

A continuous monitor for assessment of ^{222}Rn in the coastal ocean

W. C. Burnett,^{1*} G. Kim,^{1**} D. Lane-Smith²

¹ Environmental Radioactivity Measurement Facility, Department of Oceanography, Florida State University, Tallahassee, FL 32306, USA

² DURRIDGE Company, 7 Railroad Ave, Suite D, Bedford, MA 01730, USA

(Received December 13, 2000)

Radon-222 is a good natural tracer of groundwater flow into the coastal ocean. Unfortunately, its usefulness is limited by the time consuming nature of collecting individual samples and traditional analysis schemes. We demonstrate here an automated system which can determine, on a “continuous” basis, the radon activity in coastal ocean waters. The system analyses ^{222}Rn from a constant stream of water passing through an air-water exchanger that distributes radon from the running flow of water to a closed air loop. The air stream is fed to a commercial radon-in-air monitor which determines the concentration of ^{222}Rn by collection and measurement of the α -emitting daughters, ^{214}Po and ^{218}Po , via a charged semiconductor detector. Since the distribution of radon at equilibrium between the air and water phases is governed by a well-known temperature dependence, the radon concentration in the water is easily calculated.

Introduction

One of the persistent uncertainties in establishing marine geochemical mass balances is evaluating the influence of groundwater discharge into the ocean. The major rivers of the world are gauged and well analyzed, thus allowing relatively precise estimates of riverine input to the ocean. Elemental fluxes at hydrothermal systems along mid-oceanic ridges and elsewhere have been studied in considerable detail and although there is still debate concerning the absolute magnitude of hydrothermal discharge, it is well established that oceanic hot springs are significant for the marine budgets of many elements.^{1–3} However, in spite of the recognition that many land-sea interfaces of the world are characterized by leaky continental margins, it is unclear how important these “leaks” are in terms of overall marine geochemical budgets.

The direct discharge of groundwater into standing bodies of water may also have significant environmental consequences because groundwaters in many areas have become contaminated with a variety of substances (e.g., metals, radionuclides, organics). In addition, the slow, yet persistent seepage of groundwater through sediments will occur anywhere that an aquifer with a positive head is hydraulically connected to a surface water body. Thus, almost all coastal zones are subject to flow of groundwater either as submarine springs or disseminated seepage and those adjacent to contaminated areas are likely to experience environmental degradation. Prior studies indicate that groundwater seepage is usually patchy, diffuse, temporally variable, and difficult to quantify.

Furthermore, it is clear that the potential for discharging groundwaters to have a significant impact on surface waters is greatest in regions where fluids may seep into a body of water having limited circulation.

During the last few years, several researchers have been actively pursuing the possibility of using geochemical tracers for regional assessments of groundwater discharge. Research at Florida State University has shown that ^{222}Rn can be a valuable tracer of direct groundwater discharge to the coastal ocean and freshwater lakes.^{4–6} Radon, a naturally-occurring radioactive gas, is an excellent tracer because it is: (1) 3–4 orders of magnitude more concentrated in groundwater than typical surface waters, (2) completely conservative (inert), and (3) known to decay at a rate ($T_{1/2}=3.82$ d) comparable to the time scale of circulation in many coastal settings. Our investigations to date have shown that radon is a very good tool for locating seeps, springs, and other points of discharge on the sea floor. Finding these points of discharge is an important first step, especially when contaminated groundwater may be involved. In addition, a modeling approach may be used to estimate quantitatively the volumes of groundwater actually being discharged if sufficient information concerning other natural sources of radon is available for the study area.^{7–9}

Since fluids discharging from submarine springs and seeps may consist of recirculated seawater as well as fresh groundwater, salinity is not necessarily a good indicator of fluid discharge. For example, “Mud Hole Springs” on the west Florida shelf, discharges significant quantities of water with essentially the same salinity as seawater into the Gulf of Mexico. Detailed analyses have

* E-mail: wburnett@mailers.fsu.edu

** Current address: School of Earth & Environmental Sciences, College of Natural Sciences, Seoul National University, Seoul 151-742, South Korea.

shown that although the original fluid was very likely normal seawater which infiltrated the continental margin, reactions with the surrounding sediment have resulted in a solution with a dramatically different elemental composition.¹⁰ Such discharging fluids, whether fresh groundwater, seawater, hypersaline brines, or mixtures, are typically enriched in ^{222}Rn , ^{226}Ra , CH_4 , nutrients, and other constituents compared to surface waters because of chemical exchange, recoil, and other processes which occur in the aquifer during transit.

