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GAS CHROMATOGRAPHIC AND SONAR IMAGING OF HYDROCARBON SEEPS IN THE MARINE ENVIRONMENT

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LIST OF FIGURES

Although marine hydrocarbon "sniffers" have been used to detect anomalous concentrations of dissolved gases in bottom waters all over the world, the ability to predict the oil versus gas potential of buried reservoirs in frontier areas provides the most significant accomplishment of the marine seep detector (Williams et al, 1981).

All hydrocarbon reservoirs, even those which produce primarily liquids, contain low molecular weight hydrocarbon gases. The composition of these gases generally shifts toward higher molecular weight components in oil reservoirs as compared to gas reservoirs. Previous publications have demonstrated the use of several methane through butane light hydrocarbon ratios for making compositional correlations (Bernard et al, 1976; Drozd et al, 1981; Jones and Drozd, 1983). For the marine seep detector, a compositional cross-plot scheme can be demonstrated to be useful for classifying marine hydrocarbon seeps as to their oil, condensate, or gas potential and for relating these seeps to their associated source reservoir types. Marine hydrocarbon seeps from the Gulf of Mexico will be shown to correlate with producing wells using well analysis data published by Rice et al, (1978) in a USGS open file report.

Recent advances also include illustrations from a color imaging sonar system which is capable of providing a color image of all microseeps large enough to produce bubbles in the water column. These high quality images provide actual profiles of the bottom sediments and aid considerably in defining the location of the fault or fracture that issued the seepage.

A final example correlating marine seep data with hydrocarbons analyzed from dart cores will be shown for a "sniffer" anomaly which preceded the discovery of the Beta Field in offshore California.

INTRODUCTION

Marine hydrocarbon seep detectors are designed to analyze seawater near the bottom for the presence of dissolved hydrocarbons, which are an indication of potential deep sedimentary oil and/or gas deposits, or the presence of man-made leakage from oil and gas pipelines or well casings. The first information published on offshore geochemical sniffing was by Dunlap et al, (1960), followed by Dunlap and Hutchinson, (1961). Over the next ten years, programs were initiated by many of the major oil and service companies, Anonymous, (1964); Jeffrey and Zarrella, (1970); Schink et al, (1971); Rogers and Edwards, (1975); Sigalove and Pearlman, (1975); Reitsema et al, (1978); Mousseau and Williams, (1979). Additional research was conducted on stripping techniques and establishing baseline values, Lamontagne, (1973, 1974); Bernard et al, (1976); Brooks and Sackett, (1973, 1976); Sackett and Brooks, (1974, 1975); and Sackett, (1977).

Also during this period, Gulf Research scientists designed, built, and operated several marine seep detectors which were employed aboard various research vessels, such as the R/V HOLLIS HEDBERG, along with its predecessor, the R/V GULFREX, Mousseau and Glezen (1981), Mousseau, (1981a, 1981b, 1983). These ships have circumnavigated the earth and conducted extensive detailed surveying in areas such as the Gulf of Mexico (Mousseau et al, 1979). The R/V HOLLIS HEDBERG system employed three separate water inlets which continually supplied sample streams from the near surface, intermediate depths to 450 feet and a deep towed sample inlet which operated at 565 ft. depth while the ship was underway at normal seismic survey speeds. Each sample stream was analyzed for seven (7) hydrocarbon gases once every three minutes with a sensitivity which depends upon the hydrocarbon, but for example, is about 50 picoliters of propane at STP per liter of seawater. The purpose for using three inlets is to differentiate between surface contamination and microseeps. As shown in Figure-1, which is a 3-D perspective plot of propane from the hull and deep inlets, surface contamination can be a major interference to shallow sampling, but is not a factor in producing the seeps observed by the deep inlet.

The most typical form in which the "sniffer" data is deployed when used in conjunction with seismic as an exploration tool is illustrated in Figure-2. Geochemical data from a deep tow inlet in profile form is shown superimposed to scale on a seismic record. Such records were produced at sea by Gulf oil Co. to aid the explorationist in making real time evaluations of hydrocarbon potential of structurally significant areas. The anomaly represented in Figure-2 is considered a "localized" anomaly because of the relatively short duration of the hydrocarbon signal and the magnitude of the hydrocarbon concentrations relative to regional background. Several "bright spots" may be seen on the seismic section at depth as well as shallow gas-charged sands presumably sourced by migration along the observed fault plane.

