technical publication; NWRI Technical Note No.AEMRB-TN05-007. Following from this report the second year of the study has provided a better understanding of the flow and sediment dynamics of the pond during wet weather periods and will allowed for a more focused approach for the final year of the project.

To date, field, laboratory physico-chemical analysis, hydrodynamic modelling and laboratory flume experiments have taken place. This report provides information on each of these areas and how they will direct the final year of the study.

Résumé

Ce projet de trois ans a pour objet d'évaluer la performance actuelle du bassin Est de retenue des eaux pluviales (site de gestion des déchets de Halton, route régionale 25, Milton, Ontario) dans l'élimination des sédiments et des contaminants associés (métaux). La collaboration entre la région de Halton et l'INRE facilitera l'élaboration de meilleures stratégies de gestion et technologies de traitement de l'eau. La première année du projet (2005) consistait en une étude de faisabilité du projet, dont les résultats ont été rapportés dans la note technique de l'INRE n° DRGEA-TN05-007. Découlant de ce rapport, la deuxième année de l'étude fournit une meilleure compréhension de la dynamique de l'écoulement et de la dynamique sédimentaire du bassin en périodes humides. Elle nous permettra aussi d'adopter une approche plus dirigée pour l'année finale du projet. Jusqu'à maintenant, des études de terrain, des analyses physicochimiques en laboratoire, des modélisations hydrodynamiques et des expériences de laboratoire menées sur des canaux ont été effectuées. Ce rapport présente de l'information sur chacun de ces aspects et la façon dont ils influeront sur la dernière année de l'étude.

2006 Field Station Set Up and Activity

The Halton East Pond is an open stormwater detention pond with the dimension of 120 m (L) x 50 m (W) and 2 m (D), there is one inlet (2 culverts) and one outlet in the pond as shown in Figure 1.

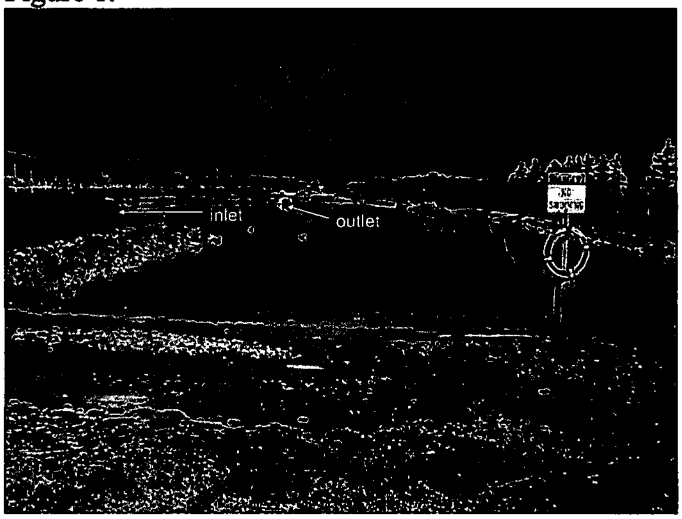

Figure 1. East stormwater detention pond.

Dog houses were set up over the inlet and outlet to house electronic and sampling equipment. An electrical line was run from the Halton Region's pumping station to power the inlet site while a solar panel was used to power the outlet site.

Area Flow Velocity Meters (Sigma 950) were installed within the 200 mm diameter pipe at the outlet of the pond and in the north inlet culvert. The south inlet culvert was blocked off at the up stream end to force all stormwater through the north culvert and allow for an accurate measurement of flow velocity and volume. Observations, however, revealed that the culverts have substantially decayed with water circumventing the blocked end of the south culvert by seeping in through the bottom at a significant rate. As such, inflows for this year are only estimates. Corrective measures will be taken in 2007 to collect accurate flows and will be described below.

An automated sampler (Sigma 900) was also installed within the outlet pipe and north inlet culvert to collect 1 L water samples at equal time intervals. The Sigma water samplers were triggered to initiate sampling once a water level threshold was surpassed. Up to 24 1L samples can be collected for each round of sampling. These samples were analyzed discreetly or in composite as described below.

Laboratory Physico-Chemical Analysis

As the majority of metals will be associated with particulate matter (Horowitz, 1991), sampling focused on the assessment of suspended solids (SS) concentrations over storm events. The rationale for this focus is that if the pond reduces SS concentration from the inlet to the outlet there will be a corresponding reduction in the loading of metals. Total suspended solids (TSS) was measured in discrete one litre samples collected by the autosamplers during rain events.

An initial assessment of a small suite of metals (Cd, Cu, Fe, Mn, Pb and Zn) on a small number of composite samples was carried out in association with SS. Atomic absorption spectroscopy (AAS) was used as the analytical method for the determination of total metals concentration.

Hydrodynamic Modelling

A three dimensional hydrodynamic numerical model (Star CD) was used to simulate flow conditions in the pond under various flow rates and macrophyte placement scenarios. Upon completion this model will be able to assess residency times, and the fate of sediment within the pond.

Laboratory Flume Experiments (Polymer Application Effects)

In the summer of 2006, the Halton Region applied a polymer (United 228 - United Laboratories) to the pond in an attempt to remove solids from the water column. The application of the liquefied polymer was through a surficial broadcasting from the shore line. Given sufficient time the polymer will react with suspended solids and be delivered to the bed of the pond either in association with created flocs, individual particles or on its own. Once delivered to the bed, this polymer may influence the stability of the bed sediment. In the first report by Droppo and Exall (2005), it was hypothesized that wind resuspension may be an issue with the East Stormwater Pond. Mobilization of bed sediment from the pond would be detrimental to its effective operation. Any method that will increase bed sediment stability and thereby minimize erosion and migration of sediments and associated contaminants out of the pond is desirable. As such, the purpose of the laboratory flume experiment was to assess if polymer application can influence bed sediment stability. Three methods of polymer application were examined; 1) broadcasting over the water surface (to simulate the Halton Region protocol), 2) mixing (water column, suspended sediment and polymer are all mixed prior to settling) and 3) injection (deposited bed sediment was injected directly with a polymer). As the properties of the United 228 could not be determined, chitosan was used as a surrogate to investigate these different polymer application techniques and their influence on the stability of the bed.

The flume geometry and operation is described in Lau (1994) and is illustrated in Figure 2a. In short, the bed sediment from the East Stormwater Pond was placed into the flume (Figuer 2b) and water was added. The polymer was added via one of the application methods and then the stability of the bed sediment was evaluated. Stability was assessed by imparting a known shear (via the rotation of the annular flume lid on the surface of the water) onto the bed sediment and determining the point or erosion (critical bed shear stress for erosion). Comparison between polymer applications were assessed as to their ability to stabilize the bed from erosion.

a b

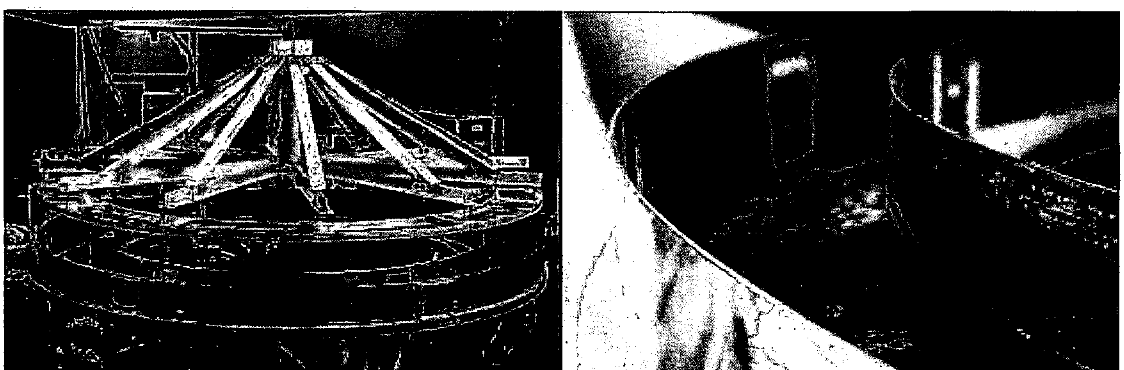

Figure 2 a) Annular flume (2m diameter) used to assess critical bed shear stress for erosion. b) Bed sediment within the flume prior to the addition of water.

Results and Discussion

Pond Efficiency as it relates to Suspended Solid Concentration Removal – Samples were collected from the inlet on five dates between September 19 and October 12. Figure 3 shows an example of the data from samples collected from the inlet pipe during an event in the morning of October 4. As discussed above, the flow values are uncertain due to issues with the equipment and the pipes. For this event, the inlet sampler was programmed to collect one litre every 10 minutes after the threshold level (2 cm) had been reached in the pipe. While TSS concentrations were initially low, an apparent spike in flow resulted in higher TSS values, which tapered off slowly with time.

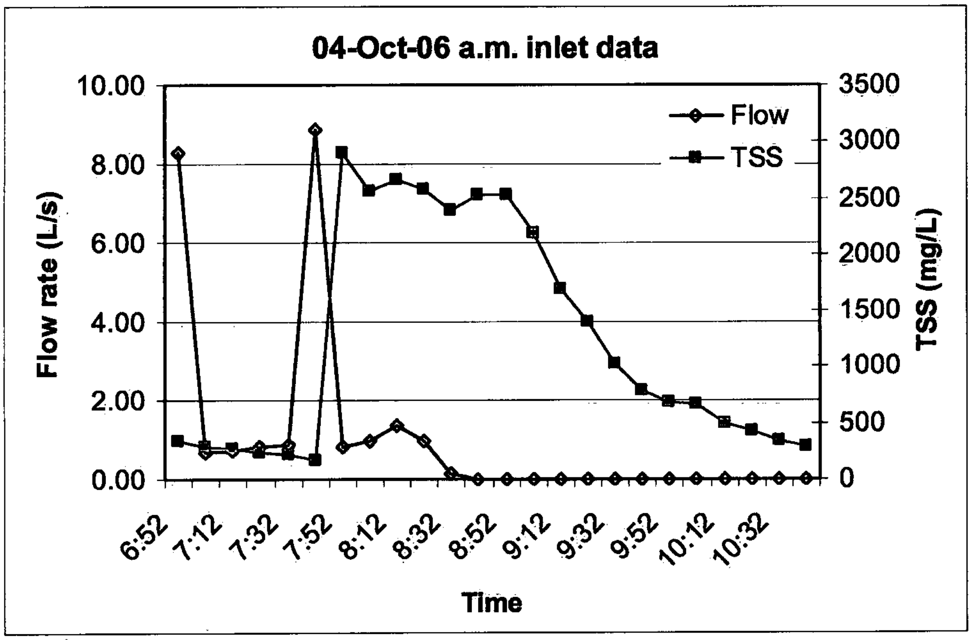

Figure 3. Monitoring data from East Pond inlet during a high solids rain event.

Paired inlet-outlet samples were collected for two events in October 2006. Figure 4a and 4b show an example of the paired data. For this event, both inlet and outlet samplers were programmed to collect one litre every half hour after the level sensor indicated that the threshold level (5 cm) had been reached in the pipe. In spite of apparently wide fluctuations in the flow, TSS values at the inlet remained quite low throughout this event increasing from approximately 50 to 80 mg/L. The data from the outlet also showed low TSS values over the entire sampling period remaining between 50 and 60 mg/L. Over the storm event there is a slight decreasing trend in the TSS data suggesting a removal of TSS by the pond prior to discharge. The increase in TSS observed in the final sample of the outlet (Figure 4b), however, suggests that a longer sampling period may have been more appropriate for this event.

