A considerable volume of recent research has demonstrated that the chemistry of natural waters, including the world's oceans, is changing as a consequence of technological activities of man. In part these changes are associated with the global dissemination of organic compounds and elements that are synthesized and/or mobilized by man. In addition, global energy demands have increased both the rate of exploitation of submarine petroleum deposits and the volume of tanker traffic; these activities have increased the incidental input of petroleum into the marine environment.

We might anticipate that almost all exogenous substances will effect changes in an aquatic system when concentrations exceed a certain threshold. For this reason the measurement and study of exogenous substances, as well as naturally-occurring biogenic compounds, in natural waters is becoming increasingly important. In this paper we consider hydrocarbons and related compounds with boiling points encompassing the range between those of the alkanes n-C14 and n-C34; they are furthermore defined by the extraction and analytical methodologies employed. Generally they are sufficiently non-polar to be detected without chemical derivatization by the gas chromatographic techniques currently in use. They consist primarily of a considerable variety of biogenic compounds; those of special interest are the synthetic organochlorine compounds and compounds that are present in petroleum or that are derived from petroleum.

The history of the determination of hydrocarbons in seawater appears to parallel the history of the determinations in seawater of heavy metals. Prior to about 1975, almost all of the determinations of lead in seawater appear to have been too high because of contamination during collections (Participants of the Lead in...
Seawater Workshop, 1974; Patterson et al., 1976). Similarly, previous determinations of zinc in seawater were anomalously high because of sample contamination (Bruland et al., 1978); extreme precautions must be taken during sampling of seawater for cadmium measurements (Martin et al., 1979). As a consequence, virtually all of the measurements made before 1975 of metals in seawater by a considerable number of investigators should now be considered as part of the learning process.

Previously (Risebrough et al., 1976) we have suggested that many recent determinations of chlorinated hydrocarbons, particularly polychlorinated biphenyls, in seawater were too high, perhaps by an order of magnitude. A number of investigators have reported PCB levels in both the Atlantic and Pacific Oceans, and in the Mediterranean Sea, in surface waters and throughout the water column, that exceeded 1 ng/l (Williams and Robertson, 1975; Scura and McClure, 1975; Harvey et al., 1973; Harvey et al., 1974; Elder, 1976). Usually, the PCB detected approximated in composition that of Aroclor 1254, a mixture consisting principally of tetra-, penta-, and hexachlorobiphenyls. If, however, the mean concentration of polychlorinated biphenyls in the North Atlantic between the equator and 65°N, (an area of approximately 47 x 10^6 km^2 and a mean depth of 3900 meters; Sverdrup et al., 1942), were 1 ng/l, the PCB content would be in the order of 130,000 tonnes, higher than the total U.S. domestic use of these PCB's between 1957 and 1974. Since global production might be assumed to have been approximately twice that of the U.S., concentrations of this magnitude would imply that most of the PCB of this chlorine content that had ever been manufactured was in the waters of the North Atlantic. Contamination of the samples during some stage of the sampling would appear to be the most likely explanation for these reported concentrations that were clearly inconsistent with global mass balance considerations. Alternatively, even with the sensitivity of the electron capture detectors, sample volumes may not have been sufficient to provide adequate resolution and signal above background.

Similarly, many of the reported values in seawater of total hydrocarbons, usually considered to be a mixture of petroleum and biogenic compounds, may also be too high, perhaps by an order of magnitude. The diversity of sampling methodologies used for these determinations has been reviewed by de Lappe et al. (1978). Almost all values obtained before 1975 with a variety of analytical techniques, have been in excess of 1 microgram/l (Levy, 1971; Keizer and Gordon, 1973; Gordon and Keizer, 1974; Zsolnay, 1972; Zsolnay, 1973; Barbier et al., 1973; Iliffe and Calder, 1974; Koons and Brandon, 1975; Brown and Huffman, 1976; Brown and Searl, 1976). From recent studies carried out in the Pacific, ranging from the Aleutians westward to Japan and Singapore, southwards to New Zealand and the Antarctic, and southeastwards of Tahiti, Brown and