At present, specialists can choose from several types of apparatus, based on different detectors, for measuring radon in air and provide spot, integrated, or continuous measurements. In contrast, there are few techniques for measuring low-level radon in water, and virtually none provide continuous measurements in this medium. Although ^{222}Rn in seawater may be measured reliably by classical collection methods and laboratory analysis via radon emanation techniques, the approach can provide information only about water bodies over limited areas and time periods.^{11–12} Ideally, an application such as tracing groundwater flow into the coastal zone would employ continuous measurements of dissolved radon concentrations in surface waters over several different time scales to evaluate short (tidal) to long-term (seasonal) patterns. Assessment of possible temporal trends is important because submarine groundwater flow is known to be extremely variable – in some cases even reversing direction in response to external forcing (tides, change in water table height, etc.). Unfortunately, fine-scale temporal analysis is invariably limited by sampling logistics and time constraints. Furthermore, large-scale mapping of potential seepage sites is hampered by the time requirements involved in the collection and analysis of large numbers of samples. It is desirable, therefore, to develop a detection system or systems which could be deployed and provide monitoring either in real time, for a rapid site assessment, or moored for a more extended periods to provide long-term, continuous measurements at one site.

We have been working on two approaches to this challenge: (1) an “active” pumping system that will continuously strip radon out of a stream of water with subsequent detection of the gas phase by an atmospheric radon monitor, and (2) a “passive” system that is based on diffusion of radon through a membrane into a submerged chamber with an on-board radon detection system. We describe the active system in this paper. The passive approach we are pursuing is similar to a design used initially by TASAKA et al.¹³ for measurement of radon in a pure water tank used for the Kamiokande underground neutrino detector in Japan. That system consists of a charged silicon semiconductor detector in a water-proof stainless steel cylindrical chamber with a provision to allow radon diffusion from the surrounding waters into the chamber via a semi-permeable

membrane. Our efforts to apply such a design for use in natural waters will be reported in a separate publication.

Experimental

The basic approach of the active continuous monitor is equilibration of a stream of flowing water with a stream of air which is being re-circulated through a commercial radon-in-air monitor. We are using a RAD-7 (DurrIDGE Co., 7 Railroad Ave., Suite D., Bedford, MA 01730; Tel: 781-687-9556) for the radon-in-air monitor because it is portable, durable, very sensitive, and operates in a continuous mode. The RAD-7 uses a high electric field with a silicon semiconductor detector at ground potential to attract the positively charged polonium daughters, $^{218}\text{Po}^+$ ($T_{1/2}=3.10$ m; alpha energy = 6.00 MeV) and $^{214}\text{Po}^+$ ($T_{1/2}=164$ μs ; 7.67 MeV) which are then counted as a measure of the radon concentration in air. Importantly, the RAD-7 has energy window settings that allow one to discriminate between all alpha-emitting polonium isotopes including the longer-lived ^{210}Po ($T_{1/2}=138.4$ d; 5.30 MeV) and the ^{220}Rn (thoron) daughter, ^{216}Po ($T_{1/2}=0.145$ s; 6.78 MeV). This feature creates a significant advantage in terms of sensitivity as the background for the specific regions of interest will remain very low, close to zero. If one did monitor the entire spectrum, the inevitable build-up of the long-lived beta-emitter ^{210}Pb ($T_{1/2}=22.3$ y) would result in increased ^{210}Po levels with time which could have a serious effect on background levels. Furthermore, energy discrimination allows one to select either or both the ^{218}Po or ^{214}Po windows for ^{222}Rn assessment. For faster analyses, the ^{218}Po is preferred as it will reach radioactive equilibrium with ^{222}Rn in only about 15 minutes. The ^{214}Po lags behind because of the intermediate beta-emitting daughters, ^{214}Pb ($T_{1/2}=27$ m) and ^{214}Bi ($T_{1/2}=19.9$ m) resulting in an equilibration time of approximately 3 hours.