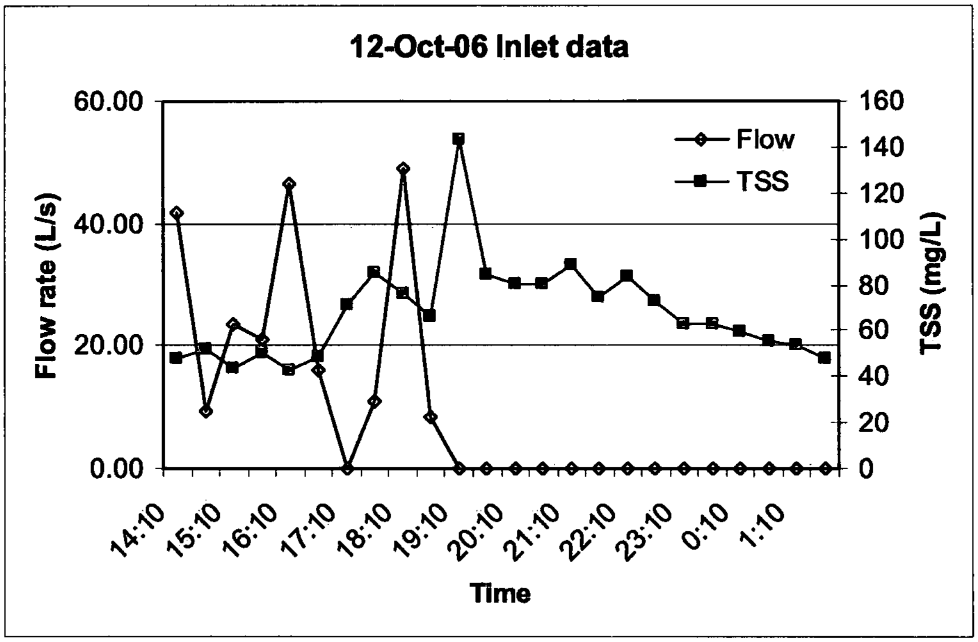

Figure 4a. Monitoring data from East Pond inlet during a high flow, low solids rain event.

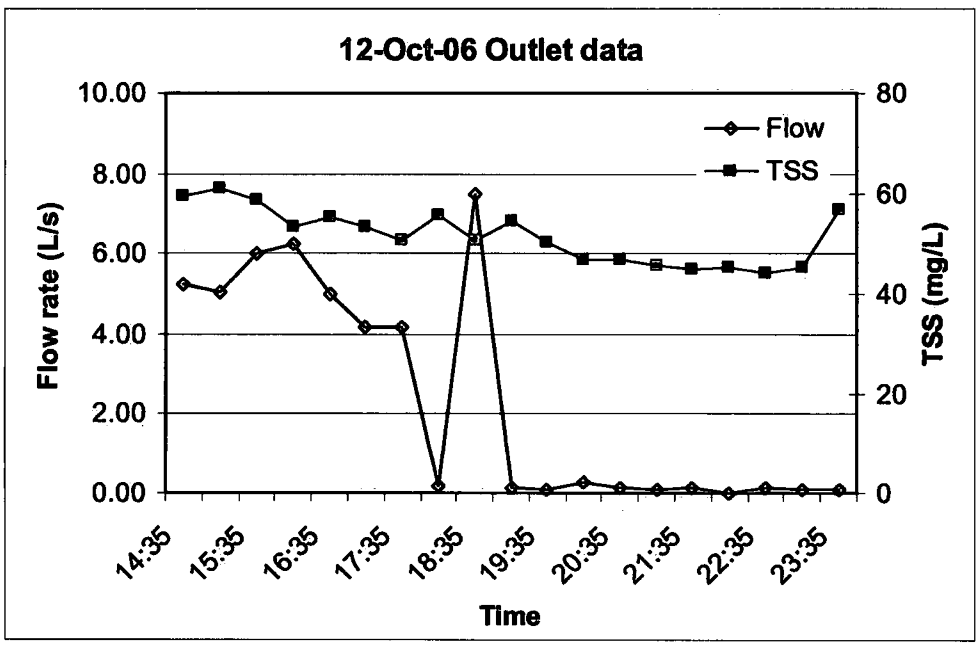

Figure 4b. Monitoring data from East Pond outlet during a high flow, low solids rain event.

Equipment and sampling protocol challenges that arose during the 2006 season will be resolved for monitoring in the 2007 season. The sampling and analysis protocols have been established, faulty equipment has been repaired and recalibrated, and the timing and frequency for inlet and outlet samplers will be further refined to better understand the solids removal efficiency of the pond.

Pond Metal (Cd, Cu, Fe, Mn, Pb, Zn) Concentrations with Inlet Suspended Solids - Metal analysis was carried out on three composite samples collected over two storm events for the inlet sample location only. Unfortunately the outlet sampling system experienced errors which did not allow us to collect a sufficient volume of sample for suspended solid metal concentration analysis. This will be rectified for the following year.

In order to assess the potential impact of the metals entering the detention pond and/or leaving the detention pond on aquatic life, the concentrations were compared to the Guidelines for the Protection and Management of Aquatic Sediment Quality (MOEE, 1993). The guidelines as outlined in Table 1 reflect a gradient of ecotoxic effects and are based on the chronic, long term effects of contaminants on benthic organisms.

Table 1. MOEE Guidelines for the Protection and Management of Aquatic Sediment Quality (MOEE, 1993).

Pollutant Categories	Sediment Quality	Potential Impact
> SEL	Grossly Polluted	Will significantly affect use of sediment by benthic organisms.
> LEL	Marginally-Significantly Polluted	Will affect sediment use by some benthic organisms.
> NEL	Clean-Marginally Polluted	Potential to affect some sensitive use.
< NEL	Clean	No impact on water quality water or benthic organisms anticipated.

SEL = severe effect level, LEL = lowest effect level, and NEL = no effect level.

Four of six suspended sediment metals (Cd, Fe, Pb and Mn) exhibited concentrations that were below the LEL (i.e. considered clean to marginally polluted), suggesting minimal impact on the organisms which live in a sediment environment with these metal concentrations (Table 2). Copper and Zn were between the SEL and the LEL (i.e. marginally to significantly polluted), suggesting a possible chronic effect on organisms (Table 2). The majority of metal levels in Table 2 are within the range or below the levels found for natural rivers and lakes as summarized by Stone and Droppo (1996). Caution must be taken, however, when comparing the results of different studies due to the operationally defined nature of metal extraction. In addition, as with this initial study, metals are expressed as total concentration and do not take into account the binding phase of the metal to the sediment particles. Metals are generally associated with sediments through 1) an exchangeable fraction, 2) bound to carbonates, 3) bound to Fe/Mn oxides, 4) bound to organics and 5) a residual phase. Generally the sequence of extraction (fraction 1 to fraction 4) can be viewed as an inverse scale of the relative availability of metals (i.e. bioavailability) (fraction 5 is considered not available) (Stone and Droppo, 1996). Generally fraction 5 represents a significant proportion of the metal concentration and thus can not pose any significant impact on biota. For example in a study by Droppo et al (2006) on street sediments the total iron concentration was reduced by an order of magnitude from 40,000 μg/g to 4,000 μg/g when only fractions 1 to 4 were accounted for. As such, for the preliminary metals examined in this study, it would appear that there is a limited risk of suspended solid associated metals having a significant impact on biota. Further assessment of this issue, however, is warranted.

Table 2. Mean total metals concentrations compared to MOEE guidelines (n=3).

Metal	LEL ($\mu g\ g^{-1}$)	SEL ($\mu g\ g^{-1}$)	Mean Total Concentration ($\mu g\ g^{-1}$)
Cd	0.6	10	0.4
Cu	16	110	38.5
Fe	20000	40000	19258
Mn	460	1100	391
Pb	31	250	18.0
Zn	120	820	160.7

Hydrodynamic Model - Prior to the modelling exercise a bathometric survey was carried out. The results of this survey are presented in Figure 5. The three dimensional hydrodynamic numerical model was applied to simulate flow conditions in the pond under various flow rates and geometries for exploring possible ways to improve the performance of the stormwater pond. While a very high flow has been modeled below (1 m^3/s), it does provide an indication of the flow patterns of the pond as it currently exists (Figure 6). In addition, an important aspect assessed by this model was the influence of the macrophyte bed directly in front of the inlet culverts. These macrophytes may play a negative or positive role in the performance of the pond by either 1) short circuiting the flow by deflecting it towards the outlet and/or 2) slowing down flow with the beneficial result of settling out sediment. To simulate the macrophyte bed, a porous block with the similar size and shape was built into the model domain as shown in Figure 7.

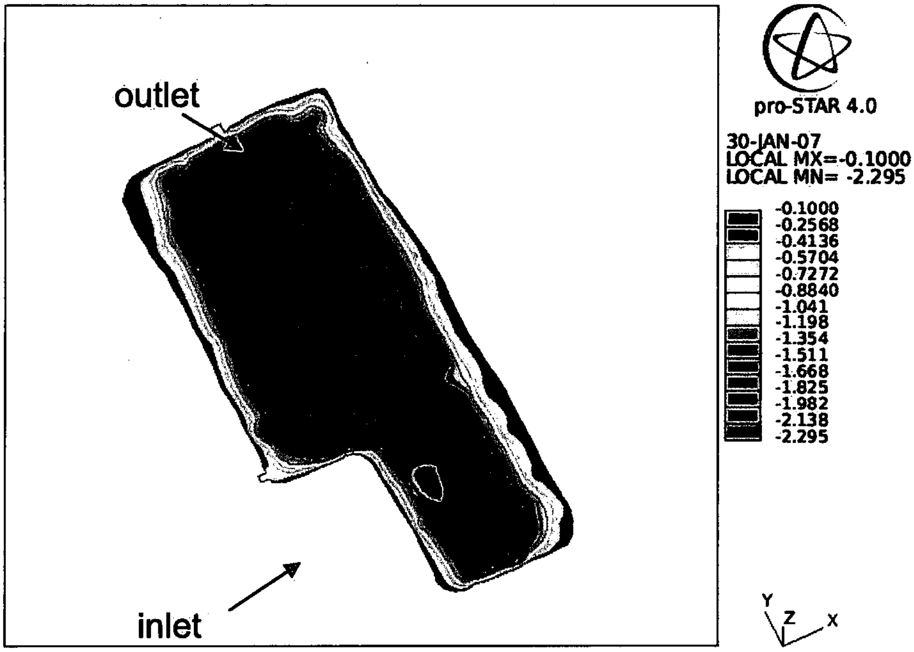

Figure 5. Depth contour of the Halton East Pond. Note that negative numbers can be taken as absolute depths.

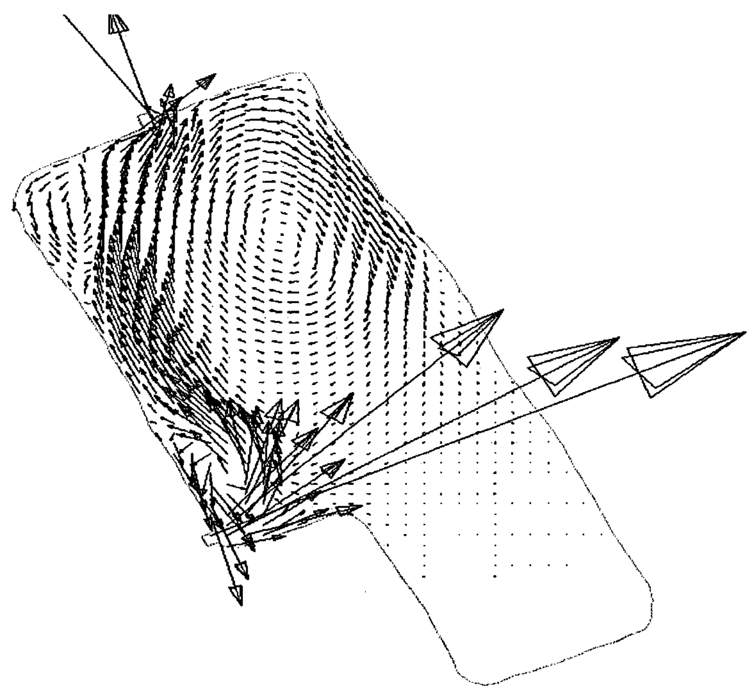

Fig. 6: The simulated velocity field in the Halton East Pond with plants right in front of the inlet pipe (flow velocity = 1 m/s; flow rate = 1.2 m^3/s).

