Chapter 13
A New Approach to Tracing Particulates from Produced Water

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Abstract It has been recently discovered that precipitates form when produced water is diluted with seawater. These precipitates are more toxic than the dissolved fraction, can flocculate and sink to the bottom, or can coalesce onto microscopic oil droplets and rise to the surface. This represents new pathways that could bring potentially toxic substances to the surface or bottom where marine life is concentrated. The surface or bottom concentration of toxins and their slow two-dimensional dispersion present potential biohazards that should be evaluated. We present a novel, proven, patent-pending technology specifically designed to trace near-surface or near-bottom particulates to greater distances and dilutions than other measurement technologies can achieve, and present preliminary results demonstrating the effectiveness of the system. We propose a method to experimentally determine the pathways and dilution factors of particulates from oil production platform produced water discharges.

Abbreviation

MAP magnetically attractive particle

1 Introduction

A mixture of oil, gas, and water comes from petroleum reservoirs and is separated in early stages of production. The water, termed "produced water," contains high concentrations of dissolved minerals and emulsified oil droplets and is diluted with seawater before being released from ocean production platforms. The plume is diluted with ambient seawater prior to discharge into the surrounding sea, where it is further diluted by turbulence and ambient currents. Canadian regulatory standards specify only that hydrocarbon concentration at the discharge point not exceed 30 ppm, which can be met by pre-discharge dilution, and do not regulate total quantities of released hydrocarbon or minerals. Post-release dilution and pathways of produced water are rarely measured or quantified. The approach proposed here can accurately track the fate of particulates from produced water, giving the relative

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probability of transport to various locations and distances from release. Knowledge of the produced water plume properties can be incorporated to give quantitative estimates of transport, and knowledge of the ambient currents will then give quantitative estimates of concentration.

Azetsu-Scott et al. (2007) found in laboratory experiments that produced water undergoes changes in its physical chemistry, including precipitation of heavy metals, after being mixed with ambient seawater. The particulate fraction was generally more toxic than the dissolved fraction, showing 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. The precipitates tended to aggregate and sink, and there was production of buoyant particles comprised of heavy metal precipitates sequestered onto oil droplets that were transported to the surface. The combination of

- increased toxicity following dilution-induced oxidation,
- rapid transport to both the surface and the bottom where living organisms concentrate,
- slower dilution due to the produced water being near the surface or bottom, and
- slower dispersion in two dimensions in comparison with three

suggest that the heavy metals in produced water may be more toxic than originally believed and have physical pathways that allow them to become concentrated in regions of high environmental sensitivity. These new findings raise the possibility that dilution may not be a sufficient method to deal with produced water from offshore oil platforms. In addition to studies of the changes in physical chemistry and potential for toxicity that occur when produced water is mixed with seawater, it is important to be able to trace the particulate products, both surface and benthic, from existing produced water plumes to assess their fate and dilution factors. Both approaches will be required to accurately assess the potential impact on aquatic life.

Conventional tracing technologies (drifters, current meters, dyes and chemical tracers, survey vessels, and numerical models) are expensive and suffer many time–space limitations, yet models of a dispersing system need appropriate observations sufficient for testing and validation. Dye studies are prohibitively expensive in terms of vessel time. Current meters provide information about currents at a few locations, but do not provide sufficient spatial resolution to deduce Lagrangian paths. Drifters provide Lagrangian paths, but it is the path appropriate to large drifting bodies, not small particles, and their expense precludes their use in large numbers. Dye can be followed in the near field, (DeBlois et al. 2007) but cannot be detected at long distance or times from the source because dilution rapidly reduces the concentration to below detection threshold (Wells, Bailey and Ruddick, 2011). While dye can be detected with purpose-built moored instruments, their expense precludes their application in even moderate numbers. The default approach, sampling from a moving vessel, suffers greatly from the "moving target" problem: the plume tends to move and disperse more rapidly than it can be mapped, and synoptic surveys are prohibitive. Dye is moreover inappropriate for tracing particulates, since it remains dissolved in the water column, dispersing and moving differently from surface or near-bottom particulates. The approach we propose below does not have these deficiencies, has been shown to trace fluid dispersion over distances of ~10 km, and with appropriate accompanying observations, promises to yield quantitative results.

