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To cite this version:

Kumiko Azetsu-Scott, Phil Yeats, Gary Wohlgeschaffen, John Dalziel, Sherry Niven, et al.. Precipitation of Heavy Metals in Produced Water: Influence on Contaminant Transport and Toxicity. Marine Environmental Research, 2007, 63 (2), pp.146. 10.1016/j.marenvres.2006.08.001 . hal-00562959

HAL Id: hal-00562959

https://hal.science/hal-00562959v1

Submitted on 4 Feb 2011

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Accepted Manuscript

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PII: S0141-1136(06)00174-7
DOI: 10.1016/j.marenvres.2006.08.001
Reference: MERE 3063

To appear in: *Marine Environmental Research*

Received Date: 12 December 2005
Revised Date: 2 August 2006
Accepted Date: 6 August 2006

Please cite this article as: Azetsu-Scott, K., Yeats, P., Wohlgeschaffen, G., Dalziel, J., Niven, S., Lee, K., Precipitation of Heavy Metals in Produced Water: Influence on Contaminant Transport and Toxicity, *Marine Environmental Research* (2006), doi: 10.1016/j.marenvres.2006.08.001

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Precipitation of Heavy Metals in Produced Water: Influence on Contaminant Transport and Toxicity

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ABSTRACT

Produced water undergoes changes in its physical chemistry including precipitation of heavy metals after being discharged and mixed with ambient seawater. Potential impacts of the precipitation of heavy metals on their transport and toxicity were studied using samples from offshore oil production sites on the Scotian Shelf off eastern Canada. Concentrations of aluminum, cadmium, chromium, cobalt, copper, iron, lead, manganese, nickel and zinc were measured in total, particulate and dissolved fractions together with Microtox® tests for assessment of toxicity.

Heavy metals in produced water were transformed from dissolved to particulate phase in a period of hours under oxygenated conditions, and aggregated to larger particles that settle rapidly (>100m/day) over a few days. In addition, there was production of buoyant particles comprised of heavy metal precipitates sequestered onto oil droplets that were transported to the surface.

The particulate fraction was generally more toxic than the dissolved fraction. This was evident at the mixing interface between produced water and seawater where elevated particulate and toxicity levels were observed. Laboratory studies suggest an increase in the toxicity of discharged produced water over time. Time-series experiments showed a sustained toxic response for more than a week following the oxidation of freshly discharged produced water that initially elicited little or no toxic response in the Microtox® Test.

Chemical processes identified in this study, namely precipitation of heavy metals and consequent settling and rising fluxes of particles, will influence the toxicity, the fate and the transport of potential contaminants in the produced water. Therefore, these processes need to be considered in assessment of the environmental impact associated with offshore oil and gas operations.

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INTRODUCTION

Produced water comprising naturally occurring formation water in the oil and/or gas reservoir and seawater injected to maintain reservoir pressure, has been classified as the largest contributor to the offshore waste stream (Krause, 1995), constituting approximately 80% of the wastes and residuals produced from natural gas production operations (McCormack et al., 2001). It is usually a hot, saline reduced water that contains high concentrations of heavy metals, radionuclides, hydrocarbons and ammonia compared to the receiving environment. It may also contain process chemicals such as demulsifers and corrosion inhibitors added during the operation of the well (Somerville, *et al*., 1987). Despite the identification of a multitude of potential contaminants in produced water, regulatory guidelines for its disposal in Canada are solely based on the concentration of residual hydrocarbons (National Energy Board et al., 2002).

The produced water flow from an oil/gas well and its trace chemical content can be quite variable. Data on chemical composition from the PanCanadian Cohasset/Panuke production facility on the Scotian Shelf (SOEP, 1996) indicate that trace metal concentrations in the produced water are 10^2 to 10^5 times those in seawater. Maximum volume discharge for offshore installations on the Scotian Shelf has been estimated to be of the order of hundreds of cubic metres per day. In consideration of the concentration of potential contaminants, future anticipated discharge volumes and number of production sites, this may represent a substantial input of contaminants to the Scotian Shelf.

Environmental impact of produced water has been assessed by measuring chemical composition of freshly discharged produced water (Tibbets et al., 1992; Jacobs et al., 1992; Flynn et al., 1992), by plume dispersion-transport models (Brandsma and Smith, 1995: Brandsma *et al*,

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1995; Washburn, et al., 1999) and by ecotoxicological measurements (Brendehaug *et al*., 1992; Neff and Sauer, 1995). Because of high variability in its chemical composition, toxicity of produced water shows a wide range of results (summarized by Patin, 1999). A response of vulnerable zooplankton, especially in embryonic and larval stages, has been reported and the accumulation of lipophilic hydrocarbons is suspected to cause a reduced survival rate (Gamble *et al*., 1987; Davies and Kingston, 1992). In California, Osenberg *et al.* (1992) described the effects of produced water on infauna populations near a discharge. Purple sea urchin (*Strongylocentrotus purpuratus*) fertilization tests at the same site showed toxicity for dilution rates as high as 1,000,000:1 (Krause *et al*., 1992). Ecosystem models by Rivkin et al. (2002) and Khelifa et al. (2003) predicted that the discharge of inorganic nutrients (e.g. ammonia and phosphorus) and dissolved organic carbon fractions (e.g. volatile fatty acids) within the produced water stream may alter planktonic community structure.

Rapid dilution of produced water with ambient water is often argued as sufficient to mitigate any impacts on the marine environment. Somerville, et al. (1987) modelled the dilution of produced water discharged from the Brent platform in the North Sea. For a 10,000 m^3/day discharge rate, they estimated a 100-fold dilution at 50 m and a 2,800-fold dilution at 1,000 m from the platform. Furuholt (1996) modelled a 2,000 m^3/day discharge and found a 1,000:1 dilution approximately 50 m downstream of the discharge point. For a 20,000 m^3/day discharge he found a 1,000:1 dilution approximately 500 m from the discharge point. However, Washburn *et al.* (1999) modeled the dispersion of produced water at the Carpinteria production site in California using a buoyant plume model, and found that concentrations can exceed lethal levels for sea urchin fertilization bioassay >1000 m from the discharge site.

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Physical dispersion models of projected discharges from the SOEP wells (SOEP, 1996) indicate that rapid dilution of the discharge will dilute contaminant concentrations to non-acutely toxic levels within very short distances from the discharge points. These models, however, treat chemicals as passive tracers. Produced waters can contain tens to hundreds of milligrams per litre of elements such as aluminum, iron and manganese that will precipitate on contact with oxygenated seawater. Based on produced water concentrations reported for the Venture well in the SOEP project (SOEP, 1996), there could be enough dissolved aluminum and iron to generate >1 g/l of suspended particulate matter (SPM). How important will the transformation of these dissolved metals to precipitates be in sequestering other more toxic contaminants, altering their toxicity, and transporting them by routes other than passive dilution in the receiving waters? The experiments being reported in this paper were designed to address these questions based on 1) measurements of major and trace element concentrations in produced water, 2) experiments to determine the chemical phase transitions that occur when produced water reacts with oxygen and seawater, and 3) toxicity tests with a regulatory assay on the produced water samples and the various chemical fractions generated in the experiments.

MATERIALS AND METHODS

Twenty produced water samples were collected from Aug. 5, 1998 to June 21, 1999 at the Cohasset and Panuke oil production sites on Sable Island Bank, Nova Scotia, Canada (Fig. 1). Water samples were collected by the rig staff using high density, polyethylene bottles (2-4 l) that were pre-cleaned with 6 N HCl, then rinsed with milli-Q water. Most samples were collected in the morning, immediately air-lifted to the Halifax airport and transported to the laboratory. Using this protocol, we could start our experiments within a few hours of sample collection at the

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oil production sites. Sample bottles were modified with a conical plastic insert in the cap that facilitated the collection of a sample without trapping air in the bottle. Most samples arrived in the lab without showing any outward signs of oxidation, however, some did contain trapped air and indications that oxidation had occurred. Flow rates at time of sampling as well as produced water temperatures were recorded by the rig staff, as were hydrocarbon concentrations for many of the samples. Oxygen saturation levels and salinity were measured in our laboratory.