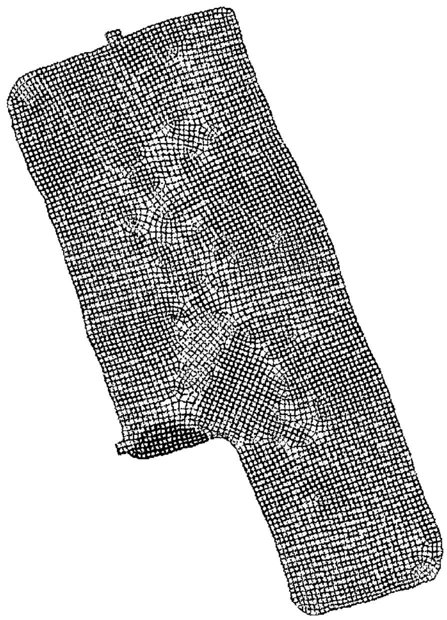

Figure 7. A mesh used for numerical modelling, the green area represents the location of the living plant in the Halton East Pond.

As the pond currently exists, while flow does enter into the macrophyte bed, likely resulting in some beneficial sediment removal, the majority of flow is diverted by this barrier (Figure 8). Figure 6 illustrates that the inflow currently takes the path of least hydraulic resistance directly to the outlet. The south end of the pond provides little beneficial use with the current situation. This shortcut flow pattern will reduce the flow resident time and the area of the pond which currently is active in particle removal.

Figure 8. Inlet flow is diverted towards the outlet due to macrophyte location.

While only preliminary at this time, an effective option for enhancing the performance of the pond would be to remove the macrophyte bed at the inlet. By removing the inlet macrophyte bed, the entire pond is involved in the circulation pattern thus resulting in a longer hydraulic residence time and a more effective sediment removal (Figure 9). Of particular interest in this scenario is that the currently inactive south portion of the pond would now be integrated into the flow pattern (evidenced by a clockwise circulation in the zone – Figure 9), extending the active area for sediment removal greatly.

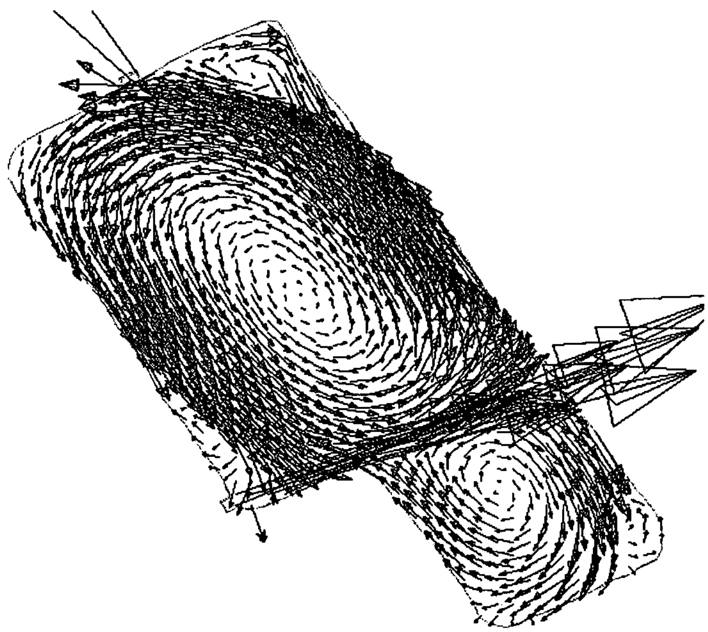

Figure 9. The simulated velocity field in the Halton East Pond with plants being removed from front of the inlet pipe (flow velocity = 1 m/s; flow rate = 1.2 m^3/s).

A more effective use of macrophytes for sediment control would be to populate the north end of the pond in front of the outlet. This would act as a filter of sediments and would increase the hydraulic residence time of the pond.

Laboratory Flume Experiments (Polymer Application Effects) – The flume study on the application of chitosan to stabilize pond bed sediment was carried out by a fourth year undergraduate thesis student (Maricris Marinas). Experiments were initially performed using kaolinite clay, then repeated with sediment collected from the HWMS East Pond using a ponar sampler in July and August 2006. The three polymer application methods described above (broadcast, mixing and injection) were applied and the sediment bed was evaluated for resistance to shear. Additionally, the flocs formed were evaluated for size and speed of settling after re-suspension. Data from the experiments are currently being analyzed; results will be made available to Halton Region when the report is complete. The results will be of value in planning the most effective use of chemical additives in the pond.

2007 Study Plan

Equipment – All equipment will be reinstalled with the following additions for 2007:

Two flow meters will be installed in each inlet pipe to better characterize the flow regime entering the pond. If the flow are such that they are not effectively measured by the electronic equipment then it is proposed that a weir box be integrated into the inlets for a more accurate assessment of input dynamics.

Two logging optical backscatter probes will be installed within the pond to continuously monitor turbidity (a surrogate of TSS) over time. One will be place close to the inlet while the other will be placed close to the outlet.

An acoustic doppler velocity meter (ADV) will be deployed within the pond in a down wind location for a period of one month. This instrument will log the velocity profile within the near bed region and will allow for the calculation of bed shear stress values. These values can then be compared to the flume experiments which provide the critical bed shear stress for erosion for the pond bed sediment. This information will provide evidence as to if resuspension is an issue for the east stormwater detention pond.

Sampling - Multiple storm inlet and outlet samples collected and analyzed for:

TSS
Volatile suspended solids (VSS)
Whole water samples for a suite of metal concentration analysis
Suspended sediment samples for a suite of metal concentration analysis
Sequential extraction AA analysis for suspended solid associated metals (sample volume dependent)

Modelling - Next step is to study the sediment dynamics within the pond under various hydraulic conditions using Lagrangian particle tracking model.

Experimentation/Research – It is proposed that a sediment tracing study be undertaken in the late summer, early fall, in order to validate the numerical model and to further determine the efficiency of the pond to remove sediment from suspension prior to its discharge. A rare-earth element (Holmium- Ho) labelled clay will be injected as a slurry into the inflow of the pond (either during a natural storm event or during a simulated storm event) and the plume traced as it dispersed within the pond. Following settling of the tracer, sediment cores will be collected and analyzed for Ho concentration. This information can then be plotted in a GIS application and overlaid with the model predicted flow patterns. The result will be a conclusive evaluation of the pond's current condition to remove fine-grained cohesive sediments (i.e. those that contain the majority of the pollution) and will lead to strategies for improving the performance further. Toxicological analysis of Ho is currently underway in order to determine if any negative effects can result from this experimentation.

The report on the flume study carried out by M. Marinas on the application of polymers to stabilize pond bed sediment will be completed and a copy provided to the Halton Region. An executive summary of this thesis will provide the Region with possible options as to the application of the polymer currently in use for the control of suspended solids within the East stormwater detention pond.

Summary

In the 2006 season, NWRI efforts focused on the monitoring, modelling and polymer application studies. Sampling and flow measurement equipment were installed in the inlet and outlet of the East Pond at the Halton Waste Management Site. Preliminary samples were collected to evaluate the sampling and analysis protocols, which will be further refined for the 2007 monitoring season. A bathometric survey of the pond was carried out and a three dimensional hydrodynamic numerical model was applied to simulate flow conditions in the pond under various flow rates and geometries. Based on the preliminary results, possible ways to improve the performance of the Halton East Pond are discussed. A laboratory study of three polymer application methods was completed; the report will be provided to Halton Region when available.

In 2007, NWRI plans to continue and refine its efforts in monitoring and modelling. A novel method of tracing sediment behaviour has also been proposed for discussion between NWRI and Halton Region.

References

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Appendix C

Toxicity Report on Holmium (WSTD Contribution # 07-541)

TOXICITY OF HOLMIUM-LABELLED CLAY TO FOUR BENTHIC INVERTEBRATES

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ABSTRACT

Montmorillonite clay adsorbed with the rare earth element holmium (Ho-clay) is a new material produced for tracing movements of fine particles in aquatic systems. However, little is known about the toxicity of Ho-clay, and its potential environmental effects. To investigate effects of Ho-clay on aquatic biota, four benthic invertebrate species (*Chironomus riparius*, *Hexagenia* spp., *Hyalella azteca*, *Tubifex tubifex*) were exposed to Ho-clay alone and mixtures of 10, 25 and 50% Ho-clay with field-collected reference sediment for 10-28 days in standard laboratory toxicity tests. Overall, only the 100% Ho-clay treatment resulted in significantly higher toxicity than the reference sediment. Mean survival at the end of the exposures to 100% Ho-clay was 7, 53, 2 and 100% for *Chironomus*, *Hexagenia*, *Hyalella* and *Tubifex*, respectively. Exposure to a negative control treatment of 100% clay resulted in minor reductions in growth, but no lethal responses. Highest concentrations of Ho at which no toxicity was observed were 1400 μg/g for sediment and 11 μg/L for water. Potential impacts of Ho-clay released into natural waters would be expected only where Ho-clay persists in sediment at proportions >50% for at least several days.

RÉSUMÉ

La montmorillonite adsorbée avec la terre rare holmium (Ho-argile) est une nouvelle matière qui permet de suivre les déplacements des particules fines dans les réseaux aquatiques. Toutefois, on ne connaît que peu de choses sur la toxicité de Ho-argile et sur ses effets possibles dans l'environnement. Pour étudier les effets du mélange Ho-argile sur le biote aquatique, on a exposé pendant 10 à 28 jours, dans un laboratoire ordinaire de toxicologie, quatre taxons d'invertébrés benthiques (*Chironomus riparius*, *Hexagenia* spp., *Hyalella azteca* et *Tubifex tubifex*) au mélange Ho-argile seul, ainsi qu'à des mélanges de 10, 25 et 50 % de Ho-argile avec des sédiments témoins recueillis sur place. Dans l'ensemble, seulement le traitement à 100% de Ho-argile a causé une toxicité notablement supérieure à celle des sédiments témoins. Le taux moyen de survie à la fin de l'exposition à 100 % de Ho-argile était de 7, 53, 2 et 100 % pour *Chironomus*, *Hexagenia, Hyalella* et *Tubifex*, respectivement. L'exposition à un témoin négatif composé de 100% d'argile a causé de faibles réductions de la croissance, sans aucune réaction létale. La plus forte concentration de Ho pour laquelle on n'observait aucune toxicité était de 1 400 µg/g pour les sédiments et de 11 µg/L pour l'eau. Les mélanges Ho-argile libérés dans des eaux naturelles ne devraient avoir des effets nocifs que s'ils persistent dans les sédiments pendant plusieurs jours, dans des proportions de plus de 50 %.

INTRODUCTION

Many contaminants discharged to aquatic systems are associated with fine sediment particles. Determining the transportation pathways of fine sediments in surface waters is an important step in understanding the environmental fate of contaminants. Clay labelled with the rare earth element holmium (Ho-clay), is a recently developed tracer material with potential use in field experiments for examining fine sediment transportation and fate (Suzuki and Spencer 2005). However, the toxicity of Ho-clay to aquatic organisms is not well known.

Ho-clay is composed of holmium adsorbed to aggregates of montmorillonite clay minerals. In freshwater and marine environments, a fraction of the bound Ho can be desorbed through cation exchange (Suzuki and Spencer 2005). Thus both particle-bound and dissolved Ho could be bioavailable. In an assessment of the toxicity of dissolved forms of 63 metal and metalloid elements to the freshwater amphipod *Hyalella azteca* (Borgmann et al. 2005), Ho ranked in the middle for relative toxicity. Environmentally important elements Cu, Ni and Zn were several times more toxic that of Ho based on median lethal concentrations (LC50s); metals showing the lowest LC50s (Cd, Ag, Pb, Hg) were 75–600 times more toxic than Ho. Whether a solid phase form of Ho, such as Ho-clay, also lies at the middle for relative toxicity is uncertain, because toxicity of a contaminant can be strongly related to its solubility and lability.