The water-air exchanger is simply a clear plastic (acrylic) tube which has water flowing through it continuously with a provision for a stream of air which is pumped, either from the built-in air pump in the RAD-7 or an external pump, and re-circulated through a bed of desiccant and then to the RAD-7 for measurement (Fig. 1). An aerator stone provides a stream of fine bubbles to help equilibrate the radon-in-water with the radon-in-air. After some time, the radon concentration in the air reaches equilibrium with the radon in the water, the ratio at equilibrium being determined by the water temperature. According to WEIGEL,¹⁴ this relationship is as follows:

$$a' = 0.105 + 0.405e^{-0.0502T}$$

where a' is the concentration ratio of water to air (about 1:4 at room temperature), and T is the temperature of the water in $^{\circ}\text{C}$.

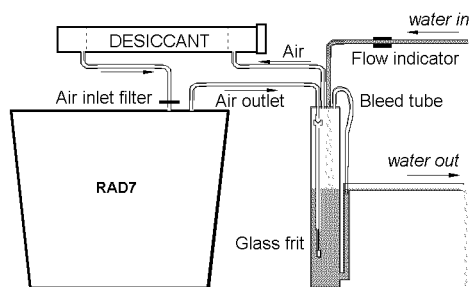


Fig. 1. Diagrammatic view of the experimental setup for the RAD-7 exchanger continuous radon-in-water monitor

Thus, the system is operated by providing a constant stream of water to be analyzed to the exchanger, continuously circulating the air through the closed loop (exchanger-desiccant-RAD7-exchanger), obtaining radon-in-air measurements, and calculating the radon-in-water concentrations based on the well-known temperature dependence. Once set up, this can all be done automatically. The water stream could be from a tap, a submersible pump which is emerged in the coastal water column, or any other source of interest. Depending upon the concentration, the RAD-7 would be programmed to integrate counts (in either or both the ^{218}Po and ^{214}Po windows) over whatever period is necessary for the required precision, or desired for the application at hand. The data are stored in a data logger on-board the RAD-7 and easily downloaded to a PC for final analysis.

Results and discussion

Laboratory tests

For an initial test of the system, we connected the exchanger to the tap water in our laboratory at Florida State University and monitored both the ^{218}Po and ^{214}Po windows on 30-minute cycles over a 24-hour period. The results (Fig. 2) show the anticipated result, i.e., the ^{218}Po in the air equilibrates with the radon in the water stream much faster than the ^{214}Po . As theory predicts, both daughters have apparently reached equilibrium in a little over 3 hours. Interestingly, the ^{214}Po count rate is consistently about 5% higher than the ^{218}Po . In a closed system where both daughters are in radioactive equilibrium with ^{222}Rn , their activity ratio would be very close to 1.0. Apparently, the excess ^{214}Po activity is a result of the unique environment around the charged detector of the RAD-7. This results in two populations of ^{214}Po ions available at the detector surface for decay and counting – those that are produced by decay from the ^{218}Po originally attracted to the detector surface, and those which arrive from the air stream via one of the intermediate daughter products (^{214}Pb , ^{214}Bi). Most

^{218}Po ions in the air chamber of the RAD-7 are deposited onto the detector. A small fraction of these ions are neutralized and remain in air until they decay to ^{214}Pb which is usually ionized and thus attracted to the detector. As long as there is no marked change in an environmental factor that influences ionization, such as humidity, the proportion of charged to neutralized ions should be constant. Humidity has been shown to influence neutralization rates of $^{218}\text{Po}^+$ in gases.¹⁵ The desiccant will maintain the humidity in the chamber at less than ~10% where there are no humidity effects. Thus, once the system has been operating long enough under constant environmental conditions to establish equilibrium (between the air and water phases as well as radioactive equilibrium), both the ^{218}Po and ^{214}Po windows can be used to enhance the sensitivity of the system.

Using the count rate from both windows at equilibrium, the standard calibration for radon-in-air supplied by DurrIDGE for our instrument ([0.085 Bq/l]/cpm for both windows, [0.174 Bq/l]/cpm for ^{218}Po alone), and correcting for the temperature dependence, we calculated a radon-in-water concentration (and 2σ counting error) of 9.27 ± 0.46 Bq/l (250 ± 13 pCi/l) for the tap water based on 42 measurements. For comparison, we collected 4 replicate samples immediately at the end of the experiment and analyzed them using a Wallac 1414 low-background liquid scintillation counter (LSC) with alpha/beta discrimination. The LSC was calibrated for ^{222}Rn measurements by use of a NIST radium standard solution. The LSC result, at 9.65 ± 0.43 Bq/l (260 ± 11 pCi/l) is within the analytical uncertainty of the continuous monitor estimates.