Manipulation of samples including sub-sampling for various experiments and filtration for various analyses was conducted in a glove box purged with nitrogen. Concentrations of Al, Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni and Zn were measured in filtered or unfiltered water samples and in the particulates collected during filtration. Thirty ml water samples were acidified with 30 µl of high purity HNO_3 and analyzed by ICP-MS (PE/Sciex ELAN 6000) without any pre-concentration or separation. Because of the high salt content of the samples, all water samples were diluted with milliQ water (50 to 150 fold dilutions) before analysis. The particulate fractions were collected by filtering aliquots of water through cleaned, tared 0.2µm Nuclepore filters. After rinsing with Milli-Q water to remove salt and drying, each filter was weighed on a microbalance to determine SPM concentration, then digested with 2.0 ml of HNO_3 and 1.0 ml of HF in a Loran teflon bomb (Loring and Rantala, 1992). We used minimum amount of Milli-Q water to rinse the salt, however, the loss of some metals is possible. The bomb was heated inside a plastic pressure chamber in a microwave oven for 45 seconds. The digested solution was heated in a teflon beaker on a hot plate (170-200 ºC) in a clean bench to evaporate the solution to dryness. The inside walls of the beaker were washed down with two 10 ml aliquots of 2% HNO_3, and left to sit for 30 min to allow re-solution of digested metals. Concentrations were measured by ICP-MS. Oxygen was measured using an oxygen meter (Orion, model 840) and

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salinity by refractometer. Toxicity was assessed with the Microtox® Test based on the reduction of bioluminescence by the marine bacterium *Vibrio fischeri* on exposure to toxicants (Johnson, 1997; Qureshi *et al*., 1998; Environment Canada, 1992).

In addition to measurements of chemistry and toxicity of untreated produced water, three separate experiments were conducted to study the changes in composition and toxicity after mixing with seawater, and on exposure to oxygen.

First, a preliminary time series study of settling particulate matter from different mixtures of produced water and seawater was conducted using the produced water sample collected on Sep. 16, 1998. Four sets of dilutions included raw produced water and three mixtures of produced water and seawater at dilution rates of 1:2, 1:10 and 1:100. Filtered seawater (0.2 µm Nuclepore filter) from the Scotian Shelf was used for dilutions. Four dilutions containing different ratios of produced water and seawater were placed in Inhoff glass cones for 148 hours. Sub-samples (50ml) were collected from the bottom of cones at time intervals: 0, 24, 95, 119 and 148 hours and particulate matter concentrations were measured gravimetrically.

Secondly, produced water/seawater interface experiments were conducted to study precipitation, flocculation and settling behaviour of heavy metals. Produced water samples used in these experiments were collected on Sep. 28, Oct. 14 and Oct. 19, 1998. For each experiment, 200 ml of produced water were layered under 200 ml of seawater in Inhoff cones (Fig. 2). In this experiment, seawater was measured into the Inhoff cones and produced water, which has a higher density than seawater, was slowly introduced from the bottom of the Inhoff cones under the seawater layer using a peristaltic pump. The density interface made by this method is stable and mixing is limited by the diffusion at the interface (Azetsu-Scott and Johnson, 1992). This stratification allowed us to observe chemical processes occurring at the interface between

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produced water and ambient seawater under a controlled environment. Two Inhoff cones were set using the Sep. 28 produced water sample to take time series samples at t=3.9 and t=25 hours and three Inhoff cones were set for Oct. 14 and 19 samples for time series samples at t=1.5, 71.5 and 144 hours. Sub-samples were taken from the bottom of the each Inhoff cone (Fig. 2) from two produced water layers (70 ml for L-1 and 90 ml for L-2), one produced water/seawater interface layer (80 ml for L-3) and two seawater layers (90 ml for L-4 and 70 ml for L-5). At the end of the Oct. 14 and 19 experiments, particles adhering to the walls of the Inhoff cones were recovered by washing with 50 ml of distilled water, although some particles could not be removed and still adhered to the walls. Heavy metal concentrations were measured for both particulate and dissolved fractions in each layer during the experiment using the Oct. 14 sample. Microtox® Tests were conducted on unfiltered and filtered samples from each layer.

Thirdly, two experiments were conducted to investigate the effect of oxygen on produced water. Aliquots of 100 ml of produced water were placed in 500 ml high density polyethylene bottles and stirred on a rotating table. Time series samples were taken at time 0 and 1 hour, and 1, 2, 3, 8 and 15 days for produced water collected on Dec. 14, 1998. For produced water collected on Feb. 8, 1999, samples were taken at 0 and 3 hours, and 1, 2, 3, 4, 7, 10, 14, 16 and 21 days. Heavy metal concentrations in the particulate fraction were measured together with particulate matter concentration, oxygen saturation and microtoxicity tests.

Metal precipitates from several of these experiments were observed using Scanning Electron microscopy with Energy Dispersive X-ray analysis and fluorescent microscopy.

RESULTS AND DISCUSSION

(1) *Temporal variability of heavy metal concentrations and toxicity of source produced water*

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Metal concentrations measured in unfiltered produced water samples (Table 1) clearly show that the concentrations can be very high (as much as 50,000 times ambient seawater) and very variable. High concentrations were especially evident for Cu, Fe and Zn. Enrichment of metal concentration in produced water compared to that in the ambient seawater is Zn>Fe>Cu>Mn>Pb,Ni>Al,Cd>Co. Although the composition of produced water varied widely, some affinity among elements was observed. These include Fe, Mn and Al, which varied in the same manner and showed highest concentrations on Oct. 14, while Cu and Zn co-varied and showed high concentrations for samples collected on Aug. 13 and Oct. 5. Observed concentrations of Al and Fe, elements that are responsible for the formation of precipitates, are lower than anticipated based on previously published data for these fields. Approximately 25-50 mg/l of SPM could be generated from the observed levels of Al, Fe and Mn. The samples were analyzed for metals by ICP-MS after diluting the samples with milli-Q water. As a result the detection limits are not as low as normally expected for analysis of aqueous samples. None of the samples had Cr or Co concentrations above their detection limits (80 and 2 μg/l, respectively). The large number of not detected results would suggest that a more sensitive technique for determination of heavy metals would be preferred. Nevertheless, it is evident that heavy metal concentrations can exceed levels at which toxic effects would be expected. Concentrations of 4.2 mg/l Cu and 26 mg/l Zn are clearly in the potentially toxic range. Copper toxicity to marine plankton is seen at tenths of μg/l (Fitzwater et al., 1982; Coale, 1991) and at even lower levels in laboratory cultures (Gavis, 1983). Zinc is not as toxic, but toxicity to plankton is seen at approximately 10 μg/l (Davies, 1983).

The Microtox Assay is a regulatory biotest for testing the toxicity of environmental samples. It is based on the reduction of light produced by a photo-luminiscent marine bacterium that is

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used in the test system on exposure to toxicants (Johnson, 1997). Results from the Microtox® Test also showed large variation, from 18.7% to >99.0% for unfiltered samples and 16.1% to >99.0 % for filtered samples (Table 2). This can be attributed to the fact that samples were recovered from different sectors of the formation as they were exploited by production operations during the experimental period. Toxicity (EC_{50}) derived from dose response curves is expressed as the percentage of produced water in a test solution that will generate a 50% decrease in bioluminescence. Thus, lower numbers indicate greater toxicity. Some of the non-toxic samples (EC_{50}>99%; no toxicity at the EC_{50} level observed in undiluted samples) did show evidence of a toxic response at the EC_{20} level (>20% decrease in bioluminescence) and these samples were expressed as >99*. EC_{50} values were not achieved in 66% of total and 83 % of dissolved produced water samples. When toxicity was observed, unfiltered samples showed higher toxicity than filtered samples, with the exception of the sample collected on Feb. 8, 1999. The difference between filtered and unfiltered samples inferred that the particulate phase had an influence on toxicity of discharged produced waters. No clear correlation was observed between toxicity results and salinity, temperature, flow rate, hydrocarbon or oxygen concentrations. Despite metal concentrations being much higher in produced water than those in the natural seawater, no significant correlation between toxicity and metal concentrations was observed, indicating that metal concentrations alone may not be responsible for the observed toxicity.