In order to assess the ecological risk of releasing Ho-labelled clay to the environment, a series of laboratory toxicity tests with four benthic macroinvertebrate species was conducted. The tests involved exposures to mixtures of Ho-clay and pond sediment following a standard methodology developed by Environment Canada for assessing toxicity of contaminated sediments in the Great Lakes (Reynoldson and Day 1998). These tests were conducted in advance of a planned field experiment in which a slurry of Ho-clay will be discharged to a stormwater pond in the Region of Halton, Ontario, in October 2007.

The purpose of the toxicity assessment was to characterize relationships between exposure to Ho-clay (in terms of the proportion of Ho-clay mixed with natural pond sediment) and the ecotoxicological responses of four macroinvertebrate taxa (midge, mayfly, amphipod, oligochaete worm) representing a range of feeding habits and lifestyles.

METHODS

Experimental design

The overall experimental design is shown in Fig. 1. Four sets of toxicity tests were conducted involving seven sediment treatments. Each set of tests corresponded to one of the following test organisms and responses:

- *Chironomus riparius* 10-day survival and growth,
- *Hexagenia* spp. 21-day survival and growth,
- *Hyalella azteca* 28-day survival and growth, and
- *Tubifex tubifex* 28-day survival and reproduction.

Five sediment treatments involved a range Ho-clay and pond sediment mixtures:

- 100% Ho-clay / 0% pond sediment
- 50% Ho-clay / 50% pond sediment
- 25% Ho-clay / 75% pond sediment
- 10% Ho-clay / 90% pond sediment
- 0% Ho-clay / 100% pond sediment

The pond sediment used in the above experiments was collected from the stormwater pond of the Regional Municipality of Halton's Waste Management Site located in Milton, Ontario, Canada. A Ponar grab sampler was used to collect the bed sediment from the middle of the pond. The collected sediment was composed primarily of deposited clays (67% <5μm), silts (32% >5μm <63μm) and an insignificant amount of sand (1% >63μm). The collected sediment was wet sieved through a 250 μm screen. Organic content was not determined for the sediment; however, given its dark hue, it is believed to possess a moderate amount consistent with pond/river sediments.

In addition to the 100% pond sediment reference treatment, two other reference treatments were tested: 100% montmorillonite clay as a negative control for effects of the Ho "carrier", and sediment from an uncontaminated site in Lake Erie (Long Point Marsh), which is used as a standard laboratory control sediment.

The test containers (=experimental units) were glass beakers containing sediment and overlying water. Toxicity tests were conducted in triplicate for each sediment treatment and test organism combination. A fourth treatment replicate was run with each test for the sampling of water and sediment for analyses of Ho concentrations. Sediment and water were allowed to equilibrate for one week before introducing test organisms. All sediment treatments were tested concurrently for each organism, although not all test sets were run concurrently.

Sediment treatment preparation

The Ho-labelled clay tracer was prepared by first making up stocks of holmium chloride ($HoCl_3$) and sodium nitrate ($NaNO_3$). From these stock solutions, 400 mL of $HoCl_3$ and 1600 mL of $NaNO_3$ were added to 10 2000-mL bottles and the pH adjusted to between 4.9 and 5.1 using a few drops of dilute HNO_3. Next, 200 g of montmorillonite clay was added to each of these working solutions. These working solutions were placed on a flat shaker at 100 rpm for 72 hours, and left to stand overnight. The supernatant was then decanted from each bottle and the sediment transferred into 4 200-mL centrifuge bottles. The 200-mL centrifuge bottles were topped up with distilled water and centrifuged for 15 minutes at 3000 rpm. Supernatant was poured off and the bottles were refilled with distilled water and centrifuged again for 15 minutes at 3000 rpm. The supernatant was poured off again and the sediment was washed into foil trays using distilled water and dried in a conventional oven at 95°C overnight. The sediment was then placed into a furnace at 500°C for 7 hours. The resulting Ho-clay sediment was grinded to <63 µm and stored until use.

The three pond sediment and Ho-clay mixtures were prepared based on dry weights of proportions. After drying a sample of the pond sediment to determine the water content (73.8%), dry weight-equivalent wet weights of pond sediment and dry Ho-clay were combined with some distilled water in 2-L containers and homogenized with a drill mixer. Appropriate amounts of the resultant slurries were then distributed to the test containers.

Toxicity tests

Static toxicity tests were conducted in aerated glass beakers with dechlorinated tap water from Lake Ontario. Ratios of water to sediment were about 4:1 by volume for all tests except *Tubifex*, which used a 1.5:1 ratio. Details of sediment handling procedures and toxicity test methods are described in Borgmann and Munawar (1989), Borgmann et al. (1989), Krantzberg (1990), Reynoldson et al. (1991) and Reynoldson et al. (1998). Brief descriptions of each test are provided below.

The *Hyalella* test was conducted for 28 days using 15 2 -10 day old organisms. On day 28, the contents of each beaker were rinsed through a 250-µm screen and the surviving amphipods counted. Amphipods were then dried at 60 °C for 24 hours and dry weights recorded. (Initial weights were considered negligible.)

The *Chironomus* test was conducted for 10 days using 15 first instar organisms. On day 10, the contents of each beaker were wet sieved through a 250-µm screen and the surviving chironomids counted.

Chironomids were then dried at 60 °C for 24 hours and dry weights recorded. (Initial weights were considered negligible.)

The *Hexagenia* spp. test was conducted for 21 days using 10 preweighed nymphs (5 - 8 mg wet weight/nymph). On day 21, the contents of each jar were wet sieved through a 500-μm screen and surviving mayfly nymphs counted. Nymphs were then dried at 60 °C for 24 hours and dry weights recorded. The relationship between mayfly wet and dry weights was determined previously by regression analysis. Initial dry weights were calculated using the equation:

$$\log(\text{dry weight}) = -0.905 + 0.968 \log(\text{wet weight});\ r^2=0.86$$

Final growth was determined as final dry weight minus initial dry weight.

The *Tubifex* test was conducted for 28 days using 4 sexually mature worms. On day 28, the contents of each beaker were sequentially rinsed through 500-μm and 250-μm sieves. The number of surviving adults, full cocoons, empty cocoons, and large immature worms were counted from the 500-μm sieve and the numbers of small immature worms were counted from the 250-μm sieve. Reproduction was measured with three endpoints: total number of cocoons per adult, percent cocoons hatched, and total number of young per adult.

For a set of tests to be acceptable, survival in the reference or laboratory control sediment had to exceed specific minimum levels: 80% for *H. azteca* and 70% for *C. riparius* (USEPA 1994; ASTM 1995); 80% for *Hexagenia* spp., and 75% for *T. tubifex* (Reynoldson et al. 1998).

In each replicate test beaker, pH, dissolved oxygen, conductivity, temperature, and total ammonia + ammonium were measured at the start (day 0 – prior to the introduction of organisms) and the completion of the test (day 10, day 21, or day 28). Evaporated water was replaced with dechlorinated tap water. Tests were run under static conditions in environmental chambers at 23 ±1 °C, under a photoperiod of 16L: 8D and an illumination of 500–1000 lux, with the exception of *T. tubifex* test, which was run in the dark.

Water and sediment sampling

Samples of water and sediment were collected from the fourth replicate beaker of each treatment during each test. Water (30 mL) was sampled in duplicate on day 0 (before placement of test organisms in beakers), day 1, midway through the test, and on the last day of the test. The water was collected using one-use10-mL sterile glass pipettes, filtered on 0.45-µm cellulose acetate filters and preserved with concentrated HNO_3 (pH to 2) within polyethylene bottles. During the tests, water removed for Ho analysis was replaced with dechlorinated tap water.

Sediment (10g wet weight) was sampled in duplicate at the beginning and end of the test. The initial sediment sample was collected by simply pouring into pill jar containers directly from the bulk sample. The final set of sediment samples were taken at the end of each test, after the last set of water samples had been taken and the remaining overlying water had been siphoned off. The sediment remaining in each treatment beaker was transferred into pill jar containers using one-use sterile plastic scoops.

Ho analyses

Sediment samples were first dried at 105° C until a consistent weight was achieved. Samples were then ground followed by microwave digestion with 0.5g of concentrated nitric acid. The nitric acid was then diluted to 50 mL by deionised water and injected into a Perkin Elmer Optima 5300v ICP-OES system. Dissolved concentrations of Ho were determined by direct injection into the ICP-OES.

Data analyses

Effects of Ho-clay on water and sediment were examined graphically by plotting Ho concentrations by sediment treatment and against proportion of Ho-clay.

Differences in responses of test organisms among sediment treatments were analyzed by one-way ANOVA of each toxicity endpoint and Tukey multiple comparison of treatment means. Differences among test organisms in sensitivity to Ho-clay were assessed by two-way ANOVA of survival data for the five Ho-clay and pond sediment mixtures. Dose-response relationships were examined for the five Ho-clay and pond sediment mixtures by plotting survival, growth and reproductive endpoints against Ho concentrations in sediment and water. Sediment and water LC50s for Ho were estimated by the trimmed Spearman-Karber method (Hamilton et al. 1977).

Joint toxicological responses were assessed by Principal Components Analysis (PCA) of the endpoints. Eigenanalysis was conducted on a correlation matrix of untransformed endpoint data. Scores for the first two principal components were plotted and tested for differences among treatments by ANOVA.

RESULTS

Ho concentrations in sediment and water

Concentrations of Ho in sediment sampled from the test beakers were low or not detected for the three treatments containing no Ho-clay, and increased approximately linearly with the proportion of Ho-clay (Fig.2, Fig. 4A). Within-beaker differences in concentrations between the start and end of tests were not significant. Among the four sets of tests, mean Ho levels in sediment agreed well for all given treatments (Fig. 4A), suggesting that the measured Ho in sediment from the fourth treatment replicate beakers were similar to those in the other three treatment replicates.

All sediment treatments containing Ho-clay resulted in dissolved Ho in the overlying water (Fig. 3). (Dissolved Ho was also detected in some samples from non-Ho-clay beakers, likely due to cross-contamination during sample analyses.) In contrast to the sediment Ho, relationships between Ho water concentration and proportion of Ho-clay in sediment were strongly curvilinear, with the 100% Ho-clay treatment resulting in dissolved Ho levels 2-3 orders of magnitude higher than those for the other treatments (Fig. 4B). Differences in mean dissolved Ho concentrations among tests were also greater than those for sediment Ho, particularly for the 100% Ho-clay treatment, where Ho in the *Hyalella* and *Tubifex* beakers were almost 2 times those for *Chironomus* and *Hexagenia.*

Among treatments overall, differences in Ho concentrations in sediment and, to a lesser extent, water indicate that the test organisms were exposed to a range of Ho levels.

Toxicological responses

Effects of treatments

Exposure to the sediment treatments had significant ($P \leq 0.0035$) effects on all toxicity endpoints except *Tubifex* survival and "percent of cocoons hatched". The general pattern was of the 100% Ho-clay treatment resulting in substantially higher toxicity than all other treatments (Table 1; Fig. 5A,B,C).

For the lethal endpoints (Fig. 5A), mean survival was ≥73% for all treatments and taxa except for the 100% Ho-clay treatment, in which mean survival was only 7, 53 and 2% for *Chironomus*, *Hexagenia* and *Hyalella*, respectively. Survival of *Tubifex* was 100% in all beakers. For all taxa, survival in the negative control sediment (100% clay) was as high as in the laboratory control and the pond reference sediments.

The sublethal endpoints showed more variability that the lethal ones to the sediment treatments. While the 100% Ho-clay treatment was again substantially more toxic than the other Ho-clay mixtures and the 100% pond sediment for all endpoints except "percent of cocoons hatched", the laboratory control sediment and 100% clay treatments also resulted in some apparent toxicity: reduced growth for *Hexagenia* and *Hyalella* (Fig. 5B). However, because the growth responses in the laboratory control sediment were within QA/QC ranges for the *Hexagenia* test, these differences may result in part from enhanced growth in the treatments with pond sediment, which appeared to be high in organic content.

Conversely to the lower growth, production of *Tubifex* young was higher in the laboratory control, 100% clay and 50% Ho-clay treatments compared to the 100% pond sediment (Fig. 5C).