2 A Novel Tracing Technology

A new, patent-pending (Ruddick and Taggart 2006) technology for aquatic environmental tracing is based on small, design-size, design-buoyancy, environmentally benign particles that can be released in either an instantaneous or a time-release fashion from one or more spatial locations. They drift and disperse in the surface (or near-bottom) layer of the ocean, to be collected (sampled) using inexpensive autonomous moored magnetic collectors. The concepts, particles, and collectors form an inexpensive system for directly determining particle dispersal at a range of temporal (minutes to months) and spatial scales (meters to 1000s km^2) in virtually any liquid.

The magnetically attractive particles (MAPs; Fig. 13.1) combine glass microspheres for floatation with fine magnetite plus a binding agent and pigment. Proportions can be adjusted to achieve the desired particle-specific gravity, ranging from positive buoyancy to trace floating particulates to negative buoyancy to trace sediments. The size can be adjusted, but we currently employ the 300–500 μm range, which allows for easy counting of collected particles.

The collectors (Fig. 13.2) consist of plastic flow-through tubes with rare-earth magnets strategically placed such that any MAP will be caught and retained with

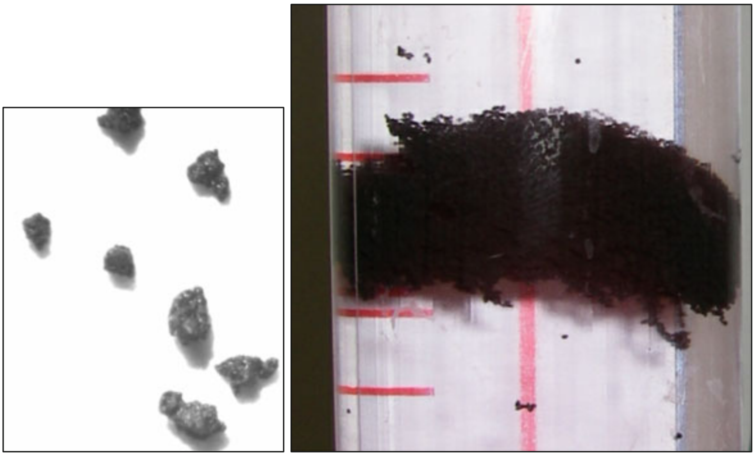

Fig. 13.1 Magnetically attractive particles (MAPs) in the 300–500 μm size range (*left panel*) and suspended at a specific gravity near 1.02 (precise values not known for this sample) in a density gradient settling column (*right panel*); size and specific gravity can be adjusted during manufacture

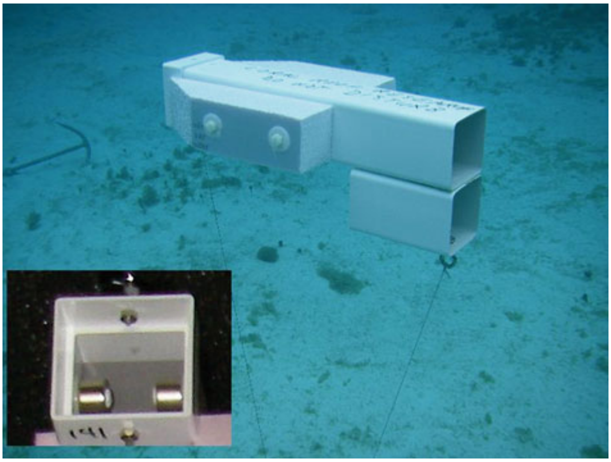

Fig. 13.2 MAP collector in situ on the Belize Barrier Reef, September 2007, with inset showing detail of the collector mouth and magnets

greater than 90% probability in 1 m/s currents. Polyurethane extruded foam is attached to provide floatation, allowing the collectors to be moored prior to particle release. The collectors are autonomous, inexpensive, require no power supply or technical expertise to deploy and use, and they automatically vane into the flow.