(2) *Formation of particulate matter from produced water*

Although there is no indication in the results described above of a strong link between heavy metal concentration and toxicity, there are substantial quantities of metals such as Al, Fe and Mn that will precipitate on contact with seawater, absorb heavy metals and other chemicals, and

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settle to the bottom, thus altering the transport of the contaminants in the produced water plume and potentially focusing their accumulation onto the sediments. The actual location for this accumulation will depend on the oxidation/precipitation rates of the Al, Fe and Mn and current speeds. A series of experiments was conducted to investigate these chemical reactions and how they affect toxicity. In the first of these experiments, produced water was simply exposed to atmospheric oxygen in 500 ml settling bottles and the production and settling of precipitates was observed. Transformation of heavy metals from dissolved to particulate phase was observed at a time scale of hours in these experiments with raw produced water, and three mixtures at dilution rates of 1:2, 1:10 and 1:100 (Fig. 3). For all dilutions, more than 50 % of the SPM settled within 24 hours. Settling velocity of a particle (≈5 mm in diameter) observed in the undiluted produced water sample was measured directly and it exceeded 100 m/day. Formation and settling of particles would increase the vertical transport of heavy metals by one to two orders of magnitude over that from simple eddy diffusion in the ocean, indicating that chemical processes that alter the physical characteristics (i.e. the settling velocity) of produced water can have an impact on the transport of potentially toxic produced water chemicals.

(3) *Heavy metal dynamics and toxicity at the seawater-produced water interface*

To investigate precipitation, aggregation and settling of metals in produced water during the interaction with ambient seawater in a more controlled manner, produced water and seawater were layered in Inhoff cones (Fig. 2). In these experiments a sharp interface between produced water and seawater layers was clearly visible because of their different refractive indices, and production and removal of particles at and from this interface was evident to the naked eye. Figure 4 shows SPM concentrations and salinity in the five layers for three experiments. Rapid removal of particles from the interface layer, where particle production was active, was observed

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as occasional downward plumes, and resulted in high concentration of particulate matter in L1. The net increase of SPM concentration in the interface and produced water layers during the experiment for the Oct. 14 sample was 50%, while the increase was 71% and 105% for the Sep. 28 and Oct. 19 samples, respectively.

Increased concentrations of SPM in the very surface layer (L5) were observed with time (Fig. 4). Seawater was pre-filtered, therefore, no particles were in L5 at t=0. Salinity variation in this layer was minimal, so the increase in SPM concentrations in L5 indicates an upward transport of particles from the produced water layers rather than mixing of produced water with seawater. Produced water collected on Oct. 14 and 19 contained high concentrations of hydrocarbons, 40 mg/l and 30mg/l, respectively, and white emulsion was evident in the Oct. 14 sample. At the end of the Oct. 14 and 19 experiments, the walls of the Inhoff cones were greasy due to the adhesion of residual particles from the L5 layer. These observations would suggest that buoyant oil droplets with attached particles are responsible for the upward transport to the surface layer. Microscopic observation of the particles in the surface slick confirmed that these particles were oil droplets (Fig. 5-a) with inorganic particles adhering to their surface (Fig. 5-b).

Particulate and dissolved metal concentrations were measured during the experiment using produced water collected on Oct. 14. The initial produced water sample contained visible black particles and concentrations of total Fe, Mn, Ni and Al were high (Table 1). Over the course of the experiment, the concentrations of dissolved Cu, Fe and Zn decreased markedly (~10 fold), while those of Mn decreased only slightly (Figure 6). Much more rapid precipitation is seen for Fe than for Mn consistent with the slower oxidation kinetics of Mn^{2+}.

Particulate Cr and Ni concentrations were positively correlated with particulate Mn concentration (Fig. 7-a), while particulate Al concentration was positively correlated with

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particulate Fe concentration (Fig. 7-b) for both produced water and seawater layers. These results suggest co-precipitation/adsorption of these metals with Fe and Mn oxides. Particulate Pb and Fe concentrations were correlated differently in the produced water and seawater layers, showing enrichment of Pb on particles in the seawater layer that are buoyant oil droplet aggregates transported from the produced water layer (Fig. 8). Similar enrichment of the surface layer particles was observed for Cu and Zn, but not for Al, Fe, Mn, Cr or Ni. It would appear that this mechanism actively transports some heavy metals (Pb, Cu and Zn) to the sea surface, separating them from the subsurface produced water layer and settling metal oxide particles enriched in Cr and Ni.

Coefficients for the pseudo-equilibrium distribution of metals between particulate and dissolved phases ($K_d = [Me_p] / [Me_d]$) are frequently used in descriptions of metal distributions and dissolved-particle interactions in marine systems. In this experiment K_ds for all of the metals increased from low values in the produced water to high values in the seawater layer at the end of the experiment. For Cu, Ni and Zn the final K_ds for the seawater layer were approaching consensus values for pelagic sediment deep water K_ds (as compiled for example by IAEA, 2004). This would imply that concentrations in the experiment are approaching equilibrium with the ambient particles and that dissolved concentrations that are still in excess of normal seawater concentrations would not be decreased further unless particles are removed from the system by settling. For Fe and Pb, dissolved concentrations at the end of the experiment were less than the detection limits employed in this project. If equilibrium implied by the consensus K_ds were achieved, the actual dissolved Fe and Pb concentrations should be ~ 1 mg/l and 0.01 µg/l, reasonable values for shelf waters. These Kds are consistent with the greater particle reactivity and shorter residence times in seawater for Fe and Pb as compared to Cu, Ni or Zn, and similar

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trends between residence times and metal concentration factors for marine plankton observed by Fisher (1986). For Mn, the final observed K_ds were much lower than the consensus values consistent with the fact that Mn concentrations over these time scales are governed by kinetic factors not K_ds.

Microtox® Tests show high toxicity at the produced water/seawater interface (Table 3). The interface layer (L-3) at t=1.5 h and 71.5 h was more toxic than the freshly discharged produced water (t=0), and even at t=144 h, the interface layer retained significant levels of toxicity (EC_{50}=88.8%). Unfiltered samples were more toxic than filtered samples. Particles that adhere to the Inhoff cone wall also showed high toxicity (EC_{50}=67.1%), which further implies the toxicity of particulate phase of metals. The surface layer (L-5) did not show significant toxicity, probably as a result of removal of oil-rich particulates to the surface film or vessel walls. The surface slick, when carefully sampled using a pipette, was found to be highly toxic (EC_{50}=38.0%). There were no clear correlations between EC_{50} and metal concentrations.

(4) *Influence of aging produced water on formation and growth of metal precipitates and toxicity under oxygenated conditions*

Observed changes in SPM concentration, oxygen saturation, Fe and Mn concentrations for produced water samples that were aged in contact with atmospheric oxygen are shown in Fig. 9. Oxygen saturation levels increased more than 80% within several hours and remained constant through the rest of the experiments. Particulate matter concentrations reached steady state in the first day of the experiment for the Dec. 14 sample, while a second phase of increase was observed after 10 days for the Feb. 8 sample. Particulate metal measurements demonstrated that particulate Fe was the major component of particulate matter in both experiments (Fe oxides making up as much as 70-75% of the SPM). Particulate Fe concentration increased with time but

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the Fe content of the SPM was virtually constant at 30-40% for the two experiments except for a decrease to only 20-25% at the end of the Feb. 8 experiment. As expected, particulate Mn concentrations increased more gradually than Fe in these experiments. Qualitatively, the increases in particulate Mn concentrations toward the end of the Feb. 8 experiment mirror the increases in SPM concentration, however, there is insufficient Mn to quantitatively account for the SPM. Particulate Cu and Zn concentrations also increase throughout the experiments, while concentrations of Al, Cr, and Ni decrease.