The adverse effects of the laboratory control sediment on growth, together with the *Hyalella* survival of <80%, are typically indicative of potentially unhealthy test organisms. However, given that survival, growth, and 2 of the 3 *Tubifex* reproduction endpoints were as high or higher in the 100% pond sediment than in any of the other treatments, it is likely that the laboratory control sediment treatment itself was affecting the endpoints. Therefore, the 100% pond sediment treatment alone was considered the appropriate reference for comparisons to the Ho-clay exposures.

The multivariate toxicological response to sediment exposures is shown in a plot of the treatment replicate scores for the first two principal components from the PCA of nine measured endpoints (Fig. 6). (*Tubifex* survival was invariant and therefore excluded from the PCA.) Of the total variance in the endpoints, 83% was represented by PC1 and PC2. PC1 is strongly, inversely related to toxicity for all endpoints. PC2 is related to increasing *Tubifex* cocoon hatch and production of young, and decreasing *Hexagenia* and *Hyalella* growth.

In terms of joint responses, the 100% Ho-clay treatment was substantially more toxic than the other treatments ($P<0.0001$ from ANOVA of PC1). Responses to all other Ho-clay treatments, though, were similar to those for the 100% pond sediment, as indicated by the overlapping distributions of the treatment replicate scores and the ANOVA results. The laboratory control sediment and 100% clay treatments produced effects that were similar to each other, but distinct from the other treatments (mainly by PC2). Although the 100% clay treatment resulted in slightly elevated toxicity compared to the 100% pond sediment, the effect is much lower than the toxicity produced by the 100% Ho-clay.

Effects of Ho concentration

Dose-responses relationships between the toxicity endpoints and measured Ho concentrations in sediment and water for the five Ho-clay and pond sediment mixtures are shown in Fig. 7 and Fig. 8. Sediment with concentration of Ho up to about 1400 µg/g was not more toxic than the pond reference sediment by any of the endpoints, whereas sediment with 4400-4800 µg/g significantly ($P<0.0015$) reduced survival and growth for *Chironomus*, *Hexagenia* and *Hyalella*, and production of cocoons and young for *Tubifex* (Fig. 7). Shapes of the curves were similar for Ho in water with concentration on the log scale. Concentrations of dissolved Ho up to 11 µg/L were not toxic to test organisms, whereas significantly reduced survival and growth for *Chironomus*, *Hexagenia* and *Hyalella*, and production of cocoons and young for *Tubifex* were observed in beakers with dissolved Ho of 330 to 546 µg/L (Fig. 8).

LC50s could be determined only for the *Chironomus* and *Hyalella* tests, for which at least one Ho concentration produced <50% survival. For Ho in sediment, LC50s (and 95% confidence intervals) were 2611 (2409-2829) and 2378 (2258-2504) µg/g for *Chironomus* and *Hyalella*, respectively. For Ho in overlying water, the LC50 for *Chironomus* was 35.0 µg/L (CI could not be estimated). The water Ho LC50 (and 95% CI) for *Hyalella* was 52.2 (42.8-63.6) µg/L. Results from the tests with *Hexagenia* and *Tubifex* suggest that LC50s for Ho in sediment and water exceed the highest concentrations measured in the treatments. For sediment, these were 4720 and 4723 µg/g for *Hexagenia* and *Tubifex*, respectively; for water, 230 and 542 µg/L, for *Hexagenia* and *Tubifex*, respectively. However, the *Hexagenia* LC50s are not likely much greater than the maximum measured Ho concentrations because survival in the 100% Ho-clay treatment was 53%.

Differences among taxa in tolerance of treatments

Variability among taxa in survival of treatments was significant ($P<0.0001$, two-way ANOVA with treatment and taxon as factors). Although the treatment-taxon interaction was significant, examination of the interaction plot, which is similar to the survival vs. sediment Ho concentration curves in Fig. 7, indicated that *Chironomus* was most sensitive to Ho-clay, followed by *Hyalella*, *Hexagenia* and *Tubifex*.

Consideration of the treatment exposure times for the tests further supports these ranks. Despite the *Chironomus* test being the shortest (10 days), mortality at test end was highest. The *Tubifex* test lasted 28 days, but resulted in lower mortality than the 21-day *Hexagenia*, 28-day *Hyalella*, and 10-day *Chironomus* tests. The difference in sensitivity between *Hexagenia* and *Hyalella* is less significant due to the unequal Ho-clay exposure periods.

DISCUSSION

Toxicity of Ho-clay

Sediment containing up to 50% Ho-clay did not prove toxic for any of the four benthic invertebrates in chronic laboratory toxicity tests, but exposure to 100% Ho-clay resulted in substantially reduced survival for three of the four test organisms. Although fine sediment, such as clay, can cause reductions in survival and growth of some benthic organisms (e.g., DeWitt et al. 1988), adverse effects with the 100% clay were observed only for the *Hexagenia* and *Hyalella* growth endpoints (Fig. 5A-C). Therefore, effects of clay do not account for low survival (nor reductions for 3 of 5 sublethal responses) in the 100% Ho-clay treatment.

Ho appeared to desorb from Ho-clay in the toxicity tests, but not very readily. Dissolved Ho was measured in water from beakers with Ho-clay, but not in proportion to the amount of Ho-clay in the sediment. Whereas concentrations of Ho reached only as high as 17 µg/L in water overlying sediment with up to 50% Ho-clay, in the 100% Ho-clay treatment beakers concentrations ranged from 116 to 954 µg/L (Fig. 3; note log-scale). In static test conditions with low water:sediment volume ratios (as in these tests), concentrations of metals in overlying waters probably reflect concentrations in porewater of sediment (Borgmann and Norwood 1999). Because concentrations of metals in porewater are often better related to toxicological responses of benthic invertebrates than bulk metal concentrations in sediment, elevated toxicity observed in the 100% Ho-clay treatment may be explained by highly elevated dissolved Ho levels. Sediment mixtures with ≤50% Ho-clay may not be toxic because Ho is not bioavailable to the test organisms.

LC50s for Ho in water were estimated to be 35.0, 52.2, >230 and >542 µg/L for *Chironomus*, *Hyalella*, *Hexagenia* and *Tubifex*, respectively. Although the exposure times were not equal for all the tests, they do provide a tentative ranking of relative sensitivities to Ho. The oligochaete worm, *Tubifex tubifex*, the least sensitive of the taxa tested, is known to be tolerant to a variety of contaminants and environmental stressors, and was not adversely affected by the 100% Ho-clay exposure.

The only known published Ho toxicity test with a benthic invertebrate was conducted by Borgmann et al. (2005). The test was conducted on *Hyalella azteca* with a 7-day, water only exposure to Ho from a 2% HCl solution. Test conditions were otherwise similar to those of the present study, including the use of dechlorinated Lake Ontario tap water. Tests were also conducted with tap water diluted to 10% with deionized water. The trimmed Spearman-Karber LC50 estimated by Borgmann et al. for *Hyalella* was 755 µg/L based on the nominal Ho concentration. If measured Ho concentrations (which were not available) were used for the estimate, the LC50 would undoubtedly be lower, perhaps about 220 µg/L based on the ratio of measured:nominal Ho LC50s obtained for the softwater tests. Our estimated LC50 for *Hyalella* exposed to Ho for 4 times the duration of Borgmann et al.'s test is about 25% of this LC50. However, the presence of sediment in our test complicates the comparison.

Risk of Ho-clay to natural surface waters

Overall results of the toxicity tests suggest that potential impacts of Ho-clay released into natural waters would be expected only where Ho-clay persists in sediment at proportions >50% for at least several days. However, the extrapolation of laboratory toxicity test results to predict *in situ* effects of contaminants is limited by differences between the two environments in various conditions, including the spatial and temporal scales of exposure to contaminants, physicochemical factors that affect contaminant transportation and fate, and the composition and organization of the exposed biological community.

Exposures of Ho-clay in the toxicity tests likely represent worst-case conditions in natural water bodies. A field Ho-clay exposure would likely be a short term pulse rather than a continuous press as in toxicity tests. Spatially, discharges of Ho-clay should be diluted exponentially across the receiving environment. Thus, the duration and area of high Ho-clay concentration and, consequently the degree biological impact, should be restricted. Our observed toxicity test responses, therefore, are likely to overestimate field impacts to benthic invertebrates.

The toxicity tests in this assessment involved several species, multiple endpoints (including lethal and sublethal responses), and exposures to sediment over a large fraction of the organisms' generation times, all of which improve the ecological relevance of the results. Responses of several taxa occupying different microhabitats and feeding niches involve more contaminant exposure pathways than responses in single species tests. Measurements of lethal and sublethal endpoints provide a broad characterization of ecotoxicological responses. Exposure of a range of life stages to Ho-clay improves the toxicity assessment by integrating potential age- and size-related variability in organism sensitivity.

Although conditions of benthic invertebrates are commonly examined in sediment assessments, their responses to contaminants and other stressors are not necessarily indicative of those of other biological groups, such as microbial communities, algae and fishes. Some contaminants, such as polycyclic aromatic hydrocarbons and contaminants that biomagnify, are rarely toxic to benthic invertebrates at concentrations that affect can fishes and other vertebrates (e.g., Fuchsman et al. 2006). Also, testing of organisms alone in artificial conditions isolated from the receiving environment, does not allow observations of interactions and other complex effects that can occur in the field (Clements 1997). Further assessment of Ho-clay effects should, therefore, involve tests with other biological groups and exposures in intact natural ecosystems.

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Table 1. Survival, growth and reproduction of macroinvertebrate test organisms after exposure to sediment treatments in Ho-clay toxicity test.

Treatment	Replicate	*Chironomus riparius*		*Hexagenia* spp.		*Hyalella azteca*		*Tubifex tubifex*			
		Survival (%)	Growth (mg/indiv.)	Survival (%)	Growth (mg/indiv.)	Survival (%)	Growth (mg/indiv.)	Survival (%)	#cocoons/ adult	% hatched	young/ adult
Laboratory control sediment	1	80.0	0.462	100	5.22	46.7	0.184	100	10.8	55.8	32.0
	2	80.0	0.555	100	4.56	100.0	0.218	100	11.0	52.3	32.0
	3	100.0	0.563	100	4.64	73.3	0.242	100	12.3	61.2	30.8
100% Pond sediment	1	66.7	0.890	100	9.17	100.0	0.933	100	10.0	57.5	14.8
	2	86.7	0.846	100	9.29	100.0	0.754	100	10.3	56.1	14.3
	3	93.3	0.816	100	10.15	100.0	0.743	100	10.0	47.5	12.5
100% clay	1	86.7	0.702	90	1.03	73.3	0.339	100	10.5	64.3	25.8
	2	100.0	0.655	100	1.51	100.0	0.283	100	8.5	64.7	20.0
	3	93.3	0.661	100	1.11	100.0	0.309	100	9.8	64.1	26.3
10% Ho-clay / 90% Pond sediment	1	86.7	0.878	100	7.86	86.7	0.649	100	10.5	59.5	13.0
	2	100.0	0.665	100	8.80	86.7	0.967	100	10.8	58.1	15.0
	3	73.3	0.745	100	8.58	93.3	0.737	100	10.5	64.3	14.0
25% Ho-clay / 75% Pond sediment	1	100.0	0.591	100	7.91	100.0	0.891	100	9.0	63.9	14.3
	2	86.7	0.685	100	6.76	93.3	0.810	100	9.8	61.5	14.3
	3	86.7	0.801	90	7.48	100.0	0.853	100	10.3	58.5	15.8
50% Ho-clay / 50% Pond sediment	1	66.7	0.940	90	7.67	93.3	0.734	100	11.0	61.4	22.5
	2	80.0	0.680	100	7.11	100.0	0.751	100	12.0	60.4	20.3
	3	93.3	0.788	100	6.85	100.0	0.773	100	10.5	61.9	17.5
100% Ho-clay	1	0	0	60	0.52	0	0	100	0.3	100.0	0.3
	2	20.0	0.047	30	0.02	0	0	100	0	0	0.3
	3	0	0	70	-0.03	6.7	0.55	100	0	0	0

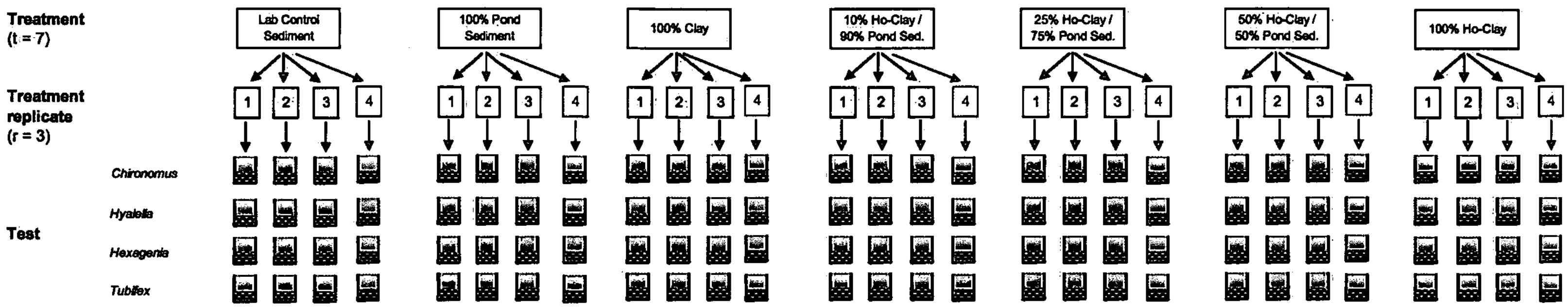

Figure 1. Experimental design for Ho-clay toxicity tests. Responses of test organisms were observed from three replicate experiment units per test. The fourth replicate was sampled for water and sediment for analyses of Ho concentrations.

