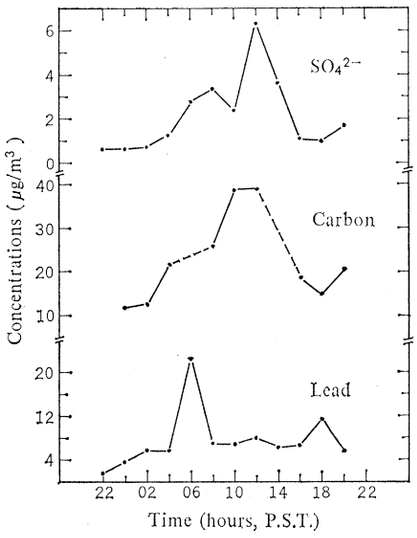

Fig. 2. Diurnal variation of particulate sulfate, carbon (*12*), and lead (*13*) concentrations. The sampling was done in downtown Los Angeles on 20 September 1972 (*14*). The similarity between the carbon and sulfate patterns is obvious.

water-soluble and could conceivably be neutralized by ambient NH_3, its chemical properties are consistent with those of ambient sulfate in the analytical sense. Moreover, ambient and laboratory-produced sulfate exhibit the same characteristic desorption in a vacuum as a function of sample temperature. The saturation effect reported for ambient sulfates (*10*) is also consistent with the proposed process. Finally, a marked correlation between the diurnal variation in the concentrations of ambient carbon and sulfate should be expected. An example of such a correlation is shown in Fig. 2. Other similar correlations have been observed more recently for other sites and pollution episodes (*11*).

The catalytic formation of sulfate on soot particles is expected to occur in the open atmosphere and especially in or near combustion sources, where both SO_2 and soot concentrations are highest. Although the sulfate formation mechanism described here may not be the only atmospheric sulfate-producing process, we believe that it plays a major role in urban atmospheres characterized by high concentrations of particulate carbon.

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Alkanes at the Air-Sea Interface from Offshore Louisiana and Florida

Abstract. *Alkanes at the air-sea interface were analyzed in 118 surface samples collected at five different intervals over a 12-month period from Timbalier Bay (Louisiana), offshore Louisiana, and offshore Florida. The alkanes were characterized by gas chromatography and mass spectrometry. Unexpectedly, methyl branched alkanes ranging in chain length from C_{15} to C_{35} and cycloalkanes were frequently the predominant components. This suggests that the alkanes are produced by natural biological sources as well as human activities.*

In recent years there has developed considerable interest in the distribution and impact of hydrocarbon residues introduced into the marine environment by petroleum production and maritime activities. Studies of the C_1 to C_5 hydrocarbons dissolved in the surface waters of the Gulf of Mexico show that the highest concentrations are apparently associated with shipping and petroleum activities (*1*). The presence of dissolved paraffins of higher molecular weights has also been reported in the Gulf of Mexico (*2*). Koons and Monaghan (*3*) concluded that the hydrocarbon content of the water in the northern Gulf of Mexico is probably less than 7 μg/liter. Concentrations of total dissolved hydrocarbons in the area of the east central Atlantic vary from 10 to 140 μg/liter (*4*), and 2 to 13 μg/liter is reported for the Nova Scotia vicinity (*5*). In the last case alkanes from C_{14} to C_{37} were present, and there was no preference for odd or even carbon numbers.

Garrett (*6*), using both a screen technique to sample the air-sea interface and a bucket sample, found that a variety of organics were present at a number of locations. More recently, samples collected at the air-sea interface in the area of the Sargasso Sea by use of a stainless steel screen were found to contain a variety of chlorinated hydrocarbons, and the highest concentrations were associated with the surface microlayer (150 μm) (*7*). Duce *et al.* (*8*), using similar techniques, showed that hydrocarbons and fatty acids, as well as pesticides, are more concentrated in the surface microlayer of Narragansett Bay than in water as deep as 20 cm below the surface.

It has been established that organics affect the physical properties of the ocean surface and many important exchange processes between the ocean and the atmosphere (*9*). For example, they reduce the capillary wave spectrum and thereby contribute to the production of sea slicks. Also, during any type of petroleum-related accident or oil spill it is the surface layer that is initially disrupted. Because of the importance of this microlayer and the general lack of qualitative and quantitative data it is important to characterize the indigenous chemical components found at the air-sea interface. This report deals with the nature and distribution of alkanes at the air-sea interface