Physical changes of the SPM were observed using Scanning Electron Microscopy. While the concentrations during the Dec. 14 experiment remained essentially constant after 1 day, morphology changed dramatically. Particles at time 0 were mainly single grains (Fig. 10-a). As time progressed, dissolved metals precipitated (Fig. 10-b), and the particles grew to large compact aggregates by t= 4 days (Fig. 10-c). The majority of these particles were confirmed to be Fe-oxides by energy dispersive X-ray analysis (Fig. 11-b). Particles formed by the attachment of metal oxide particles to oil droplets were also frequently found in the samples (Fig. 11-a).

Toxicity of unfiltered samples increased with time and the peak toxicity occurred one to two days after the experiments were started (Table 4). Reduced but significant toxicity was retained until 8 days later for the Dec. 14 sample and until 14 days later for the Feb. 8 sample. Unfiltered produced water showed higher toxicity than filtered samples in more than 85% of samples. This agrees with results from the measurements and experiments described previously – toxicity is greater for unfiltered than filtered samples and maximum toxicity is observed hours to a few days after the experiments were started. Positive correlation of toxicity and particulate Zn concentration ($p<0.02$) (Fig. 12) indicates that particulate Zn may have some influence on toxicity. Marine bacteria are known to have affinity to large aggregates (marine snow) and

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bacterial concentration is one to three orders of magnitude higher in aggregates than in the surrounding water (Alldredge and Silver, 1988). Luminescent bacteria, used in this study to measure toxicity, may adhere to suspended metal precipitates produced from the oxidation of produced water and become exposed to the enhanced concentration of metals such as Zn, resulting in development of the observed toxicity.

CONCLUSIONS

Our experiments demonstrated that produced water undergoes chemical and physical transformations upon exposure to seawater and oxygen. The principal process is the phase transition of metals from dissolved to particulate form. This transformation occurs rapidly under oxygenated conditions and influences the transport and the fate of metals in produced water. Because the produced water also contains oil droplets, two types of particles are produced, purely inorganic particles that are denser than seawater and settle quickly, and buoyant particles that are aggregates of oil droplets and inorganic particles and rise to the surface.

Toxicity assessment using the Microtox® Test showed that unfiltered samples containing metal precipitates generally had higher toxicity levels than filtered samples. This indicates that the particulate fraction of produced water contains toxic substances that were inhibitory to the primary metabolic function of the bioluminescent bacteria. Zn toxicity seems to be indicated by some of our experiments, but most of the observed toxicity appears to have been caused by an unidentified, presumably non-metallic, toxicant. Our experiments demonstrated that the toxic response elicited by the produced water may increase following exposure to aerobic marine waters, even in cases where the freshly discharged produced water has little or no toxicity. The

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laboratory studies showed that toxicity peaked after the sample was oxidized for one to two days in association with the production of metal precipitates and could last for more than a week.

Chemical processes that were identified in this study are important for the understanding of transport and fate of heavy metals in produced water, and the toxicity of produced water discharges to biological communities. Fig. 13 identifies the major physical and chemical processes that occur when produced water is discharged at an offshore production facility. Initial dilution of the produced water with seawater is accompanied by precipitation of metals and association of some of these inorganic precipitates with oil droplets. These particles will separate from the produced water plume and either rise to the surface or settle to the bottom depending on their aggregation and buoyancy, potentially causing biological effects at the sea surface or in the benthic boundary layer.

Acknowledgement

The authors thank Dr. Peter Strain for comments on the earlier version of the manuscript. This work was supported by Panel of Energy Research and Development (PERD), Natural Resources of Canada.

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Figure Captions

Fig. 1 Map showing the produced water sampling location.

Fig. 2 Schematic diagram for produced water/seawater layering experiment using an Inhoff cone.

Fig. 3 Time-series of settled particulate matter from produced water collected on Sep. 16, 1998. Experiments included raw produced water and produced water diluted with seawater at 1:100, 1:10 and 1:2 ratios with a total volume of 400 ml. Cumulative particulate matter amount (mg) was plotted against time. Particles at t=148 hours (last points) indicate those adhered to the wall of settling bottles washed off with 50 ml super Q water after all samples were drained.

Fig. 4 Time series study of particulate matter concentrations and salinity in 5 layers in the Inhoff cone experiments using produced water collected on September 28 (A), October 14 (B) and October 19 (C).

Fig. 5 Verification of oil droplets with metal precipitates within the surface slick of the seawater layer using light microscopy with UV epi-fluorescence illumination (A) and phase contrast microscopy (B).

Fig. 6 Concentrations of Fe, Mn, Cu and Zn in dissolved and particulate fractions in each layer during the time series experiment using the produced water collected October 14. Concentrations of particles attached to the walls of Inhoff cones were calculated from differences between total metal concentration at t=0 and those at t=1.5h, 71.5 and 144 h.

Fig. 7 (a) Co-precipitation of Cr and Ni with Mn. For Ni, Y= 0.89X+208.89, r^2=0.84. For Cr, Y= 0.61X+103.02 , r^2= 0.66, (b) co-precipitation of Al and Fe. Y=0.15X-6.03, r^2=0.53

Fig. 8 Relationship between particulate Pb and Fe concentrations in produced water and seawater layers. For seawater layer, Y=0.88X-24.48, r^2=0.5 and for produced water layer Y=0.39X-18.61, r^2=0.66.

Fig. 9 Time series of particulate matter concentration, oxygen saturation and particulate Fe and Mn concentrations during aging experiment using produced water samples collected Dec.14, 1998 and Feb. 8, 1999.

Fig. 10 Scanning Electron Microscope observations of changes in the size of metal precipitate aggregates formed during the experiment using the produced water collected on December 14 at t=0 (a), t=1d (b) and t=4d (c).

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Fig. 11 Environmental Scanning Electron Microscopy (ESEM) coupled with Energy Dispersive X-ray analysis to illustrate and characterize the (a) precipitation of Fe around oil droplets and (b) Fe oxide. Sample was collected during the aging experiments.

Fig. 12 Relationship between toxicity and particulate Zn concentrations.

Fig. 13 Schematic diagram for chemical and physical processes influencing the transport and the fate of produced water after it is discharged.

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Tables

Table 1. Chemistry data for produced water samples

Date	units	Aug 5 1998	Aug 13 1998	Sep 16 1998	Sep 28 1998	Oct 5 1998	Oct 14 1998	Oct 19 1998	Nov 25 1998	Dec 14 1998	Jan 13 1999	Seawater values
Flow	m^3/d	9472	10250	10347	10545	10839	3020	7050	10000	11300	3870	
Temp	ºC	70	69	67	67	67	77	63	65	67		
HC	mg/l	19				19	40	30			28	
O_2	%	20								19	27	
Sal		87	90	90	90	89	94	89	87	88	91	
Al	µg/l	<80	180	<80	<80	270	2100	<80	<80	<80	<80	1.0#
Cd	µg/l	<2	4.5	<2	<2	6	<2	<2	<2	<2	3	0.01-0.04*
Cu	µg/l	<8	1500	93	69	4200	420	<8	<8	<8	9	0.18-0.31*
Fe	mg/l	15	15	12	14	14	28	14	12	14	15	0.25-1.10*
Pb	µg/l	<8	22	<8	<8	45	12	<8	<8	<8	<8	0.02+
Mn	µg/l	1400	1600	1400	1400	1400	2700	1300	1300	1500	1600	0.24-0.45*
Ni	µg/l	<20	75	<20	<20	100	420	<20	<20	<20	<20	0.2*
Zn	µg/l	90	7200	320	220	26000	4100	270	90	90	90	0.21-0.64*

Flow, temperature and hydrocarbon (HC) data provided by PanCanadian.
: Moran and Moore (1989)
* : Yeats (1987)
+ : SOEP (1997)

Table 2. Microtoxicity test results for the source produced water. Expressed as EC_{50} values (percentage of produced water in test solution that produces a 50% reduction in the bioluminescence of the test organism).