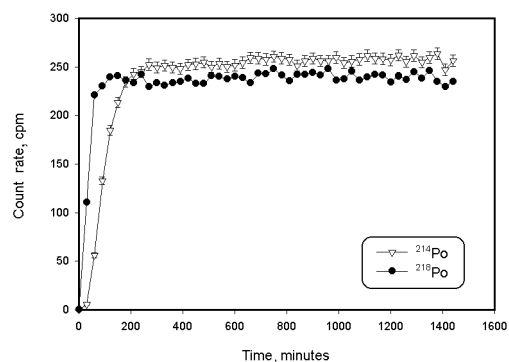


Fig. 2. Variation of the count rates in the ^{218}Po and ^{214}Po windows in air circulating through the RAD-7 from the air-water radon exchanger which is receiving a constant water stream from tap water in our laboratory. The cycle time was set at 30 minutes and the counting continued over a 1-day period. A slower response of ^{214}Po relative to ^{218}Po is due to the longer half lives of the intermediate radioactive daughters, ^{214}Pb (27 m) and ^{214}Bi (19.7 m). Uncertainties shown for ^{214}Po (^{218}Po errors are comparable) are based on counting statistics and are at the 2σ confidence level

The response time of the system depends on the half-life of the ^{218}Po , the volume of the air loop, the speed of transfer of radon from the water to the air (which depends on the efficiency of the aeration, and the speed of the pump), the flow rate of the re-circulating air, the volume of water in the exchanger, and the flow rate of water to the exchanger.¹⁶ The half-life of ^{218}Po , 3.1 m, dictates an ultimate theoretical limit, for the 95% response time, of about 15 minutes, assuming everything else was instantaneous. Since there is about four times more radon in the air phase than the aqueous phase at equilibrium, at least four times more water must flow through the system to deliver all the radon that is required. Again, that is assuming everything is working at maximum efficiency which is unlikely.

Of all the possible parameters which may effect the equilibration time, the only ones which could easily be controlled to some extent are the flow rates of the re-circulated air and water. In our experiments thus far, we have relied on the internal pump of the RAD-7 which is fixed at a flow rate of about 1 l/min. One could use an external pump as well and thus have some control over this parameter. We report here our observations on the effect of different water flow rates on the equilibration time.

We again connected the exchanger to the tap water system in our laboratory and ran equilibration time experiments, based on monitoring the ^{218}Po window, at four different water flow rates from 0.25 to 1.5 l/min. The RAD-7 pump was set to pump continuously and counts were integrated over 5-minute periods. The results (Fig. 3) show that there is no significant difference in the count rate in the ^{218}Po window once equilibrium is established at the four different water flow rates. However, there is an improvement in the time required for equilibration as one increases the water flow rate up to a point. Since the aeration rate was held constant, the shorter equilibration times at higher water flow rates must indicate that a substantial fraction of the radon degases from the water stream during its flow through the exchanger. For the conditions of this experiment, it appears that increasing the water flow rate above about 1.0 l/min has little effect, i.e., an equilibration time of about 35–40 minutes appears to be the shortest time achievable. Presumably, increasing the air flow and transfer speed of the radon from water to air (perhaps with improved aeration) could improve this further (although one will still be limited by the time necessary to reach radioactive equilibration, about 15 minutes for ^{222}Rn – ^{218}Po). We have now lowered the equilibration time to 25–30 minutes at a water flow rate of 1.5 l/min by using a spray nozzle to disperse the water entering the exchanger in a fine spray.