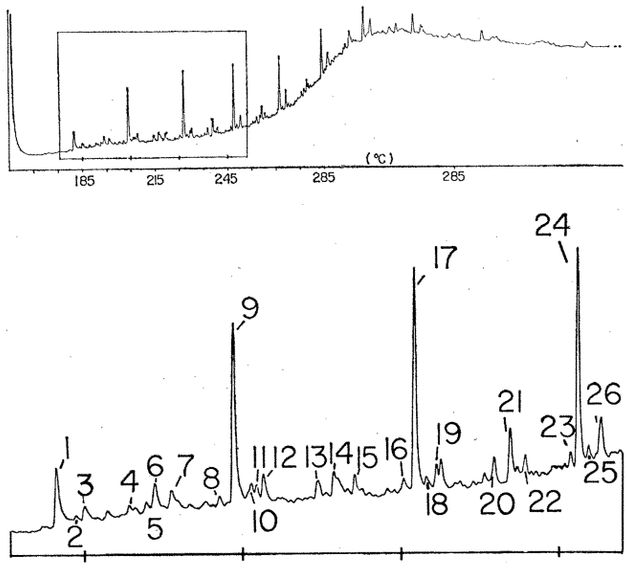

Fig. 1. Gas chromatographic separation of a typical paraffin fraction collected from the air-sea interface of offshore Louisiana in October 1972. Separation was on a stainless steel capillary column 250 m long, 0.5 mm in inner diameter, and coated with Apiezon L. A flame detector was used. The chromatograph was held at 155°C for 10 minutes and programmed from 155° to 285°C at 2°C per minute. The injector was at 250°C and the detector at 325°C. Numbered components are identified in Table 1.

in selected areas of Timbalier Bay and offshore Louisiana and Florida. Samples were collected at five intervals between August 1972 and July 1973.

An aluminum-backed Teflon disk was employed for sample collection. Approximately 90 percent of weathered crude can be recovered by this technique, and there appears to be little or no discrimination in retrieving petroleum paraffins above C_{15} (*10*). Residues collected were fractionated by using a silica gel column (*11*), and the alkanes were eluted with *n*-heptane. After removal of the solvent under a stream of purified nitrogen, the residue was weighed and further fractionated by gas chromatography. A portion of each sample eluted from the gas chromatographic column was passed through a DuPont 21-491 mass spectrometer attached to a PDP-12 computer. Alkanes from local production facilities and fuel and lubrication oils from the ships used to collect samples were also analyzed as possible sources of sample contaminants. The average (dry) weight of the *n*-heptane eluate was 0.70 mg per square millimeter of sea surface for residues collected from offshore Louisiana during five field experiments, whereas the 43 samples from the two exercises in Timbalier Bay averaged 0.36 mg/m^2 (*12*). Similar fractions averaged 0.18 mg/m^2 for Florida, while ten samples collected at the same time from Louisiana averaged 0.21 mg/m^2. No significant relation between proximity to a drilling or production platform and the quantity of alkanes at the surface was noted.

Figure 1 illustrates a typical distribution of compounds observed in a surface sample; more than 90 percent of the compounds are alkanes, and 118 such samples were analyzed. Samples obtained during a single collection trip showed only minor variations in the distribution of alkanes, qualitatively or quantitatively. Treatment with molecular sieve to remove normal alkanes followed by hydrogenation to remove the unsaturated compounds failed to significantly alter the observed chromatographic pattern. The sample represented in Fig. 1 contained about 70 percent branched alkanes, of which 50 percent by weight are 3-methyl branched, 13 percent are cycloalkanes, and 3 percent are normal alkanes. The components numbered in Fig. 1 are identified in Table 1. To date, some 50 compounds ranging from C_{16} to C_{36} in carbon number have been identified by mass spectrometry. When normal alkanes were present and in sufficient concentration to be detected they usually ranged from C_{16} to C_{21} and exhibited no odd-even carbon preference. In only a few samples, collected during August 1972 from offshore Louisiana and during October 1972 from Timbalier Bay, did the quantity of normal alkanes exceed 20 percent by weight of the paraffinic fraction. Samples collected at approximately the same time and location from a 10-m depth were found to contain predominantly normal alkanes from C_{14} to C_{36} (*13*). Tar ball samples from the Gulf of Mexico, even though they vary considerably in chemical composition, show substantial proportions of normal alkanes (*3*).

Table 1. Mass spectrometric identification of the components in Fig. 1.

Chromatogram peak number	Compound
1	3-Methylpentadecane
2	Nonadecylcyclohexane
3	*n*-Hexadecane
4	3-Methylhexadecane
5	Decylcyclohexane
6	Pristane
7	2,6-Dimethylpentadecane
8	Dimethyloctadecane
9	3-Methylheptadecane
10	Undecylcyclohexane
11	Phytane
12	*n*-Octadecane
13	3-Methyloctadecane
14	Dodecylcyclohexane
15	2,6-Dimethylheptadecane
16	Dimethyleicosane
17	3-Methylnonadecane
18	Tridecylcyclohexane
19	Dimethyleicosane
20	3-Methyleicosane
21	Tetradecylcyclohexane
22	2,6-Dimethylnonadecane
23	Dimethyldocosane
24	3-Methylheneicosane
25	Pentadecylcyclohexane
26	Dimethyldocosane