In operation, collectors are moored at locations of interest prior to a release. This can be done in good weather, and their simplicity and robustness ensures their likely survival in the event of poor weather. Their low cost means that the number of sample locations is mainly limited by the time required to set and recover the moorings. At the start of an experiment, particles are released in one or more locations, either in an instantaneous release or over a time chosen to sample a variety of flow conditions (e.g., over one or more tidal cycles). During the time of dispersal and particle collection, typically several days to a week, it is possible (but not necessary) to sample the plume using conventional net tows guided by drifters. We emphasize that this is expensive in terms of vessel time and provides limited ancillary information. The collectors are then retrieved and the numbers of particles from each release location are counted in the laboratory.

The system has several advantages over conventional tracing technologies:

It is exceedingly economic. In environmental field applications, the collectors negate the use of expensive instrumentations and their spatial limitations and/or ship time for surveying an ever-increasing area with an ever-diminishing signal from conventional tracers. The low cost of the collectors allows a large number of mooring locations for sampling. A single particle and collector experiment is far cheaper than developing a numerical flow model and making the necessary field observations required to validate such models.

It can validate numerical models. A significant limitation in the plethora of numerical flow models used for open ocean systems is the paucity of model validation, particularly with respect to Lagrangian paths. The technology we propose can function across a large range of scales for the validation and improvement of the models.

It offers direct dispersion measurement. This technology offers direct observation of sub-grid scale dispersion; a poorly known quantity that must be accurately parameterized if numerical models are to work well. Typical current measurements (flow sensor arrays, conventional drifters, etc.) provide information at scales too large to provide this information.

It is resistant to weather. The moored collectors continue to work over day to year periods (no power requirements) in all weather and in environments when or where vessels or other technology cannot. The simple and sturdy collectors are similar to lobster pot marker buoys and are dragged beneath the surface and its wave activity, when currents become extreme. In two coral-tracking experiments, collectors survived the passage of hurricanes with minimal losses.

It can accommodate discrimination of multiple sources and multiple sinks. Variations in color and/or size and/or design density of the particles can allow different batches of particles to be released at identical and/or different times and/or locations, or as a series, in liquids or water masses of different densities. Thus, assessing advection and dispersion of particulates to, from, and among a variety of flows, locations, and water masses can be achieved within a single study.

It is suitable for use in difficult or inhospitable environments. Many environments are too difficult and/or expensive to access, to instrument, and to model easily. Inclement weather can obliterate a dye study making the expensive release and initial observations useless.

It is significantly more immune to dilution than dye. Because we are detecting particles rather than dye, particles are either detected or not, are concentrated by the magnetic collectors, and can be detected at larger distances and greater dilution factors than dyes.

It is appropriate technology for tracing particulates. The design buoyancy and small size of the tracer particles makes them float (or sink, in the case of sediments or flocs), drift, and disperse in the same fashion as the particulates they mimic. This cannot be said of any other tracing technology.

The collectors integrate the particle concentration over time. This accumulation allows detection to lower concentration levels so the resulting data are more statistically robust, spatially smooth, and more representative of average dispersion and dilution.

3 Proof of Concept: The Key Largo Experiment

The particle/collector technology was initially inspired by and developed to answer questions about coral reef connectivity – the numerous factors that determine propagation distance from spawning to settlement in corals and the animals that live on the reefs. A prototype experiment in the reef system off Key Largo, Florida was