Several sea water hydrocarbon analysis systems, which can be deployed from either standard workboats or seismic vessels, are currently available to the industry. Depth capability for the towed sampler/sensors range from 300 ft. to

1200 ft. All of these systems consist of a towed pump/sensor system, connected by a fared umbilical to an onboard laboratory module. The hydrodynamic towfish usually contains a submersible pump, a conductivity, salinity, temperature and depth sensor (CSTD), and echo sounder transducer. Under normal operational conditions, the fish is maintained within the range of 4 to 8 meters above the seabed. The towfish is connected to the winch and handling gear by an umbilical which consists of a central nylon hose surrounded by power and signal conductors encased in a polyurethane sheath with a woven stainless braid. The umbilical usually is fully fared with low-drag hydrodynamic farings, which results in the towfish following close to the stern of the vessel, achieving the maximum depth for a minimum amount of deployed umbilical. Water is pumped through the umbilical to the laboratory module at approximately 6 to 9 liters per minute. The water sample is usually split into two independent streams to supply a dual gas extractor system.

Duplication of the gas extractor system allows additional independent analytical equipment to be used, and provides redundancy when required due to failure, or for routine maintenance. Each extractor consists of a glass stripper chamber into which the seawater is sprayed through a fine jet nozzle. The water level in the stripper is maintained at a constant height by a pressure regulated flow control system.

The design of the strippers available to the industry follows either a vacuum stripping or gas partitioning scheme. In the Gulf Oil Co. marine geochemical sniffer system, which is shown diagrammatically in Figure-3, a helium carrier gas is equilibrated with a water phase in such a way as to allow the stripper to be operated under pressure preventing any contamination from the onboard laboratory getting into the extracted gas stream. This dissolved gas analysis system has been demonstrated to be very reliable for conducting sniffer surveys because the stripper has no moving parts or pumps which can fail.

The dissolved gases from the stripper are then sent to a gas chromatograph by the helium stream. Analysis of these gases by Gulf included methane, ethane, ethylene, propane, propylene, iso-butane, and normal butane. Additional special gas analysis which could be included are total hydrocarbons, gasoline range C5+, benzene, toluene, helium, hydrogen, radon, and carbon dioxide.

A computer system is used to continually monitor the conductivity, salinity and depth of the fish sensor signals, with navigation data in UTM coordinates acquired every 3 minutes at the start of the GC analysis. The time lapse between collection of the water sample and the navigation time must be accounted for by the computer system.

In addition to measuring the light hydrocarbons and their ratios for recognition of different gas sources, there is usually an onboard capability to collect a methane gas sample which is specially purified and burned to convert the methane to carbon dioxide. This carbon dioxide is trapped in a special container and returned to an appropriate onshore laboratory where it is analyzed for its delta carbon 13 ratio (13C/12C). This ratio of the stable carbon isotopes allows a distinction between shallow biogenic methane and the more significant methane from a deep petrogenic source.

MARINE CROSS PLOTS AND PREDICTION OF RESERVOIR TYPE

The ability to predict oil versus gas potential of subsurface reservoirs provides the most significant demonstration of the value of sniffer geochemical data (Williams et al, 1981). Compositional cross plots have been established for classifying marine hydrocarbon seeps and predicting their source reservoir type as an alternative to simply plotting ratios of the individual hydrocarbon components. All hydrocarbon reservoirs, even those which produce primarily liquids, contain low molecular weight hydrocarbon gases. The composition of these gases generally shifts toward higher molecular weight components (more propane and butane relative to methane) in oil reservoirs (Nikonov, 1971; Pixler, 1969; Bernard et al, 1976; Drozd et al, 1981; Jones and Drozd, 1983).

In order to establish this compositional marine cross plot scheme in the Gulf of Mexico, Williams et al, (1981) compared the sniffer data base shown in Figure-4 to the well data base shown in Figure-5 (Rice et al, 1978). Rice has published the composition of the production gases for each of the 32 fields shown in this figure, including gas, oil, and combined oil and gas to condensate fields.