Collection date	unfiltered	filtered
Aug 5, 1998	>99	>99
Aug 13, 1998	>99*	
Sept 28, 1998	>99	>99
Oct 5, 1998	>99*	>99*
Oct 14, 1998	83.5	>99
Oct 19, 1998	18.7	59.8
Nov 25, 1998	90.1	>99
Dec 14, 1998	>99*	>99*
Jan 13, 1999	66.1	>99*
Feb 1, 1999	>99*	>99*
Feb 8, 1999	>99*	16.1
Feb 15, 1999	>99*	>99*

*Toxic response at the EC_{20} level (>20% decrease in bioluminescence at 100% produced water test concentration).

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Table 3. Microtox results for produced water/seawater layering experiment – Oct 14, 1998.

Time (h)	Layer	Total – EC_{50} (%)	Filtered – EC_{50} (%)
0	PW	83.5	>99
1.5	L-1	89.7	>99
	L-2	88.8	>99
	L-3	69.6	>99*
	L-4	>99	>99
	L-5	>99	>99
71.5	L-1	51.6	94.0
	L-2	>99*	>99
	L-3	80.4	>99
	L-4	>99*	>99
	L-5	>99*	>99*
144	L-1	>99*	>99
	L-2	>99*	>99
	L-3	88.8	>99
	L-4	>99	>99
	L-5	>99	>99
	wall	67.1	>99*

*Toxic response at the EC_{20} level (only >20% decrease in bioluminescence attained in undiluted produced water samples).

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Table 4. Metal in particulates and toxicity results for the seawater aging experiments.

time	Al	Cd	Cr	Co	Cu	Fe	Pb	Mn	Ni	Zn	EC_{50}	EC_{50}
	mg/g	µg/g	µg/g	µg/g	µg/g	%	µg/g	mg/g	µg/g	µg/g	total	filtered
Dec. 14												
0	1.7	0.28	210	0.91	21	38	120	0.23	12	73	>99*	>99*
1h	1.1	0.18	180	34	23	39	170	0.29	38	210	84.2	80.5
1d	0.63	0.23	130	4.8	28	36	76	0.68	17	410	29.4	57.6
2d	0.63	0.52	130	2.1	32	36	84	0.71	36	410	58.3	84.3
3d	0.67	0.15	100	3.2	51	36	90	0.71	11	450	72.8	98.0
8d	0.54	0.19	91	2.0	36	36	89	0.63	19	330	71.1	80.2
15d	0.48	0.16	94	2.9	46	35	84	0.54	8.3	230	>99*	>99
Feb. 8												
0	2.9	0.21	250	1.2	14	29	28	0.29	130	26	>99*	16.1
3h	1.3	0.14	150	1.0	5.6	36	18	0.54	62	150	90.4	98.8
1d	1.3	0.35	180	1.6	8.8	33	19	0.69	25	250	76.6	>99*
2d	1.3	0.45	220	1.1	9.4	34	20	1.1	59	270	64.0	65.4
3d	1.1	0.30	150	0.85	8.9	34	18	1.4	48	230	68.7	>99*
4d	1.3	0.41	140	1.0	9.9	37	22	1.5	59	300	65.6	74.3
7d	1.2	0.29	150	2.4	23	33	24	1.7	38	270	79.5	>99
10d	1.2	0.08	130	1.7	11	32	22	2.5	35	260	70.6	63.7
14d	0.78	0.07	110	0.78	9.9	21	17	2.7	16	190	75.7	>99*
16d	0.99	0.10	130	1.1	13	24	27	2.3	96	200	>99*	>99*
21d	1.1	0.94	150	0.66	62	23	20	1.6	21	200	>99*	>99*

*>20% decrease in bioluminescence at 100% PW test concentration.

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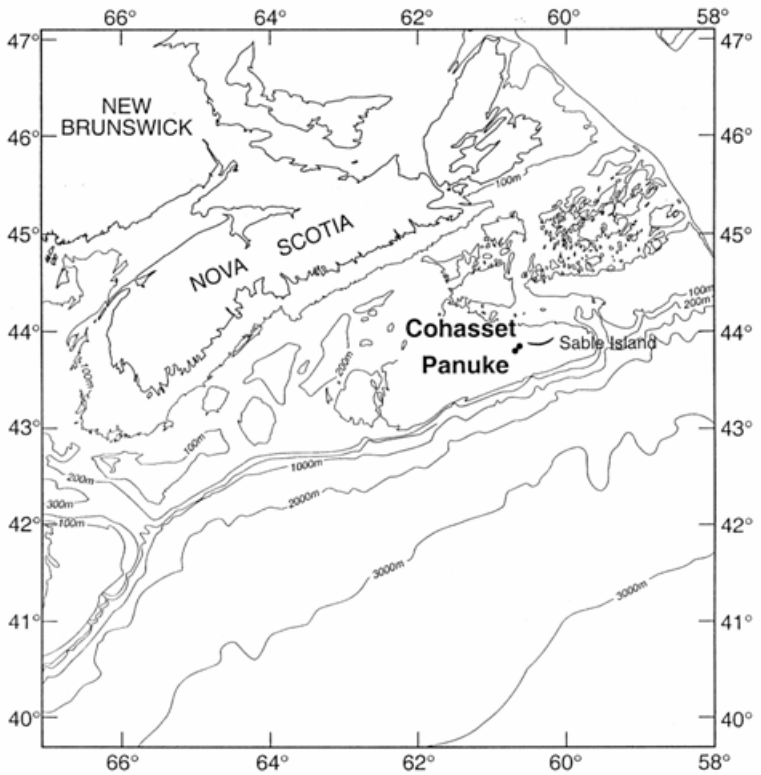

Fig 1

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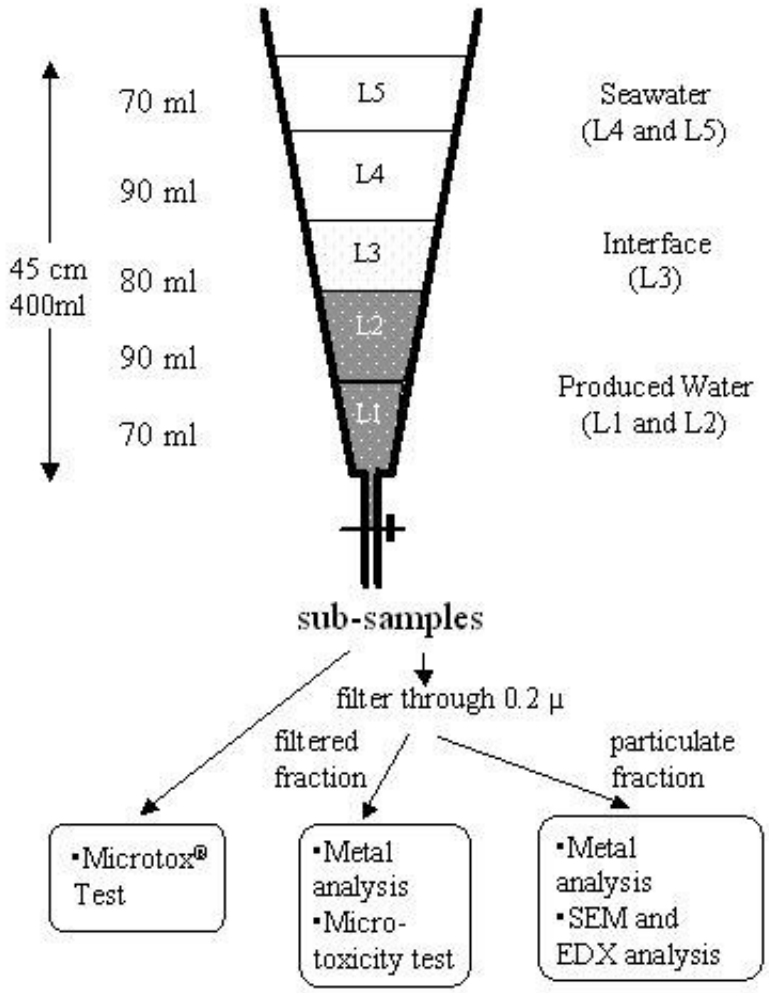