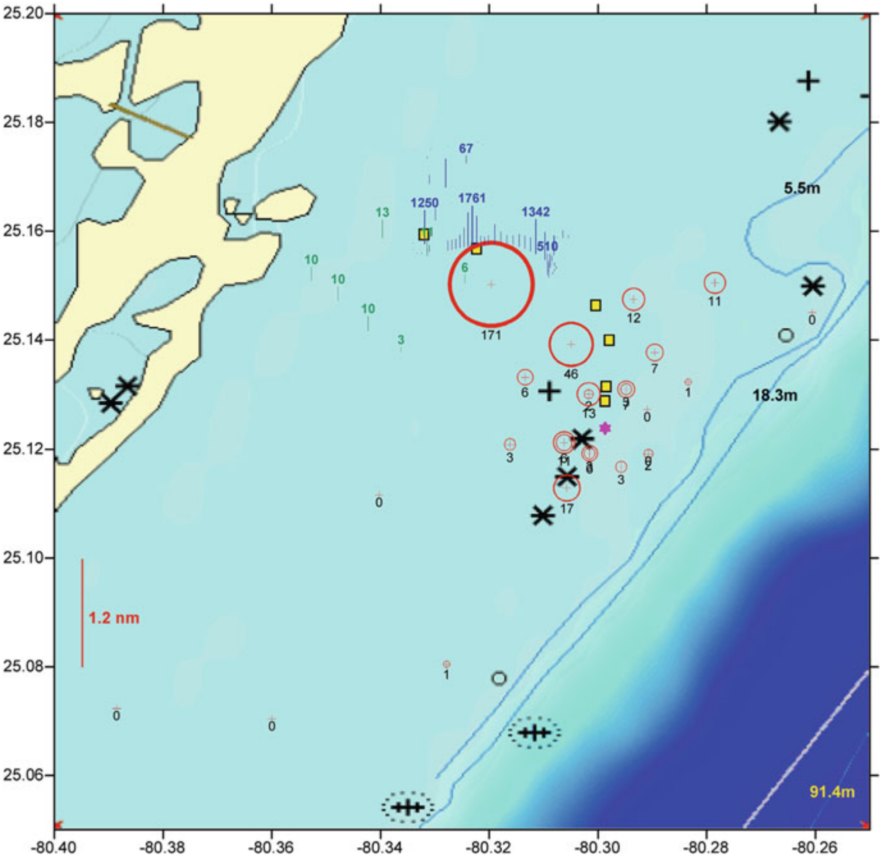

Fig. 13.3 Results from the Key Largo proof of concept tracing experiment; MAPs and drifting buoys were released at the location marked by the *magenta star*; path of one drifter is shown as *yellow squares*; *vertical bars* indicate particle counts (square-root scale) from conventional net tows in the 8 h post-release (*blue*) and ~20 h post-release (*green*); *red circles* indicate numbers (area proportional to count, circle subscript) of particles found in collectors; collectors with zero counts are indicated by a *red* +

planned to use a 40-collector mooring array surrounding a known coral spawning area, where a release of MAPs was planned to coincide with coral spawning. Three hurricanes and 2 mandatory evacuations forced a reduction to an array of 25 collectors and conventional dispersion survey monitoring for <24 h. The severe weather proved the value of the collector technology in that the collectors worked flawlessly when virtually every other aspect of the program was compromised. One collector, moored in <10 m of water, survived and functioned through winds exceeding 45 knots. We believe that the small size and appropriate buoyancy of the collector allowed it to sink beneath the surface during high current events, protecting it from wave damage.

Figure 13.3 shows the release location (magenta star) and the track (yellow squares) of one of four drifters released with the particles that helped to guide the location of conventional net tows. Particle counts from the net tows during the first 8 h post-release (blue vertical bars, square root scale) and longer tows at about 20 h post-release (green) are also illustrated. The small-scale variability on day 1 is due to the released patch being distorted into thin streaks, as confirmed by visual observation. This “streakiness” is a common feature of a tracer patch during initial dispersion (Garrett 1983), makes conventional survey methods more difficult, and makes point sampling of a field so variable as to be almost useless. The particle counts from the moored collectors (red circles, area proportional to particle number) are spatially smooth, almost certainly a result of the advection of individual streaks being swept past collectors and averaged. Notice that significant numbers of particles were collected at locations that were not surveyed by net tows. This was because the survey vessel was mapping the plume as defined by drifter tracks and visual observation, leaving no time for a complete spatial survey – the plume was moving and dispersing faster than the speed at which the vessel could map it.

The comparison of tow collections with moored particle collector counts illustrates the advantage of the MAP/collector technology over conventional dye survey observations. The collectors take observations and average over the whole experiment, even during inclement weather, resulting in a statistically robust, spatially smooth, objective, and synoptic survey and can sample a dispersing plume over longer distances and at lower concentrations than dye.

Prior to deployment, it was discovered that a significant proportion of the particles sank (MAP formulation has since changed), so several near-bottom collectors were deployed. These were found upon recovery to have captured particles from the near-bottom region surrounding the release site, confirming the potential for the MAP/collector system to trace sinking and or sediment-like particles.

