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Project Summary

A Hazardous Materials Spill Warning System

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The U.S. Environmental Protection Agency (EPA) has developed a list of materials that, based on their aquatic toxicity, are defined as hazardous substances. In addition, certain materials have been designated as "priority pollutants." Often, a spill of toxic materials into a moving water stream can occur without the knowledge of the spiller, or without notification of the authorities, or both. Accordingly, a system was needed to detect the presence of hazardous or toxic materials in streams and rivers. This need has been filled by providing a spill alarm system that was designed, fabricated, and tested before delivery to the Oil and Hazardous Materials Spills Branch in Edison, New Jersey. The system consists of nonselective components that together detect all the materials on the designated hazardous materials list and the priority pollutants. The warning system has been shown to be capable of detecting a wide variety of hazardous materials, and untended operation is possible of a 2-week period.

This Project Summary was developed by EPA's Municipal Environmental Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The report summarized here describes the design, development, and field testing of a practical hazardous spill warning system. The system provides an effective early warning of a hazardous material spill and thus facilitates a quick response.

Under the authority of the Federal Water Pollution Control Act Amendments of 1972, EPA began the process of designating 271 materials as hazardous. In addition, 65 groups of compounds were identified as toxic and formed the Toxic Pollutant List. The latter list was eventually expanded to 129 items. These chemicals are commonly referred to as priority pollutants because of the frequency of their occurrence in worldwide water analysis.

The federal program to combat spills, which was developed as a result of the 1972 amendments, is dominated by three goals: to prevent, detect, and contain, remove, and clean up spills.

Rockwell International, under the sponsorship of the EPA's Oil and Hazardous Materials Spills Branch in Edison, New Jersey, undertook a project to design and develop a warning system to detect spills of hazardous materials in natural waterways. The spill alarm system was designed to advance the state of the art in spill detection, thus allowing for a quick mitigating response.

System Description

The entire alarm system is housed in an air-conditioned, 8.2-m (27-ft) automotive trailer, which allows the system to be conveniently moved from one site to another. A submersible pump placed in the watercourse feeds the instrument package approximately 38 L/min (10

gpm) through a 5-cm- (2-in.-) diameter plastic hose.

The detection components that have been incorporated into the integrated system are:

1. pH sensor, Leeds & Northrup*
2. Oxidation-reduction potential, ORP sensor—Leeds & Northrup
3. Electrical conductivity sensor, Leeds & Northrup
4. Ultraviolet absorptimeter, Teledyne
5. Total organic carbon analyzer, TOCA Dohrman

The pH electrodes can detect strong acids and bases or substances that form strong acids or bases at levels approximately 1 pH unit above or below that of the natural waterway. Weak acids and bases will also be detected by the pH electrode, but at higher concentrations.

The ORP electrode was included in the warning system because of its usefulness in detecting chemical spills. But because redox equilibria are often established slowly, it is difficult to calculate the precise concentration at which substances are detectable. The complexity of the processes that normally occur in natural water lead to the measurement of a mixed potential rather than of a single potential that can be used to identify individual compounds.

The conductivity detector responds to water soluble electrolytes. Hazardous substances that fall into this category are most salts, weak and strong acids and bases, and substances that react with water to form them. The sensitivity of the sensor to spilled substances depends on the background conductivity of the natural water, which is in turn related directly to total dissolved (inorganic) solids in the water. For these reasons, the sensitivity of the detector must be adjusted relative to the natural water conductivity. More than 150 hazardous substances are detectable by the electrical conductivity increase produced when they are spilled in natural water.

The ultraviolet absorption instrument records the ratio of the sample absorption at two wavelengths, which are determined by choice of optical filters. For the alarm system, a 390-nm reference wavelength filter and a 230-nm measuring wavelength filter were chosen. The sensitivity for detection of many aromatic organic compounds is high at the 230-nm measuring wavelength.