Fig. 2

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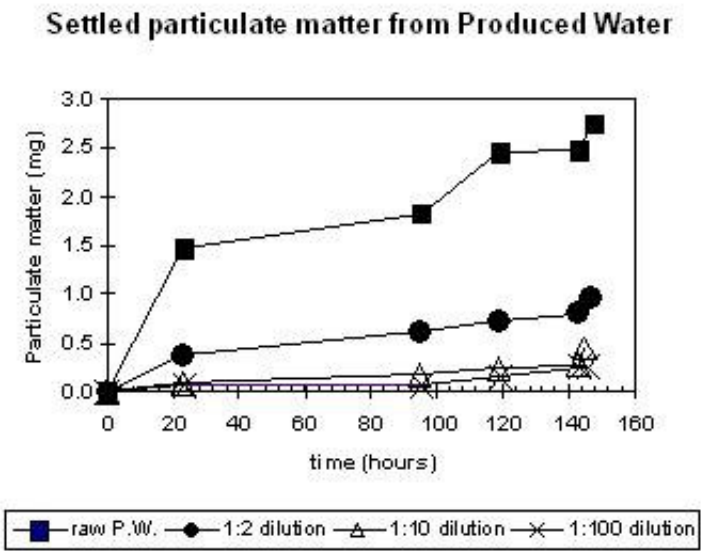

Fig. 3

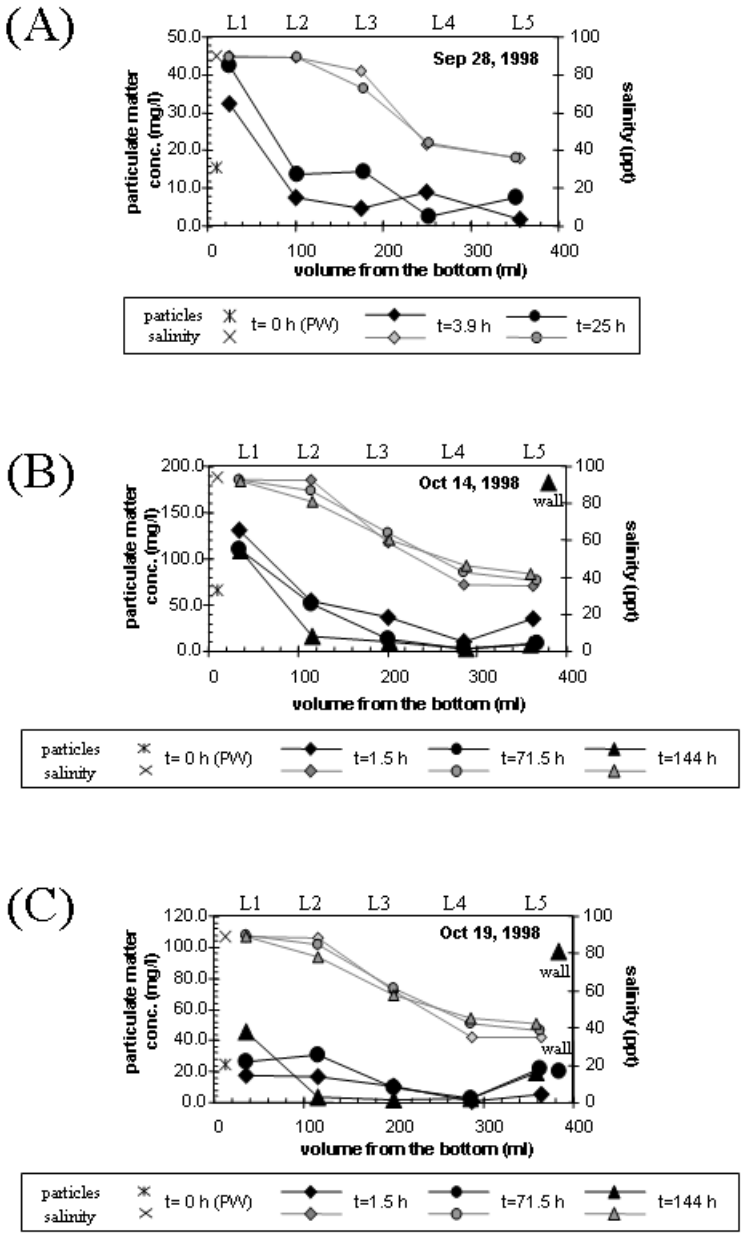
(A)
L1 L2 L3 L4 L5
Sep 28, 1998
particulate matter conc. (mg/l)
salinity (ppt)
volume from the bottom (ml)
particles
salinity
t= 0 h (PW)
t=3.9 h
t=25 h
(B)
L1 L2 L3 L4 L5
Oct 14, 1998
wall
particulate matter conc. (mg/l)
salinity (ppt)
volume from the bottom (ml)
particles
salinity
t= 0 h (PW)
t=1.5 h
t=71.5 h
t=144 h
(C)
L1 L2 L3 L4 L5
Oct 19, 1998
wall
wall
particulate matter conc. (mg/l)
salinity (ppt)
volume from the bottom (ml)
particles
salinity
t= 0 h (PW)
t=1.5 h
t=71.5 h
t=144 h

Fig. 4

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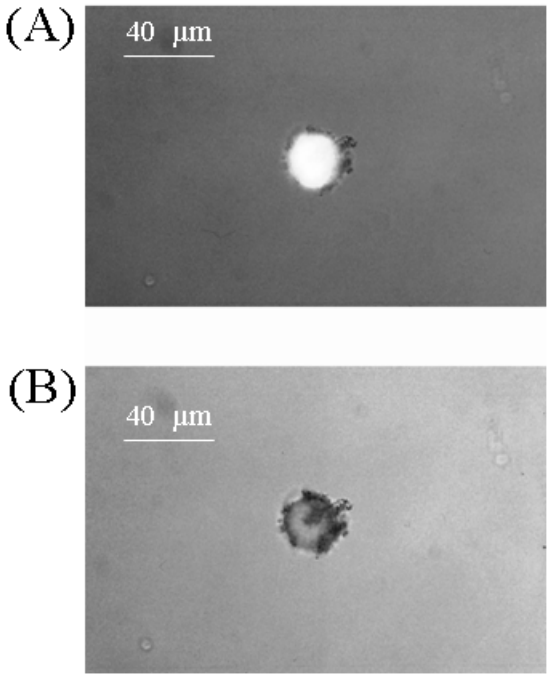