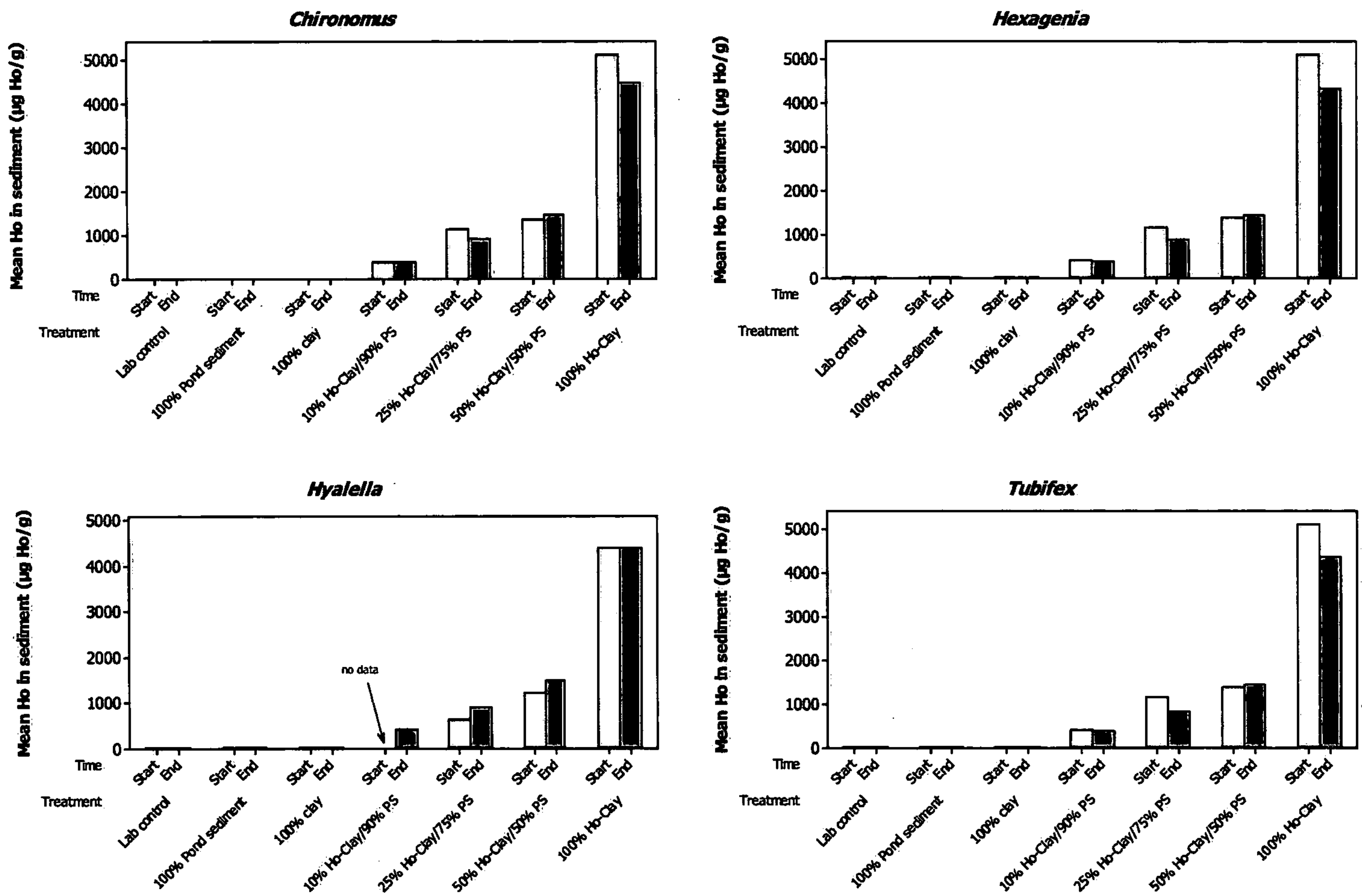

Figure 2. Measured concentrations of Ho in sediment of beakers (mean of duplicate samples) at start and end of toxicity tests for exposures of seven sediment treatments to four test organisms.

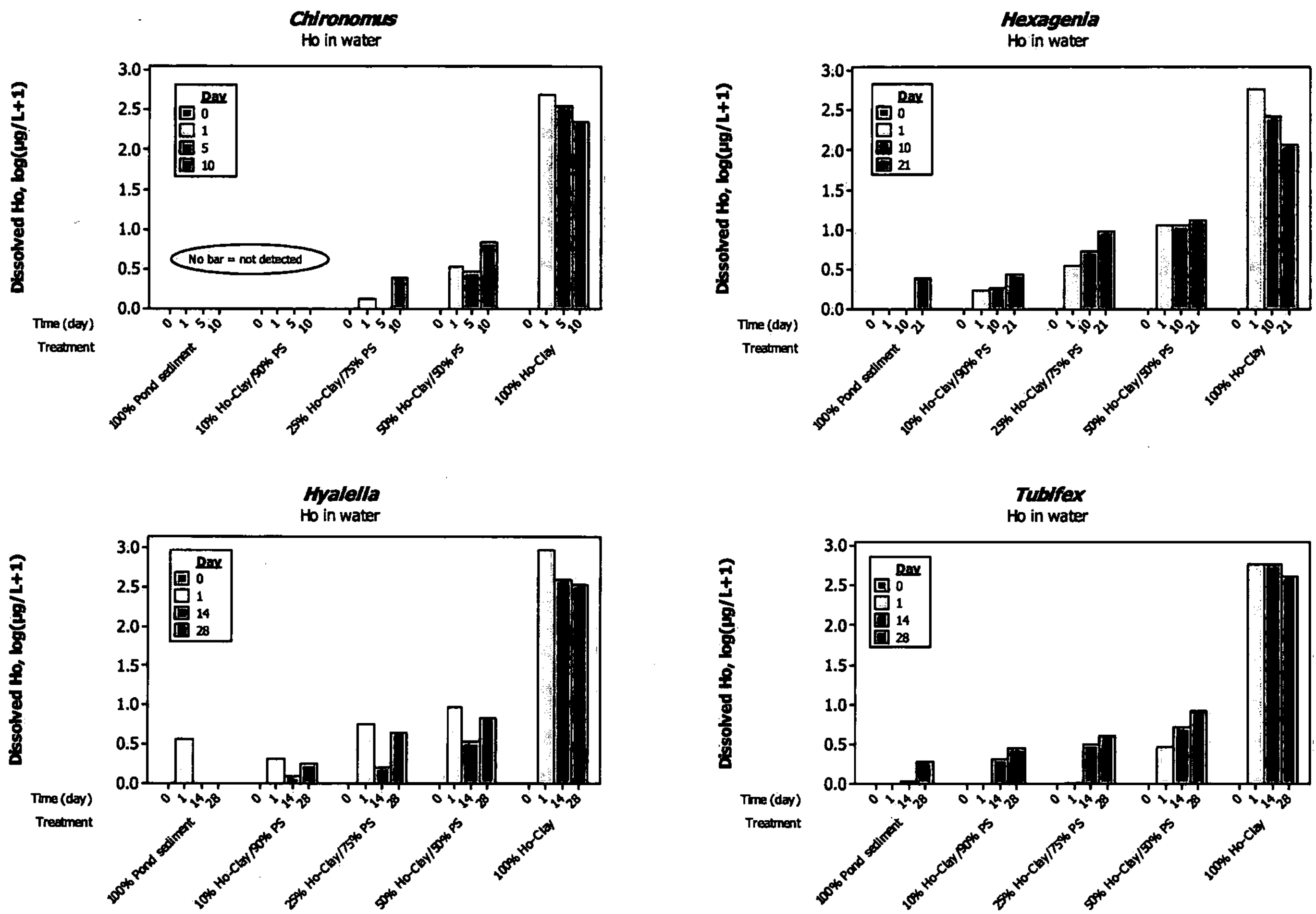

Figure 3. Measured concentrations of Ho in filtered water from beakers (mean of duplicate samples) at start, middle and end of toxicity tests. Note log-scale for Ho concentration.

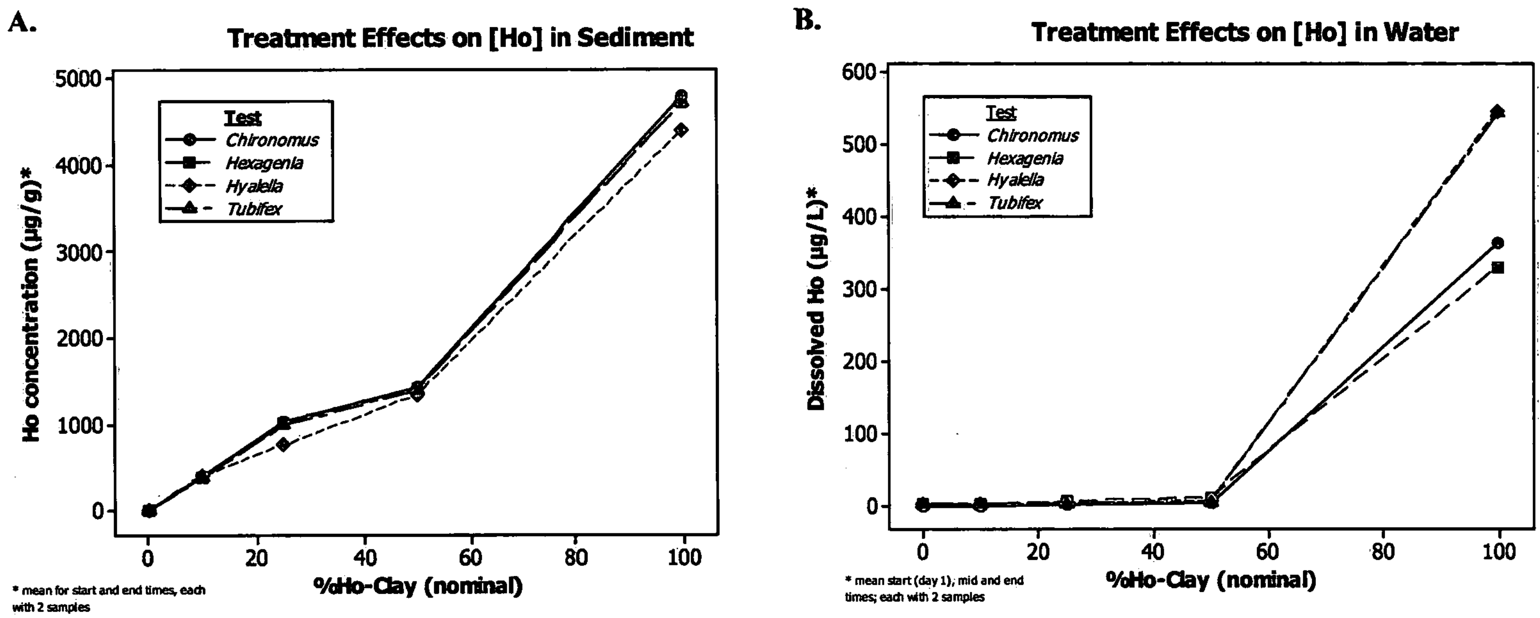

Figure 4. Concentrations of Ho in sediment (A) and overlying water (B) of toxicity test in relation to percent of Ho-clay in treatment sediment. Concentration values are means of all samples, except the day 0 water sample.

