

Pollutant Transport

For studying the transport of pollutants

Natural Radionuclides as Tracers of the Self-Cleaning Capacity of Galveston Bay

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One of the main concerns over the discharge of contaminants into semi-enclosed basins, such as Galveston Bay, is the potential impact of contaminants on biota. Contaminants are dispersed throughout a natural system by a variety of processes. These processes may be physical, chemical, or biological in character.

A very important pathway for dispersing certain types of contaminants throughout heterogeneous systems is transport by sorption onto particles. One widely-used technique for studying the fate of particle-reactive contaminants is the use of naturally-occurring, radiogenic isotopes as particle tracers and as chemical analogues for the contaminants of interest.

Our objectives in this study were two-fold: 1) the utilization of two radiogenic isotopes, ^7Be and ^{210}Pb , as *in situ* tracers in Galveston Bay; and 2) comparison of these data with previous particle-tracing studies using ^{234}Th . Heavy rain events were used as a source of pulse inputs for the lead and beryllium isotopes, and their activities were followed in the Galveston Bay water columns throughout and after the rain period.

^{210}Pb (22.1 year half-life) and ^7Be (53.3 days half-life) are particle-reactive radionuclides which are produced in the atmosphere and subsequently removed from the atmosphere by dry and wet washout of aerosols to which they are attached. These nuclides have been used extensively to study the rates of sediment accumulation and mixing, the dynamics of particle transport, and the fate of particle-reactive elements in estuarine and coastal waters. While ^{210}Pb is derived from its progenitor ^{222}Rn , which is a noble gas and emanates from the soil, the cosmogenic nuclide ^7Be reaches the earth's surface from troposphere, where it is produced. In contrast, ^{234}Th (with a 24.1 days half-life) is produced at a known and constant rate from the radioactive decay of its parent ^{238}U , which is present in sea water as a soluble uranyl carbonate. ^{238}U is conservative in seawater, and its activity is proportional to salinity.

Rain water samples were collected during heavy rains in a high density polyethylene drum (with an area of 0.27 m^2) at the roof of Kirkham Hall on the Mitchell Campus of Texas A&M University at Galveston. Samples were collected once a month, and ^7Be and ^{210}Pb activities were determined by gamma counting in a high purity germanium well detector. Large volumes (up to 10 m^3) of water from Galveston Bay were filtered and extracted through MnO_2 impregnated polypropylene cartridges, which were ashed in the laboratory and gamma counted for radionuclide assay using the same set-up.

Based on the measurement of $^{234}\text{Th}/^{238}\text{U}$ ratios in filtered water, the residence

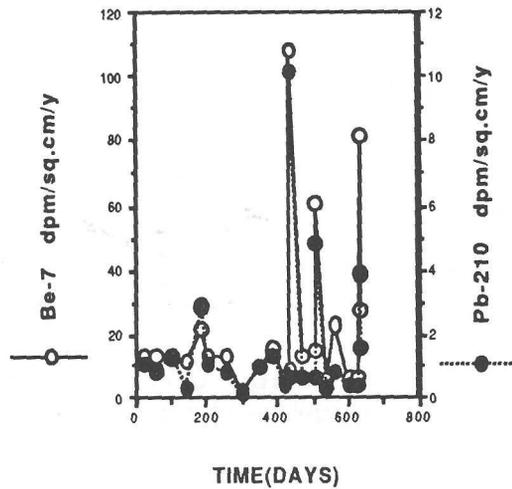


Figure 1. ^7Be and ^{210}Pb vs. time. Average fluxes are indicated by the position of the symbol at vertical axis.