Fig. 5

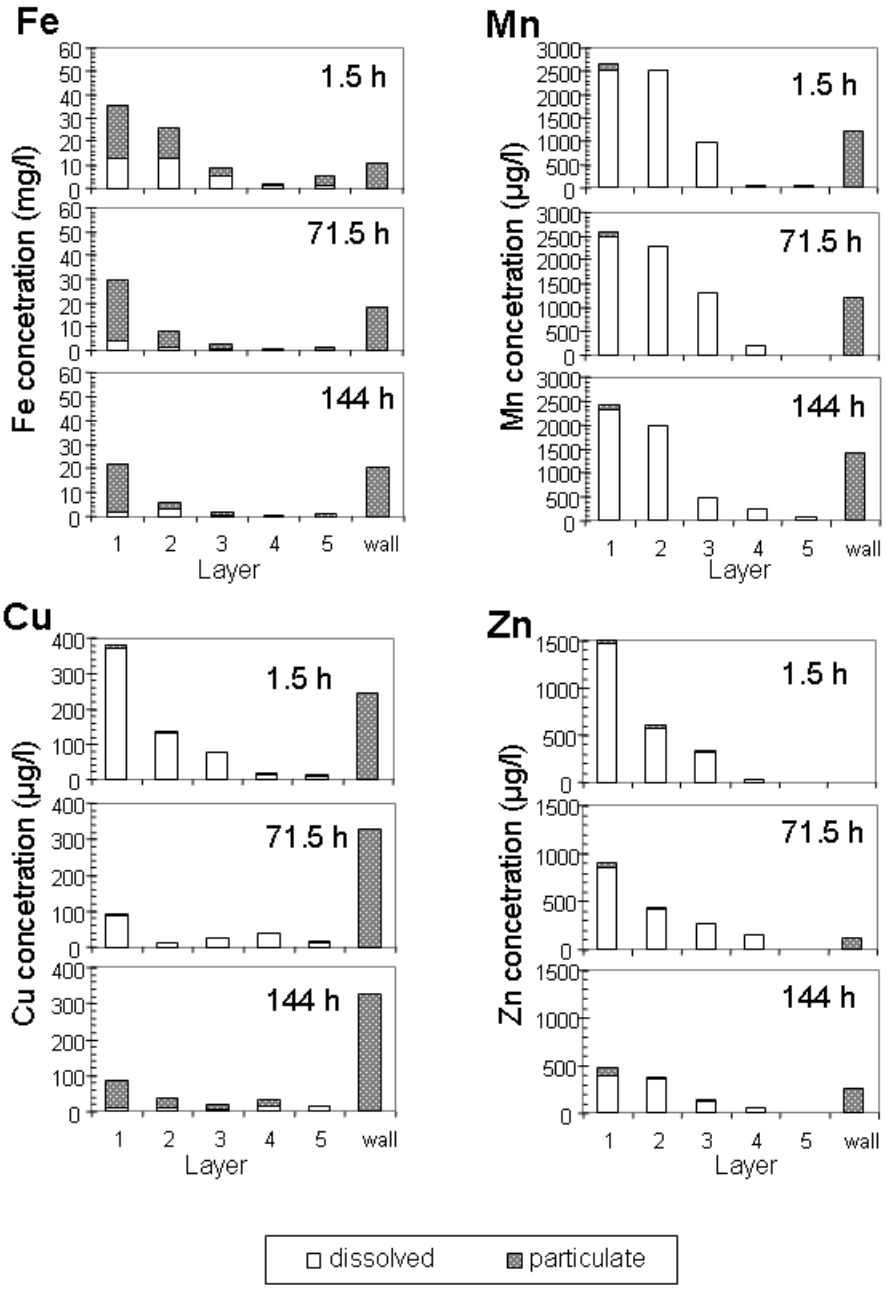
Fe
Fe concetration (mg/l)
1.5 h
71.5 h
144 h
Mn
Mn concetration (µg/l)
Cu
Cu concetration (µg/l)
Zn
Zn concetration (µg/l)
1 2 3 4 5 wall
Layer
dissolved
particulate

Fig. 6

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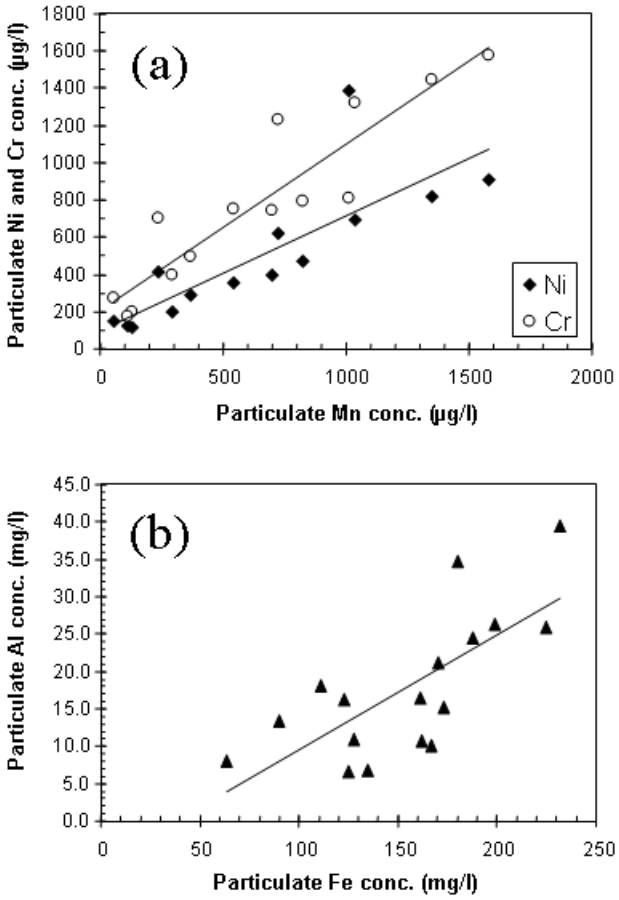

Fig. 7

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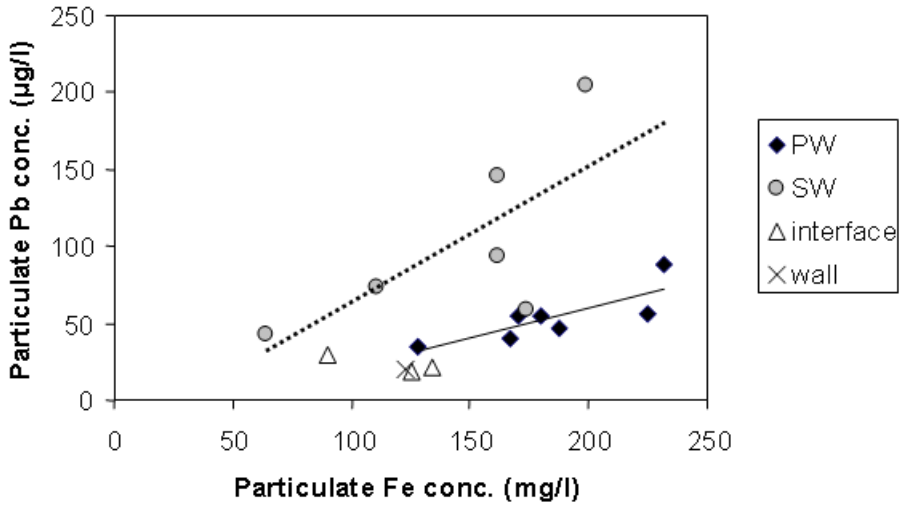

Fig. 8

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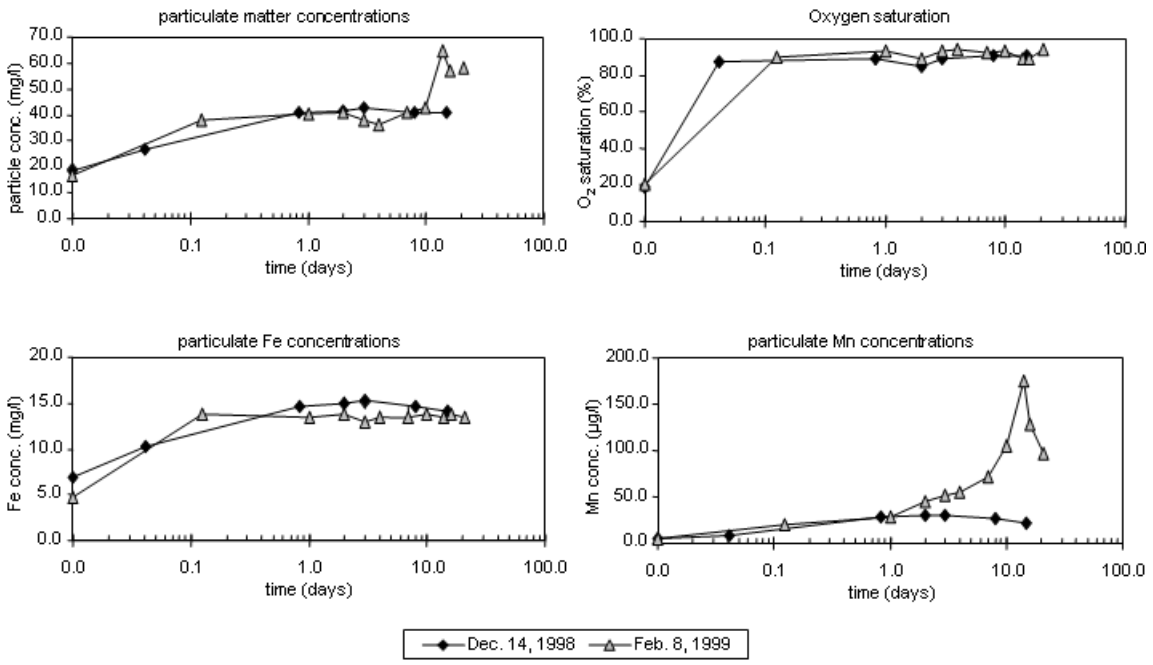