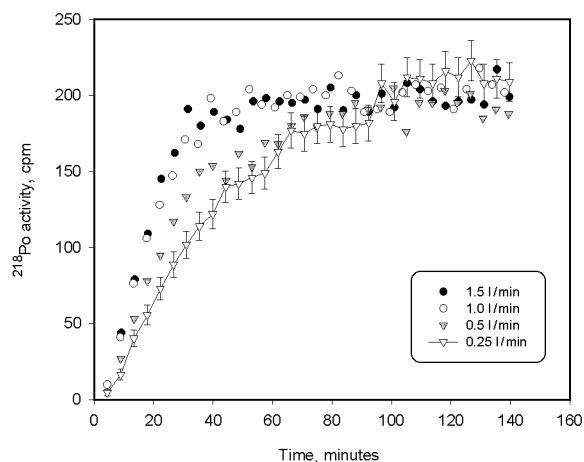


Fig. 3. Results from equilibration time experiments to assess the effects of different water flow rates. Each experiment was performed with the RAD-7 pump on continuously, a 5-minute integration period, and count rates monitored from the ^{218}Po window. Uncertainties shown for the 0.25 l/min flow rate (other flow rates would have slightly lower errors) are based on counting statistics and are at the 2σ level

For purposes of mapping radon distributions over a large area, it would be desirable to have the shortest possible equilibration time. If this cannot be significantly improved, another approach would be to establish a correction for some constant equilibrium fraction after a fixed time interval of say 15–20 minutes. This would certainly be possible if sufficient sensitivity could be obtained in that amount of time. That would largely depend on the concentration of radon in the case at hand. For coastal seawater, with ^{222}Rn activities in the 0.05–0.15 Bq/l range, somewhat longer integration times are necessary to bring the measurement precision to an acceptable level. For example, in order to reach a counting precision of $\pm 10\%$ for seawater containing 0.1 Bq/l, it would be necessary to collect counts in the ^{218}Po window for about 40 minutes after equilibration.

Field tests

As a first field test in a coastal oceanographic environment, we set up the continuous monitor at the Florida State University Marine Laboratory (FSUML), on the Gulf of Mexico near Carabelle, Florida, about 40 miles south of Tallahassee. For this initial test (December 6–10, 1999), the intake to the exchanger was connected to the seawater circulation system at the laboratory which continuously pumps in fresh seawater from a shallow intake located about 300 meters offshore. The seawater is pumped initially into large closed storage tanks and then circulated to points throughout the building and then discharged back into the Gulf. The entire flow through FSUML has a residence time of approximately 2 hours.

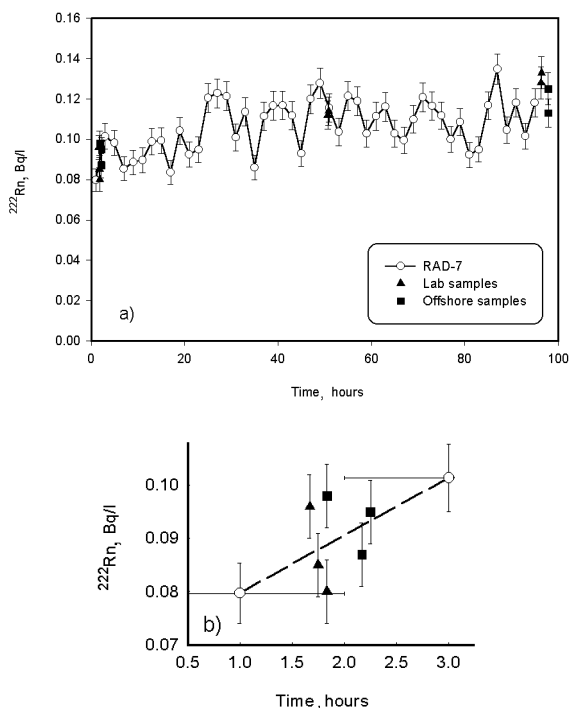


Fig. 4. Results from 4 days of continuous radon measurements of coastal seawater from the Florida State University Marine Laboratory seawater circulation system. The measurements were initiated at December 6, 1999 with the RAD-7 on “auto” mode, 2-hour integration periods, and radon concentrations calculated from counts in the ^{218}Po window and independent seawater temperature readings. Uncertainties shown for the continuous monitor are based solely on counting statistics and are at the 1σ level (a). Expanded view of the data collected during the first few hours of the experiment showing a detailed comparison of the radon results from the continuous monitor to those from grab samples collected in the laboratory and from offshore. The ^{222}Rn results for the grab samples were calculated from the sum of the measured ^{226}Ra activities (assuming equilibrium with ^{222}Rn) plus the “excess” ^{222}Rn , decay corrected to the time of sampling. The uncertainties shown for the grab samples are $\pm 1\sigma$ based on counting statistics and estimated errors in the system calibration (b)