A cross plot of the compositions of the production gases from all of these fields in Figure-5 is shown in Figure-6 (Williams et al, 1981). The log of the ratio of ethane to propane plus butane is plotted against the log of the ratio of methane to ethane plus propane. A distinctive compositional clustering of gas anomalies signifies different kinds of production: oil anomalies occur near the origin and become gassier as the points move up and to the right in Figure-6. This cross plot scheme has been used to successfully classify producing wells and their associated seepage anomalies as to their type; oil condensate, dry gas, or biogenic gas based upon the composition of the log of C1/(C2 + C3) and the log of C2/(C2 + IC4 + NC4 ratios. Identification of biogenic gas from producing wells in the northern Gulf of Mexico on this plot was based on both their molecular and isotopic ratio data. An arbitrary boundary between oil-condensate and gas-condensate (based upon the Rice well data base) has tentatively been drawn midway between the other boundaries, as shown by the interpretive line within the condensate window.

A comparison of 146 recorded geochemical sniffer anomalies taken from the data shown in Figure-4 from the Gulf Oils, Gulf of Mexico data base are plotted in Figure-7 and show an overall distribution similar to the producing wells from this area. The type of typical contrast in composition of dissolved hydrocarbon anomalies from an oil area in Vermilion and a gas area surveyed in the West Cameron area of the Gulf of Mexico is shown in Figure-8 and Figure-9.

The boundaries previously suggested by Williams for each reservoir type have been demonstrated to work on worldwide productive areas as regards major changes in composition, oil vs. gas. In order to use these cross plots to tie surface geochemical data to well data, one must also assume that migration and mixing do not significantly alter the ratios of light hydrocarbons during migration to the surface. As shown above, this approach does yield good correlations in the Gulf of Mexico where mixing of reservoir types is expected to have considerable impact (Williams et al, 1981). Alternatively in localized areas where mixing or migration do alter the ratios of seepage gases, one must gather sufficient data over known fields to create new classification boundaries.

Jones and Bray (1985) have further tested this cross plot scheme by applying it to several onshore basins, including the Sacramento, San Joaquin, Uinta, Paradox, San Juan, and Arkoma. Reasonable accord with known production have been reported in all of these basins (Bray, 1986). The apparent similarity in composition of observed interstitial gases from both onshore and offshore implies that upward migration does not significantly segregate the four lightest hydrocarbons. More importantly, it suggests the dominant regional composition of near-surface gas is that which occurs in the reservoir, or the source rock which charged the reservoir. There may, however, be samples that contain significantly different compositions, predominantly due to mixing of deep gases, or microbiological oxidation. In these cases, contributions of deep dry gases along basement -related faults, or alternatively, areas of shallow biologic activity, could explain excess methane.

SONAR IMAGING OF GEOCHEMICAL SEEPS

It is well known that gas bubbles can become resonant scatters of acoustic energy (Tinkle et al, 1973; Albright, 1973; Geyer and Sweet, 1973; Guinasso and Schink, 1975). The Gulf Oil Co. marine gas sampling system also contained a color imaging sonar system which was used to provide a color picture of all marine seeps large enough to produce bubbles in the water column. Actual illustrations of seeps detected by the gas sampler and imaged by this color sonar system are included in this paper. These high quality images provide actual profiles of the bottom sediments and aid considerably in defining the location of the fault or fracture that issued the seepage.

CONCLUSIONS

Dissolved gas analysis systems have been used to detect anomalous hydrocarbon concentrations in bottom waters all over the world. The final product of a marine system is contour maps and line profiles which delineate areas in which there are natural petroleum and gas seeps. This information may be correlated with geological and geophysical data for exploration decision-making or may be used as the basis for recommending additional survey work.