All organic compounds are detectable by the total organic carbon analyzer. After removal of the inorganic carbon compounds, a controlled sample volume is injected into a high-temperature furnace where oxygen converts all the organic carbon into carbon dioxide. The carbon dioxide is measured in a nondispersive infrared unit, and it is related to the organic content of the original water sample.

Strip chart recorder channels for each detection component have built-in alarm circuits that transmit electrical signals when certain levels have been exceeded. The specific response level for each detector can be preset. When an alarm condition is reached, the following sequence of events occurs:

1. A signal light on the control panel indicates which detector component produced the alarm.
2. A solenoid valve is opened for a selected time to permit collection of a 3.8-L (1-gal) sample of water for later chemical analysis.
3. A telephone dialer system is actuated and transmits a prerecorded message to any chosen telephone station. The designated telephone receiver has an automatic answering system so that the alarm message is recorded at the receiving stations.
4. Recorder chart speeds are increased to show more detail. After the spilled material has passed the sampling point completely, the alarm lights are automatically turned off, and after a preset time, a second relay is energized to prepare to collect a second water sample for later analysis.

In the complete report, the alarm system design and performance specifications are described in detail. The description includes the system components and their operation, figures illustrating system design, water flow diagrams, alarm control circuitry, etc.; lists of the hazardous materials detectable by the alarm system; a list of manufacturers of the various components; operating instructions for the system; and a summary of the field testing of the completed alarm system.

System Testing

The alarm system was first tested in the laboratory. Water was recirculated from a 208-L (55-gal) drum. Sensitivit levels of the detectors were determine by the addition of known quantities c hazardous substances to the water i the drum.

The system was then field-tested a two separate locations. The first tes was conducted on a simulated natura waterway located at the Rockwell Inter national Santa Susana Field Laboratory This waterway was part of a wastewate control system within which are severa ponds where effluents from rocke firings and other operations can be hel for cleanup before discharge into th municipal sewage system. Rocke engine test firings were preceded an followed by water purges that carrie quantities of organic solvents an hydrocarbon fuels. While sampling th effluent stream during the test firing of rocket engine, the alarm system wa able to detect a petroleum fuel dis charge.

With the cooperation of the Wate Quality Section of the Los Angele County Flood Control District, th second field test site was located on th Los Angeles River. At this site, th ultraviolet absorptimeter was able t detect a highly ultraviolet-absorbin material that passed the sampling poin

The completed spill alarm system wa transferred to the Environmental Emer gency Response Unit in November 197 for further testing. The alarm syster was successfully used for emergenc field response at Pittston, Pennsylvania from October 19, 1979, to Novembe 16, 1979.

Conclusions and Recommendations

The warning system has been show to be capable of detecting a wide variet of hazardous materials, and untende operation is possible of a 2-week perioc Furthermore, the system has bee designed, fabricated, tested, and foun to meet specific design criteria:

1. Detection components must b off-the-shelf items ready for us with a minimum of modification
2. Detection components must b rugged enough for remote, un tended monitoring.
3. System components must b resistant to fouling, scaling, etc. t such a degree that cleaning i necessary only once every 14 day or longer.
4. Detection components must re main sensitive under advers conditions.

**Mention of trade names or commercial products does not constitute endorsement or recommendation for use.*

5. The final system must contain several detectors capable of sensing wide classes of hazardous substances.
6. Detection components must not degrade any of the beneficial uses of a natural watercourse.

The usefulness of the detection system was demonstrated during a field test on the Los Angeles River, where it detected a highly ultraviolet-absorbing material that took more than 40 min to pass the sampling point.

The warning system should undergo further field testing under a wide variety of conditions to clarify improvements that would permit longer periods of untended operation. The testing should be conducted on waterways that differ in dissolved solids content, temperature, and frequency of pollution by hazardous materials.

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The complete report, entitled "A Hazardous Materials Spill Warning System," (Order No. PB 82-108 424; Cost: $8.00, subject to change) will be available only from:
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5285 Port Royal Road
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