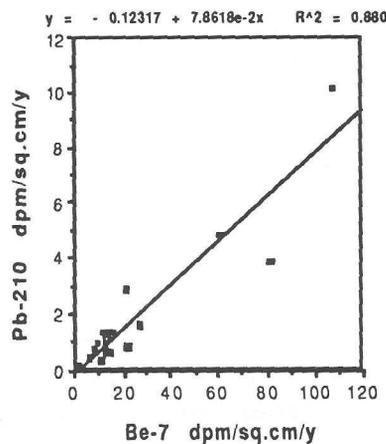


Figure 2. ^{210}Pb flux is plotted against ^7Be flux.

time of ^{234}Th in waters of Galveston Bay, from the time it is produced until it is sorbed by particles, was estimated to be as short as one hour. Total removal residence times of ^{234}Th in the water ranged between one to three days. The input functions ^7Be and ^{210}Pb , which are plotted in Figures 1 and 2, allowed us to calculate their overall residence times from the times of introduction into the water until they were removed from the water column. Furthermore, ^{210}Pb data on precipitation in coastal stations yields information on the source(s) of the air masses. Figure 1 shows that short events of rain input inject relatively large amounts of these isotopes as pulses. The similarity in the input functions of these two atmospherically derived isotopes would not be expected for marine stations

because of the low concentrations of ^{222}Rn , the mother radionuclide of ^{210}Pb , in marine air. The good correlation of ^{210}Pb with ^7Be (Figure 2) indicates that a large fraction of air is probably continental rather than oceanic.

The analysis of water samples from Galveston Bay showed that most of the ^7Be (between 74 and 86% of the total) as well as ^{210}Pb (between 77 and 90%) were associated with particles. We expect that the transport of many other particle-reactive trace metals with similar particle-water distribution coefficients (K_d) as that of Pb and Be will also be controlled by the rates of particle movements. The K_d of ^7Be varied between 3 and $12 \times 10^5 \text{ cm}^3/\text{g}$. This value is 1-2 orders of magnitude higher than some of the values reported by other workers. K_d values for ^{210}Pb varied between 2.3 and $8.6 \times 10^5 \text{ cm}^3/\text{g}$. Further studies to understand the decrease in K_d values with increasing particle concentration are in progress. Preliminary results indicate that ^7Be and ^{210}Pb have total removal residence times in the water of Galveston Bay which are of similar magnitude as those of the strongly particle-reactive ^{234}Th .

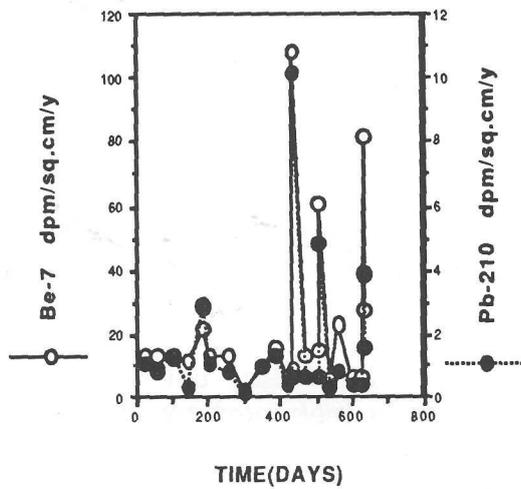


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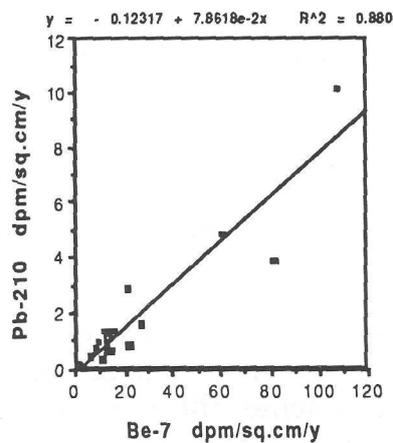


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Tracer Gas Transfer Technique for Shallow Bays

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Modeling the transport and fate of dissolved pollutants in Galveston Bay and other bodies of water depends on many factors. Among these factors are the features which influence the hydrodynamics (such as the bathymetry, wind and current patterns, tidal conditions, etc.) and the factors which influence the pollutant relative to the hydrodynamics (such as mixing and diffusion, biological and chemical processes, and physical-chemical processes such as adsorption and volatilization). This research was directed at developing a method for field measurement of volatilization of dissolved substances.