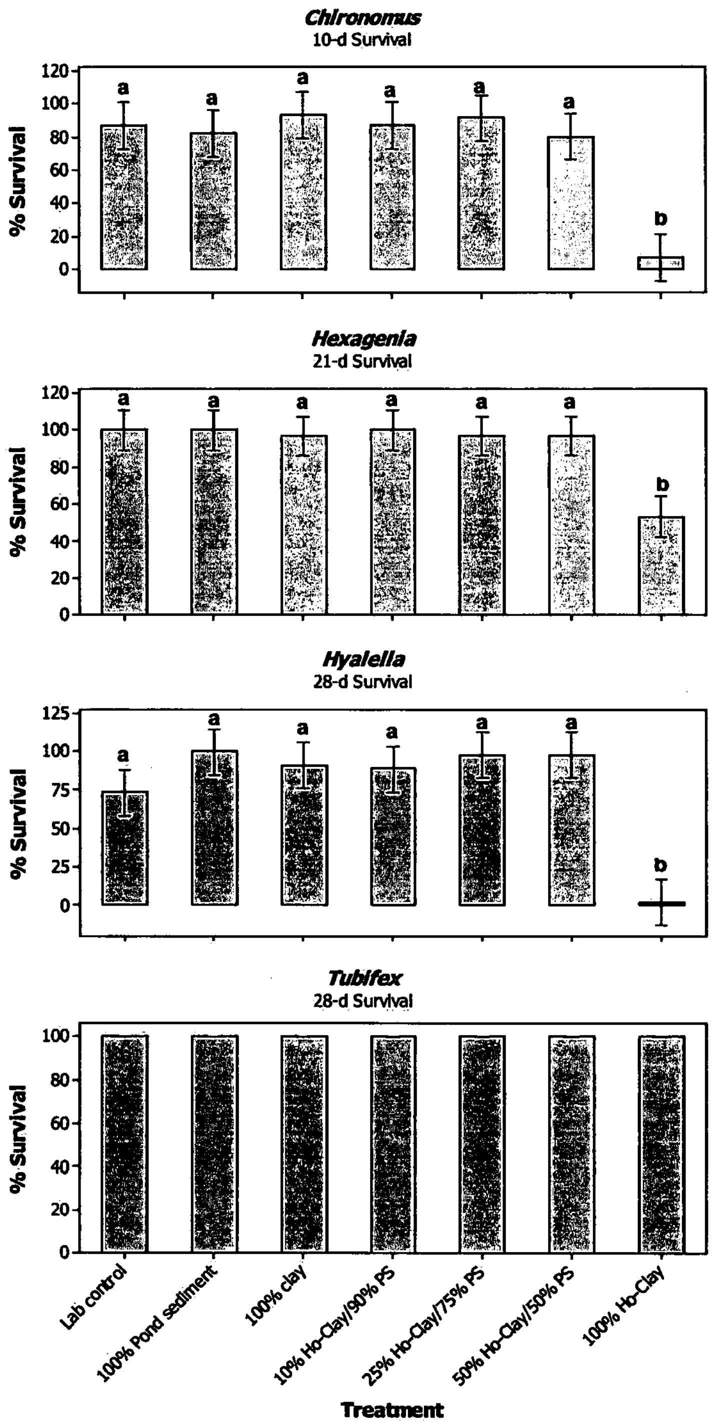

Figure 5A. Effects of seven sediment treatments on survival of four benthic invertebrates in toxicity tests. Bars are means for treatment replicates with pooled-error 95% CIs. Bars labelled with different letters are significantly different by Tukey comparisons with family error rate α=0.05.

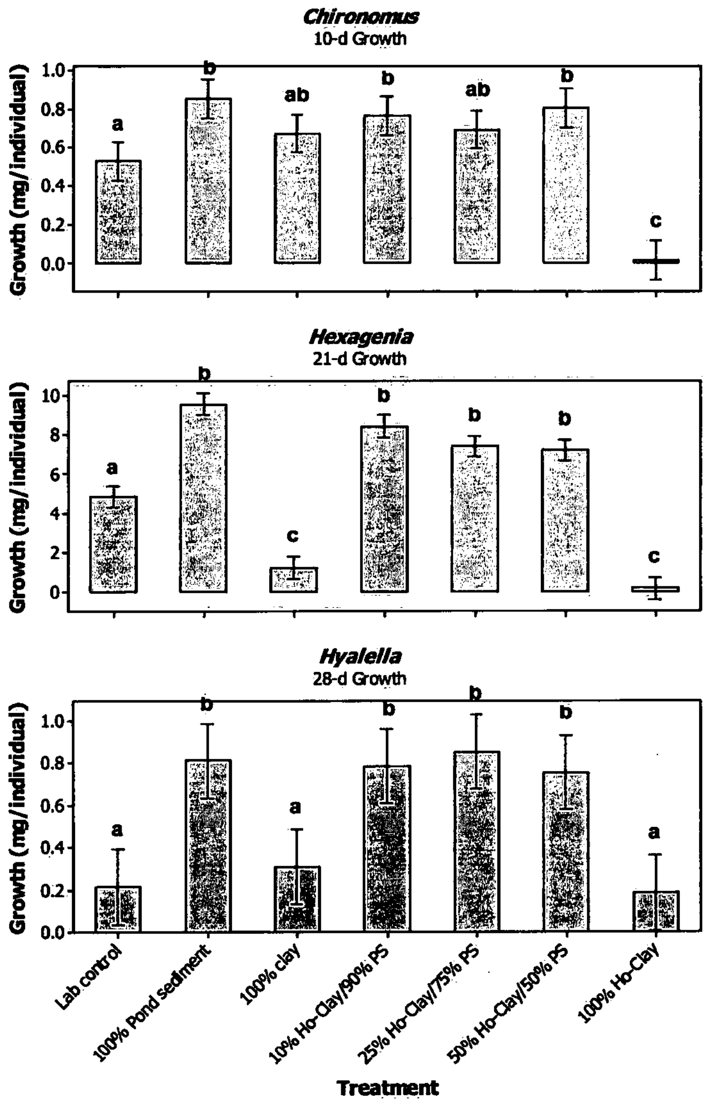

Figure 5B. Effects of seven sediment treatments on growth of three benthic invertebrates in toxicity tests. Bars are means for treatment replicates with pooled-error 95% CIs. Bars labelled with different letters are significantly different by Tukey comparisons.

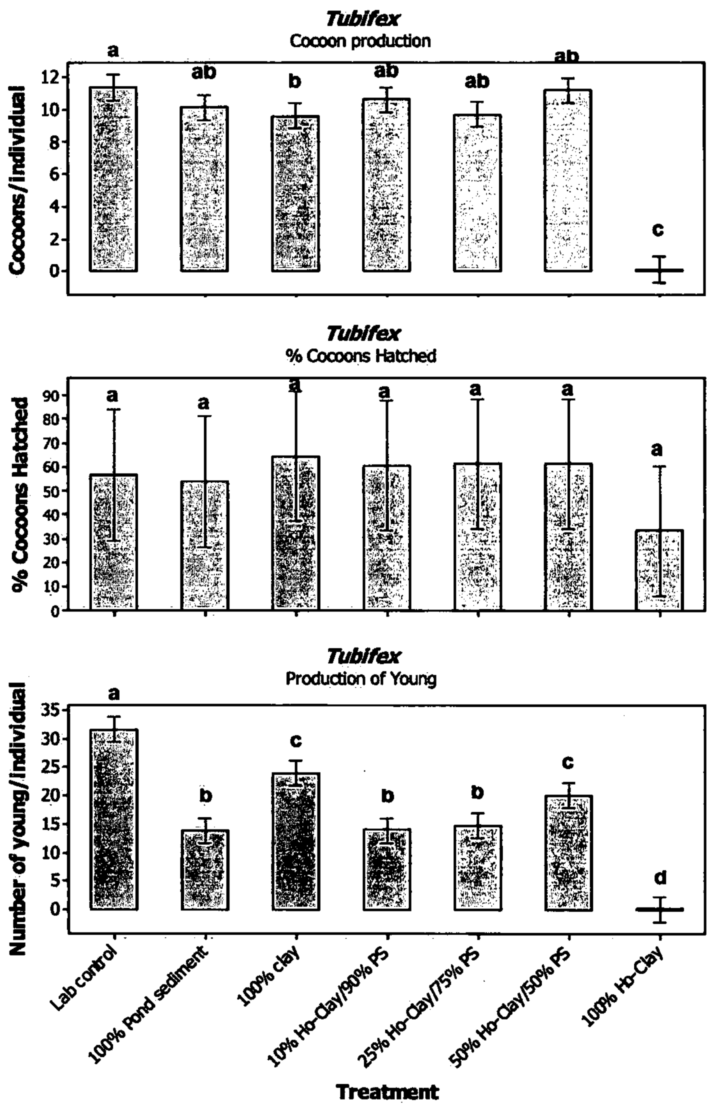

Figure 5C. Effects of seven sediment treatments on reproduction of *Tubifex* in toxicity tests. Bars are means for treatment replicates with pooled-error 95% CIs. Bars labelled with different letters are significantly different by Tukey comparisons.

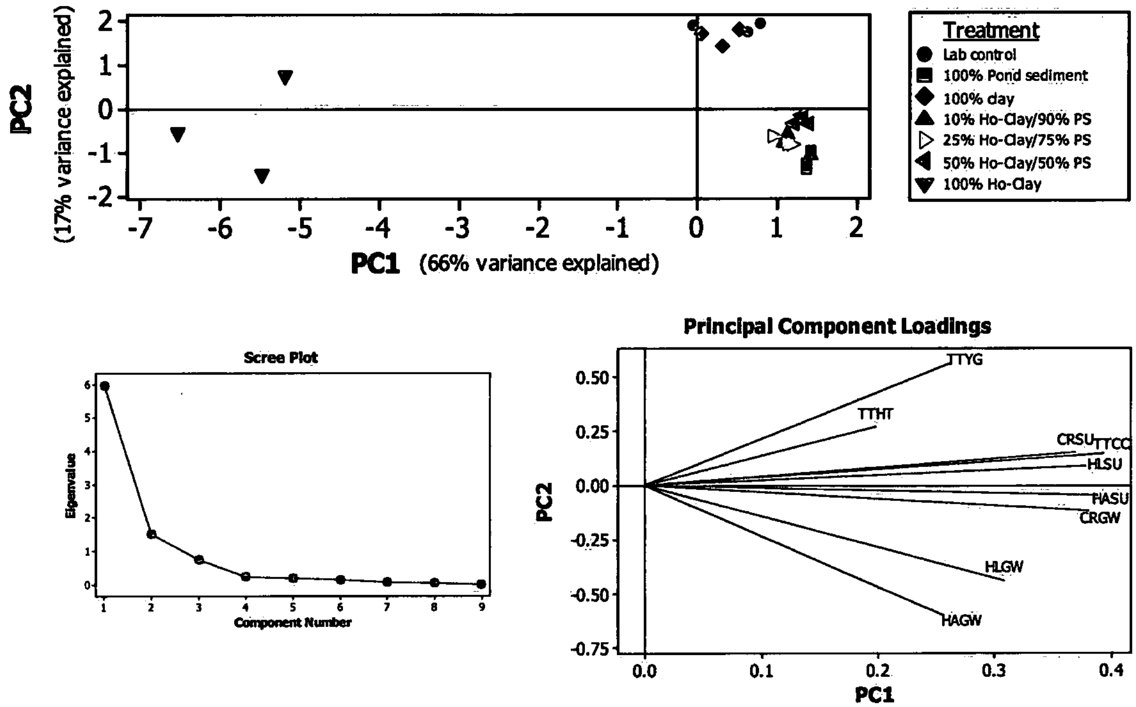

Figure 6. Results of PCA of nine toxicity endpoints from Ho-clay toxicity tests. Upper figure shows variation among treatment replicates in scores for the first two principal components. Scree plot shows amount of variance explained by each component. Loadings plot (lower right) relates the measured variables to the component variables. Endpoint abbreviations: CRSU = *Chironomus* survival; CRGW = *Chironomus* growth; HASU = *Hyalella* survival; HAGW = *Hyalella* growth; HLSU = *Hexagenia* survival; HLGW = *Hexagenia* growth; TTSU = *Tubifex* survival; TTCC = *Tubifex* cocoons/adult; TTHT = *Tubifex* % hatch; TTYG = *Tubifex* young/adult.