We set up the monitor inside a laboratory which had an outlet for the seawater system and adjusted the water flow rate to about 1.5 l/min. We set the RAD-7 to the “auto” mode, so it pumps for 1 minute out of every five, and it was programmed to integrate counts on a 2-hour schedule. To evaluate the results further, we also collected a series of grab samples, both from the laboratory seawater system itself as well as from offshore, in the vicinity of the seawater system intake. All grab samples were collected in evacuated bottles specifically designed to prevent loss of radon. The bottles were kept sealed until they are put onto a radon extraction system where radon is sparged from the water by a stream of helium, collected on a liquid nitrogen cold trap, and then transferred to alpha scintillation cells for counting. The system is calibrated by extraction and counting of radon from NIST radium solution standards in the same types of bottles. This “radon emanation”

technique is a standard approach for analysis of ^{222}Rn in seawater which has been used by marine scientists over the past three decades.^{11–12}

The results (Fig. 4) show very good agreement between the ^{222}Rn activities determined by the continuous monitor and those based on the grab samples. Over the 4-day period of the experiment, the ^{222}Rn concentration ranged from about 0.08 to 0.14 Bq/l, with a generally increasing trend towards higher concentrations later in the experiment. Furthermore, there is strong suggestion of a tidal component in the data, i.e., the radon concentrations appear to vary systematically with a period of about 12 hours. The tides in this area are mixed semidiurnal (two high tides and two low tides with unequal amplitudes each day). Although it is too early to draw final conclusions from this one experiment, tidally-driven influences on groundwater seepage have been observed before in other areas. For example, LEE¹⁷ observed an inverse correlation between seepage rates and tidal stage in an estuary in North Carolina. Moreover, an experiment performed off FSUML in January, 2000, using automated seepage meters designed by TANIGUCHI and FUKUO¹⁸ also showed an obvious tidal influence on the seepage rates. Unfortunately, we were only able to collect about 40 hours of radon data on that occasion because of a problem that developed with the laboratory circulating seawater system.

The comparisons between the continuous monitor results and the ^{222}Rn concentrations from the grab samples appear to be excellent. Three-liter grab samples were collected from a nearby laboratory outlet at FSUML (Dec. 6, 8, and 10) and from a boat offshore near the seawater intake system (Dec. 6 and 10). In order to plot the results shown in Figure 4, we adjusted the time of the offshore sample collection by +2 hours, the assumed residence time of seawater through the system (the point where our monitor was set up was near the end of the seawater flow).

Conclusions

We consider the comparisons shown in Fig. 4 especially good in view of the uncertainty of the relative timing of the samples, and the fact that the continuous monitor integrated each analysis over a 2-hour period while the individual samples represent a snapshot view. If one also considers the number of things that can go wrong either during the collection or analysis of radon-in-water grab samples (bottle leaks or breaks, radon loss during emanation or transfer on the extraction line, etc.), the automated, simple system described here appears even more attractive. A few simple improvements have now provided even better performance. Durrige increased the sensitivity of our

RAD-7 by use of a larger (450 mm² versus 300 mm²) semiconductor detector and by a slight volume and shape modification of the internal air chamber. We have now modified the exchanger design by increasing the water-to-air ratio and by use of a spray nozzle to disperse the water entering the exchanger into a fine spray. These modifications have reduced the observed equilibration time to only 25–30 minutes at a water flow rate of 2.0 l/min. This enables us to run the RAD-7 in “auto” mode (pumping 1 minute out of every five) which conserves desiccant since the air is only passing through the drying column 20% of the time. The drying column we use holds approximately 570 g of Drierite and lasts up to three weeks of continuous operation. Overall, this system represents a significant improvement over existing methods for measurement of ^{222}Rn in coastal waters.

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The authors wish to thank personnel from the Florida State University Marine Laboratory for their assistance during this study. Jamie CHRISTOFF, Mike LAMBERT, Nathan TASSOBI, and Makoto TANIGUCHI helped with the fieldwork and radon emanation analyses. This project was funded through grants to Florida State University from DOD’s Defense Threat Reduction Agency (DSWA01-97-1-0022) and the Chemical Oceanography Program of the Office of Naval Research (N00014-00-1-0175).

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