The tracer gas technique was originally developed in the mid-1960s for rivers to provide a means for directly measuring surface gas transfer for situations where reaeration was the primary transfer process of interest. In the method, a conservative tracer and a tracer gas with surface gas transfer characteristics similar to oxygen are simultaneously injected into the river. The two most commonly used gas and conservative tracer pairs are propane with Rhodamine WT and radioactive krypton with trivium. As the tracers move downstream, the concentrations of the tracer gas change due to dilution, mixing, and surface transfer, while the concentrations of the conservative tracer change due to only dilution and mixing. With simultaneous measurements for the two tracers, the conservative tracer can be used to compensate for the effects of dilution and mixing so that the surface transfer of the tracer gas can be isolated. Field techniques exist for narrow rivers where the concentration distributions are essentially one dimensional and for wider rivers with two-dimensional distributions. The techniques use either short-duration releases, giving tracer clouds which move downstream, or long-duration releases, giving steady-state tracer distributions. Little previous work has been done on developing field methods for determination of gas transfer coefficients for bays.

The tracer gas method has also been of interest in recent years in conjunction with determining volatilization rate coefficients for some types of volatile dissolved toxicants. Although there is sometimes a need to know reaeration rates for bays, it was primarily the interests related to volatilization that prompted this research into the development of tracer gas techniques which can be used in bays. The research used propane and Rhodamine WT as the tracers and included both laboratory and field studies.

The laboratory part of the work was directed at improving the methods for measuring dissolved propane concentrations and at investigating the influence of salinity on the ratio of transfer coefficients for the tracer gas and other gases.

This paper will emphasize the field work, which was the primary part of the work. The developmental field tests were conducted in Lavaca Bay, which is a secondary embayment in the northerly section of the Matagorda Bay system. The same techniques are applicable to Galveston Bay. In the field tests, propane is

dissolved in the bay water by bubbling the gas through porous stone diffusers.

The first field tests were directed at evaluating the relative benefits of short- and long-duration injections. For long-duration injections, the travel time must be known for the samples which are collected for concentration determination. Both drogues and a second fluorescent tracer were tried for determining travel times. Neither method was satisfactory. Also, reversing tidal flows can cause the tracer plume to double back on itself. Thus, it was decided to use short-duration (15 to 20 minute) injections. During the tests it was observed that if vertical density gradients are present, the rising bubbles cause mixing of the heavier lower and lighter upper water and thereby cause the tracers to gradually sink below the surface. To prevent this problem, a special injection box was built to allow mixing of the tracers during the injection with only the water near the surface. The downward migration of the tracers then is due to only mixing and not density currents. The first tests were also used to determine the time for the tracers to become mixed in the vertical direction. The tidally induced velocities are small (on the order of a few hundred feet per hour) and are less effective than wind-induced mixing. For water up to 6 ft deep and wind speeds up to 25 mph, it was found that the vertical mixing times varied in the range of approximately one to four hours.

The next sets of tests were aimed at developing methods of sampling the tracer cloud to obtain reliable and consistent results. The first plan was to mark spots in the cloud and to collect samples along vertical profiles at essentially the same relative positions in the cloud each time, with samples being collected at 45-minute to one-hour intervals. Because of the problems mentioned above with drogues and second tracers, no satisfactory method was found for marking a part of the cloud. Thus, mathematical modeling was done as an aid to understanding the transport process and to developing field techniques. It was determined that the surface transfer coefficient can be calculated from measurements made at the points of maximum concentration at various depths in the water column, after vertical mixing has been achieved. In the field tests, sampling is done at a variety of horizontal points in the cloud and also for different depths within the cloud, in order to locate the points of maximum concentration.

Most of the research was directed at developing field methods, but some limited quantitative results were obtained. These results indicate that the surface gas transfer coefficients for a given wind speed for shallow bays are smaller than would be predicted based on data from either the open sea or from laboratory experiments.