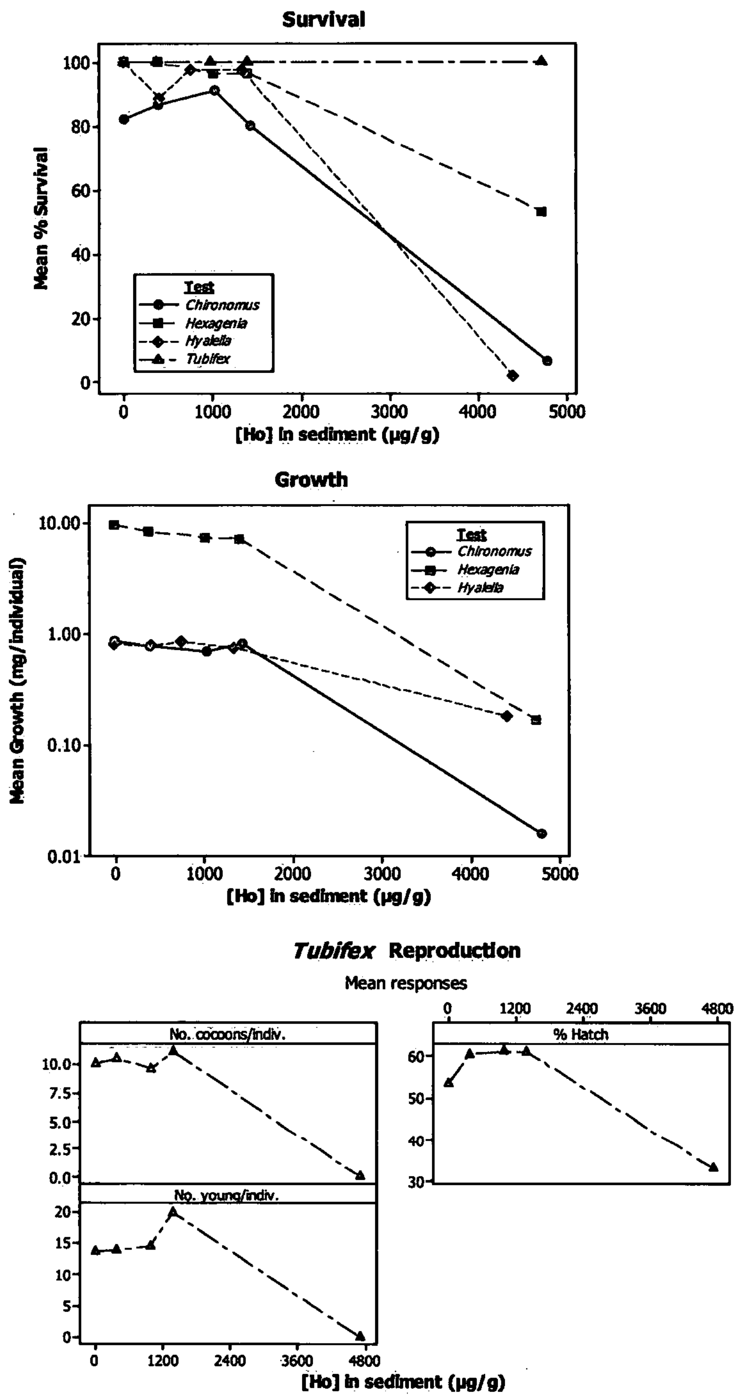

Figure 7. Relationships between toxicity endpoints and Ho concentration in sediment from test beakers for Ho-clay and pond sediment treatments. Note log scale for growth.

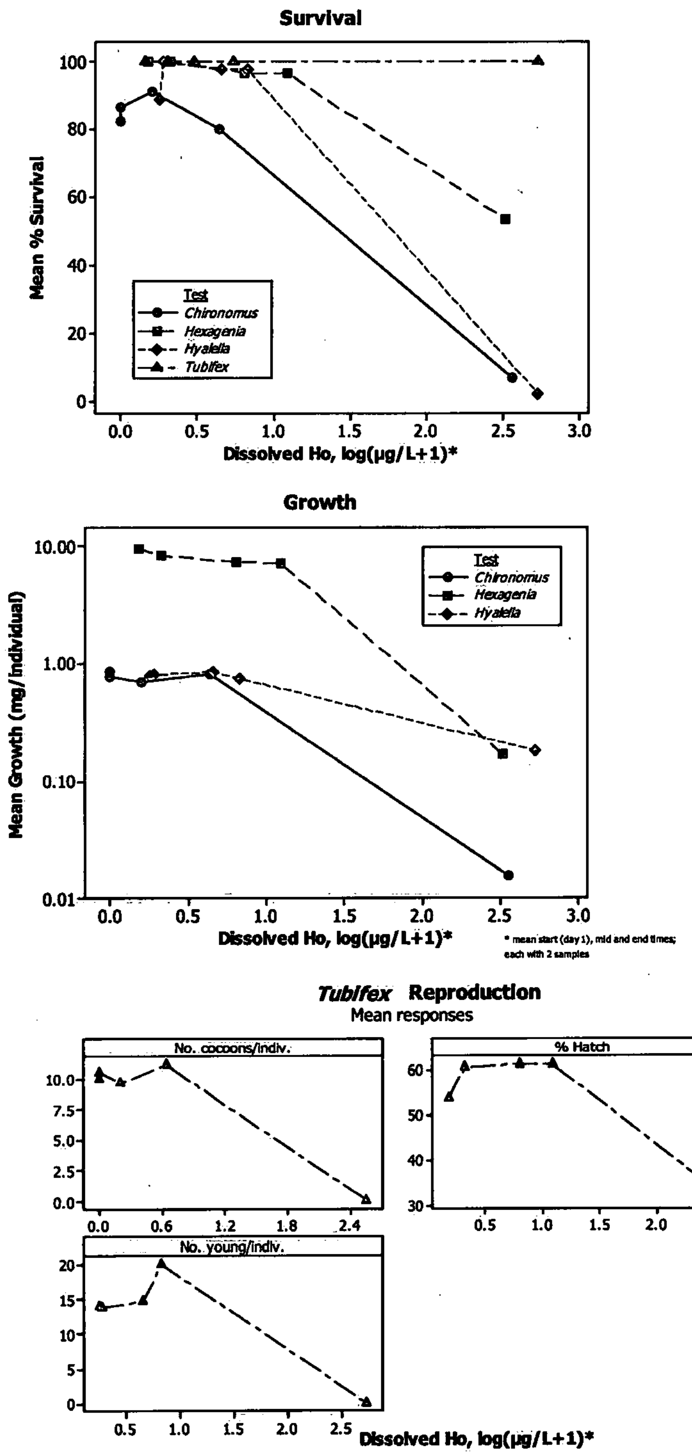

Figure 8. Relationships between toxicity endpoints and Ho concentration in overlying water from test beakers for Ho-clay and pond sediment treatments. Note log scales for growth and dissolved Ho concentration.

Appendix D
Raw Holmium Data

Raw Holmium data for all sediment samples [T = bed sediment core samples (example – T2-15 represents Transect 2 on Figure 8, 15m from shore near inlet), S Reed = Reed bed sediment samples (above water line) and S = shore sample (bed sediment at edge of pond in 10cm deep water].

Sample Name	Northing	Easting	Holmium (µg/g)	Sample Name	Northing	Easting	Holmium (µg/g)
T 1-2	4814226	594546.4	1.39	S Reed-Lower	4814234	594503.6	3.71
T 1-5	4814226	594548.7	0.997	S Reed-Mid	4814237	594508.1	1.72
T 1-10	4814229	594553.1	0.835	S Reed-Upper	4814236	594504.2	1.1
T 2-2	4814229	594541.9	0.959	S1	4814219	594546.5	1.38
T 2-3	4814232	594541.8	1.61	S2	4814237	594519.3	1.24
T 2-10	4814238	594546.2	1.01	S3	4814225	594539.7	2.06
T 2-15	4814241	594550.7	1.39	S4	4814238	594523.8	1.6
T 3-2	4814238	594532.8	0.679	S5	4814226	594555.4	0.968
T 3-3	4814241	594535	1.15	S6	4814228	594537.4	1.94
T 3-5	4814241	594537.2	1.53	S7	4814235	594557.5	0.656
T 3-10	4814244	594539.4	0.874	S8	4814235	594530.6	1.56
T 4-2	4814237	594508	0.608	S9	4814222	594544.2	1.63
T 4-5	4814237	594512.5	11.2	S10	4814241	594521.5	1.03
T 4-10	4814241	594517	3.27	S11	4814237	594517	1.33
T 4-15	4814244	594521.4	3.14	S12	4814234	594514.8	1.27
T 4-20	4814250	594525.8	1.05	S13	4814231	594508.1	3.15
T 4-25	4814250	594528.1	1.06	S14	4814234	594508.1	3.74
T 4-32	4814253	594534.8	0.888	S15	4814234	594505.8	0.686
T 5-3	4814234	594512.6	7.68	S16	4814231	594532.8	2.81
T 5-10	4814241	594514.7	2.69	S17	4814234	594501.3	0.721
T 5-15	4814244	594519.2	1.96	S18	4814274	594462.6	0.542
T 5-20	4814247	594523.6	0.988	S19	4814237	594499.1	0.62
T 5-25	4814250	594525.8	1.05	S20	4814259	594480.8	0.666
T 5-30	4814256	594530.2	1.22	S21	4814238	594526	2.37
T 6-5	4814240	594512.5	6.98	S22	4814240	594494.5	1.43
T 6-10	4814244	594514.7	5.88	S23	4814283	594455.7	0.665
T 6-15	4814247	594514.7	1.68	S24	4814295	594462.3	0.555
T 6-20	4814250	594514.6	0.764	S25	4814308	594486.8	0.669
T 6-25	4814256	594519	0.937	S26	4814293	594502.8	0.668
T 6-32	4814265	594523.4	0.833	S27	4814278	594516.5	1.04
T 7-3	4814237	594512.5	1.95	S28	4814262	594530.2	0.882
T 7-5	4814240	594510.2	1.95	S29	4814250	594543.8	0.768
T 7-10	4814243	594508	2.56	S30	4814244	594550.6	0.751
T 7-25	4814259	594507.7	0.797				
T 7-40	4814277	594507.5	0.474				
T 8-1	4814237	594505.8	2.29				
T 8-5	4814243	594501.2	1.13				
T 8-25	4814262	594496.5	0.803				
T 8-40	4814274	594491.8	0.545				
T 8-65	4814296	594482.5	0.502				
T 9-3	4814237	594505.8	1.61				
T 9-5	4814237	594505.8	1.19				
T 9-10	4814240	594501.3	0.987				
T 9-25	4814256	594492.1	0.831				
T 9-40	4814268	594482.9	0.507				
T 9-65	4814286	594466.9	0.643				

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