Our data suggest that the branched and cyclic paraffins comprise the bulk of alkanes at the air-sea interface, whereas the normal paraffins accumulate in the water column. There are several possible explanations for this enrichment, such as selective removal by autoxidation or photooxidation, emulsification by wave action, and adsorption on particulate matter. However, one of the more important factors may be biological. Marine bacteria preferentially oxidize normal alkanes (*14*), and microbial attack is most effective against oil in thin films or adsorbed on solid particles (*15*). The pristane/phytane ratio in the alkane fraction at the air-sea interface (which varies from 1.5 to 2.3) and the presence of a large number of dimethylalkanes suggest that crude oil or petroleum products may serve as the hydrocarbon precursor pool. If so, however, it is difficult to explain the presence of such high concentrations of 3-methyl branched alkanes with even carbon numbers. Certain plants contain substantial quantities of 3-methyl branched alkanes with even carbon numbers ranging from C_{28} to C_{34} (*16*), and it has been suggested that such alkanes occur in marsh plants that are common to the Gulf Coast (*17*). We suggest that the alkanes at the air-sea interface are probably entering the marine en-

vironment from a wide variety of biological sources as well as from petroleum released by natural seeps and man's activities, and that branched and cyclic alkanes accumulate at the interface as a result of a complex combination of physical and biological influences. The data that have been collected so far show that the types and amounts of hydrocarbons in the surface film along the northern Gulf Coast have remained fairly constant during the study period.

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Specificity of Antibodies: Primary Structural Basis of Hapten Binding

Abstract. *The primary structure of the 83 residues of the NH_2-terminus of the V_H region was determined for each of three different antibodies to hapten which were produced in inbred guinea pigs. Each antibody had a different and distinctive primary structure within each of the two "hypervariable" regions (Hv1 and Hv2) included in the analyzed part of the variable region of the heavy chain. The sequences of Hv1 and Hv2 in the three antibodies were either unique or of restricted variability compared with those of "normal" immunoglobulin G2. Further implication of Hv1 and Hv2 in contributing to ligand-binding specificity of antibodies came from the placement of residues modified by affinity labeling reagents in these hypervariable regions.*

The accurate correlation of the primary structures of antibodies with their ligand-binding specificities has been a long-term goal of immunologists. This correlation would allow them (i) to better describe the "active" sites of antibodies and eventually place amino acid residues contributing to antigen binding in their actual three-dimensional array; (ii) to infer the magnitude of genetic information for amino acid sequences of antibodies transmitted through the germ line; and (iii) to use distinctive sequences of antibodies as markers for lines of B (bone marrow derived) lymphocytes and plasma cells in order to better understand the regulation of the immune response in vivo.

We used inbred guinea pigs as donors of antibodies specific for the dinitrophenyl (DNP), *p*-azobenzenearsonate (ARS), or *p*-azobenzenetrimethylammonium (TMA) haptens to circumvent that genetic polymorphism present in an outbred population which is expressed as allotypic differences among proteins. Different individuals, immunized with the same antigen according to the same regimen, might be expected to produce antibodies with the same or similar binding-site structure because inbred animals inherit the same structural genes for antibodies and any alterations of these genes during somatic cell division followed by clonal selection would occur within animals with the same genetic background.

In a primary structural analysis of the heavy chain (γ_2 chain) from the most abundant isotype of guinea pig antibody, immunoglobulin G2 (IgG2), we isolated and rigorously aligned eight fragments from a CNBr digest of "normal" γ_2 chain, accounting for its entirety (*1*). Since "normal" IgG2 is a mixture of molecules with different binding specificities, we reasoned that fragments with a single amino acid sequence obtained from such a pool would not be directly involved in determining antigen binding. On the other hand, variability at a given residue position might be a marker for those segments of the molecule imparting antigen-binding specificity. A single primary structure was found for five COOH-terminal fragments, totaling 306 residues (*2*), and was expected because others have characterized two "active" fragments of antibody, Fab and Fv, each of which retained a ligand-binding site but lacked COOH-terminal regions of the parent molecules (*3*).

Our attention was focused on three CNBr fragments of guinea pig γ_2 chain comprising V_H, the NH_2-terminal quarter of heavy chain wherein sequences of myeloma proteins differ, because they contained those residue positions specifically modified by affinity labeling reagents (*4*). These chemically reactive analogs of antigen determinants are concentrated in binding sites of antibodies where they may react covalently with an appropriate amino acid residue, provided one is situated close enough to the rigidly bound reagent (*5*). When we used the affinity labeling reagents MNBDF (*6*), BADL, and BAAT to modify anti-DNP or anti-ARS, the specifically substituted residues were found within C-1-n, C-1-a_1, and C-1-a_2 (*7*). These three fragments contain the ~ 140 residues of the NH_2-terminus of γ_2 chain (*1*), and when derived from "normal" heavy chain each contains all or most of one short segment of highly variable primary structure—residues N31 to N35, N48 to N59, and N99 to N118—called "hypervariable" regions Hv1, Hv2, and Hv3, respectively (*8*). These Hv regions are surrounded by sections of V_H which appear to each have a single sequence, except where alternative residues have been detected at N2, N16, and N79 (Fig. 1). Analogous "hypervariable" segments in human and murine light (L) chains have been detected by comparison of numerous sequences of V_L region from