4 A Proposed Experiment to Trace Particulates from Produced Water

Produced water can form precipitates rich in heavy metals upon dilution with seawater and consequent oxidation, and the particulate form is more toxic than the dissolved form. These particulates can become concentrated near the surface or bottom where life is most plentiful. The MAP/collector system is an appropriate technology for tracing the path, dispersion, and eventual fate of these potentially toxic particulates; we outline a tracing experiment that could prove its value as a monitoring technology.

An inexpensive but feasible tracing experiment would begin with mooring 25–40 collectors at surface and (optionally) near-bottom at several locations surrounding a production rig out to approximately 10 km distance. Particles would then be released at a known rate into the produced water effluent stream over a minimum of one tidal cycle, so as to effectively sample a variety of flow conditions. Both positively and (optionally) negatively buoyant MAPs could be released, allowing both surface and near-bottom particulates to be traced. After several days, the collector array would be retrieved and the numbers of captured particles counted.

Knowledge of the rate of produced water discharge, rate of discharge of MAPs, and concentration of both MAPs and precipitates in the near field of the discharge would allow the MAP and particulate concentrations to be related, so that particle capture numbers could be related to precipitate concentrations. Furthermore, knowledge of the ambient currents past the collectors would allow particle capture numbers to be related to fluxes and to average concentrations.

How well can we expect this system to perform in such an experiment? The rate of discharge of produced water varies during the lifetime of a well ("Managing Produced Water," Canadian Association of Petroleum Producers information Pamphlet), but a typical value may be 1000 m^3/h, or about 0.3 m^3/s (Zhao et al. 2008). We imagine releasing into a 0.3 m^3/s effluent stream 14 kg ($\sim 10^9$) of MAPs over 12 h duration. The stream will therefore have $10^9/0.3\times 12\times 3600\ m^3 =$ 77000 particles/m^3 at inflow. With a dilution factor of 10,000, ten times more dilute than the normal limit for dye detection, there will be 7.7 particles/m^3. In an ambient current of 20 cm/s (typical for the Nova Scotia and Newfoundland shelves in the absence of storm conditions), a collector with a mount area of 25 cm^2 samples $\sim$50 m^3/day, and so would be expected to catch 380 particles in a day; a substantial number. This suggests that the plume of particles should be detectable at significantly greater distances and dilutions than achievable by dyes.

Another approach would be to estimate the dimensions of the released patch of particles after approximately 1 week dispersion. If the eddy diffusivity in the vicinity of the production rig were $K = 100\ m^2/s$, then at a time of 1 week post release, the dispersed patch would occupy an area of $K_t = (100\ m^2/s) \times (1\ week) = 6\times 10^7\ m^2$, or 60 km^2. If the particles occupy the upper water column (keeping in mind that they float) then the concentration at this late stage of dispersion would be 16.5 particles/m^3. A collector would then be expected to capture 830 particles per day in a 20 cm/s current. The MAP/collector system is therefore expected to track the fate of particulates to dilutions and distances well beyond what can be achieved with dyes or chemical tracers, and at a reasonable cost. Recent (Wells, Bailey and Ruddick, 2011) experiments to trace ballast water released from vessels in Goderich Harbor (ON) used Rhodamine dye to track ballast water to distances of several hundred meters, and particles to track it to distances nearing 10 km. The estimates above and the successful applications of this tracing technology in field experiments suggest that using the MAP/collector system to trace produced water will allow tracing to greater ranges than previously possible, and with appropriate ancillary measurements, would allow fluxes and concentrations of PW constituents to be quantitatively estimated.

5 Summary

We have described a potential environmental problem with produced water (metallic particulate formation and concentration near surface and bottom), and a novel, patent-applied, field-proven technology capable of tracing the particulates to greater distances and dilutions than any other means. This technology is robust, simple, and relatively inexpensive. It can be combined with direct observations of particulates in the effluent stream and near field to result in "calibrated" results. The observations are extremely well suited for testing and/or validating numerical flow/dispersion models used to forecast the fate of dissolved and particulate production rig products.

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