Fig. 9

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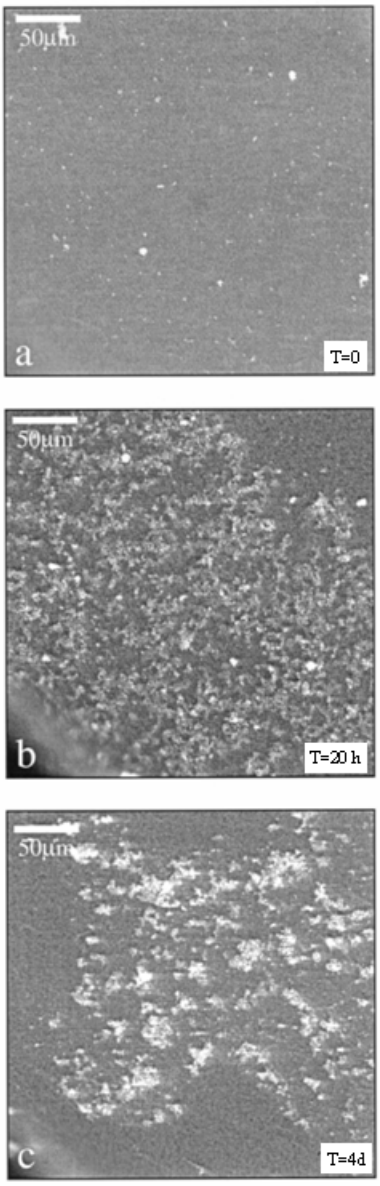

Fig. 10

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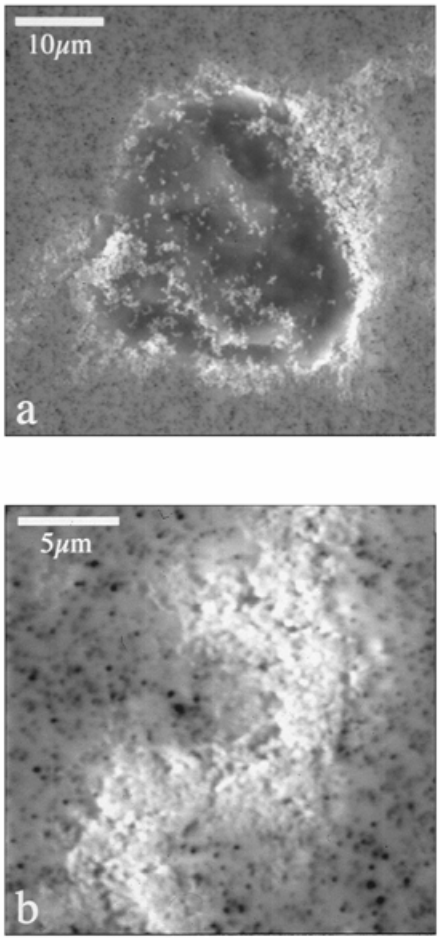

Fig. 11

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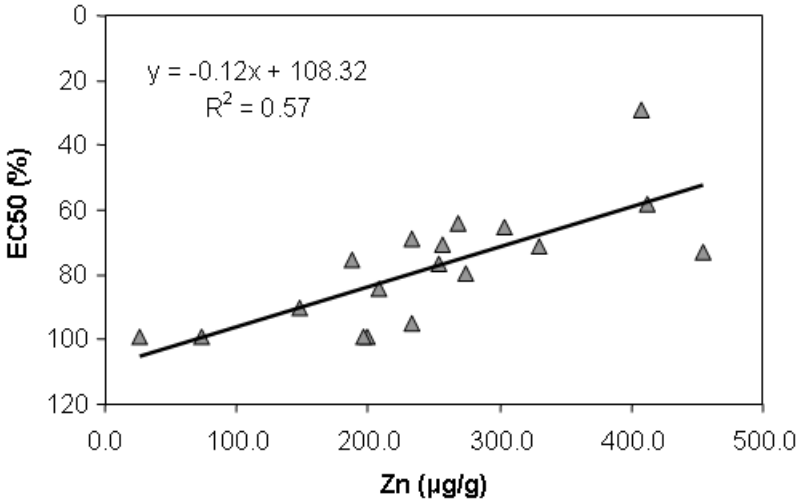

Fig. 12

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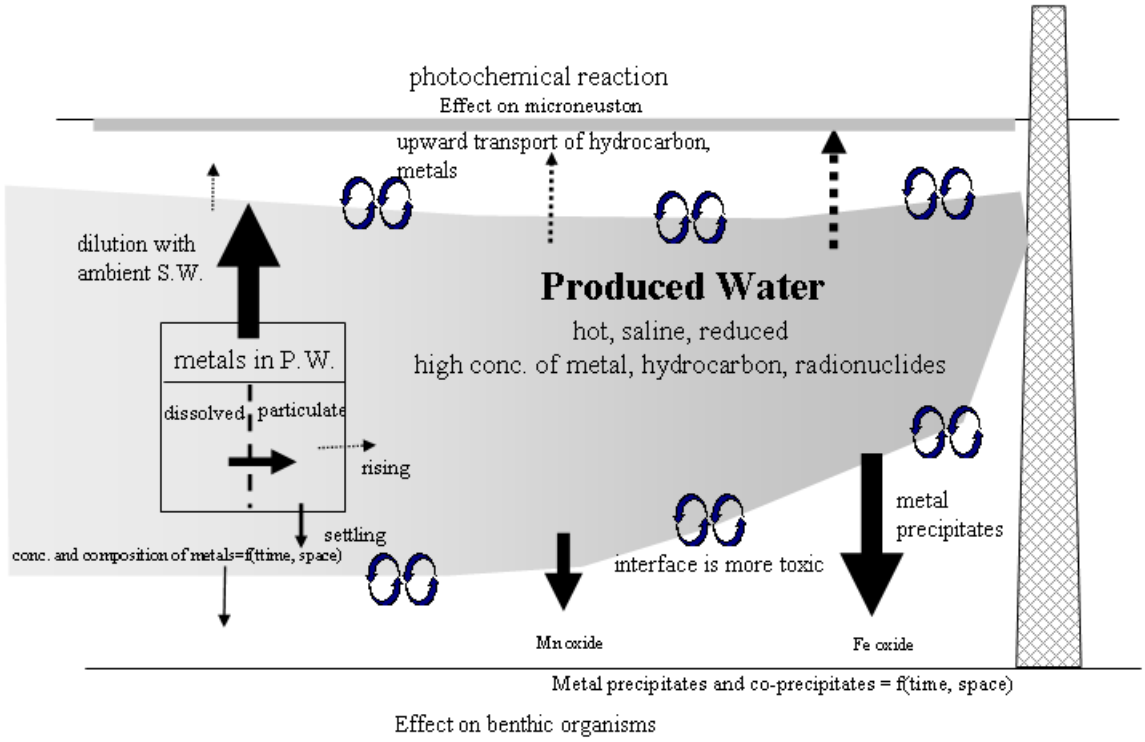

Fig. 13

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