Offshore seep detection allows areas of the continental shelf to be surveyed for seeping hydrocarbons as part of an integrated exploration program. Seepage data can be interpreted to differentiate areas with a mature source rock from those without, and to provide evidence for differentiating between mature gas prone source rocks. Integrated with seismic/structural data, survey results can be used to identify or confirm likely migration routes, (e.g. gas chimneys), and in areas of sea floor pock marks, differentiate a biogenic from a thermogenic source for the gas. In exceptionally simple geological cases, such surveys have been used to identify hydrocarbon-filled structures at depth, although in most regions the relationship between surface anomalies and deep structure is complex, requiring an integrated interpretation of all available geological and geophysical data.

The advantages of ship towed seawater monitoring are that it is relatively inexpensive and provides large numbers of statistically significant analyses on a precisely located grid. Real-time analysis also allows for informed modification of the sampling program.

Additional applications of seawater hydrocarbon detecting systems include the use for under sea pipeline leak detection, and for marine pollution monitoring and prevention (Aldridge and Jones, 1987).

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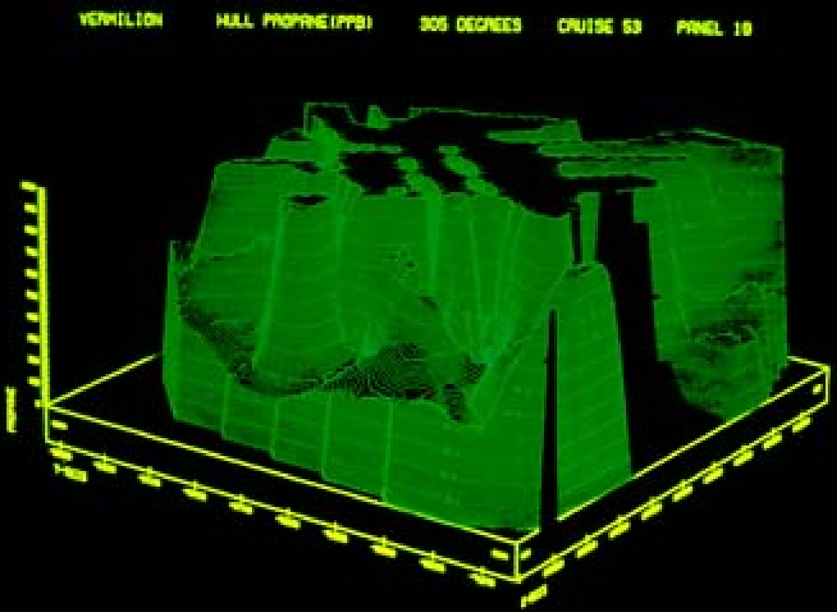
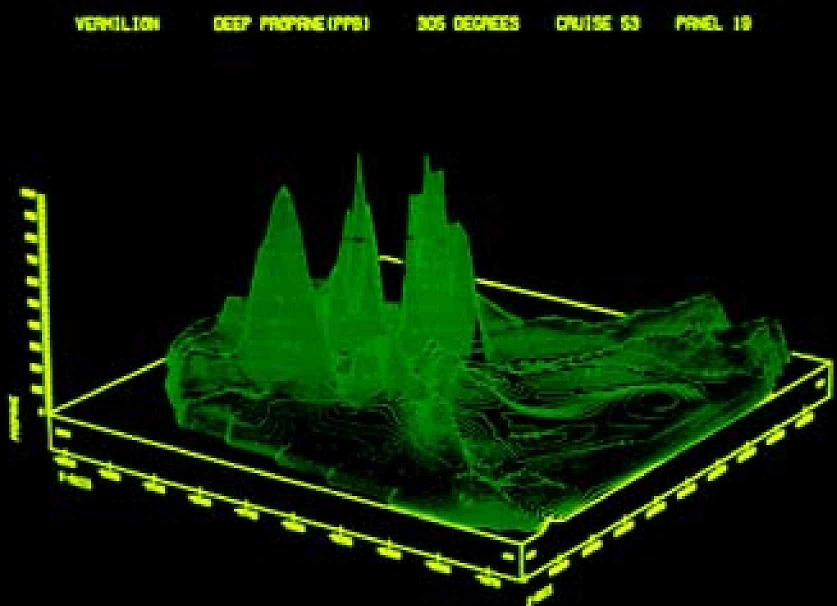

VERMILION
HULL PROPANE(PPB)
305 DEGREES
CRUISE 53
PANEL 19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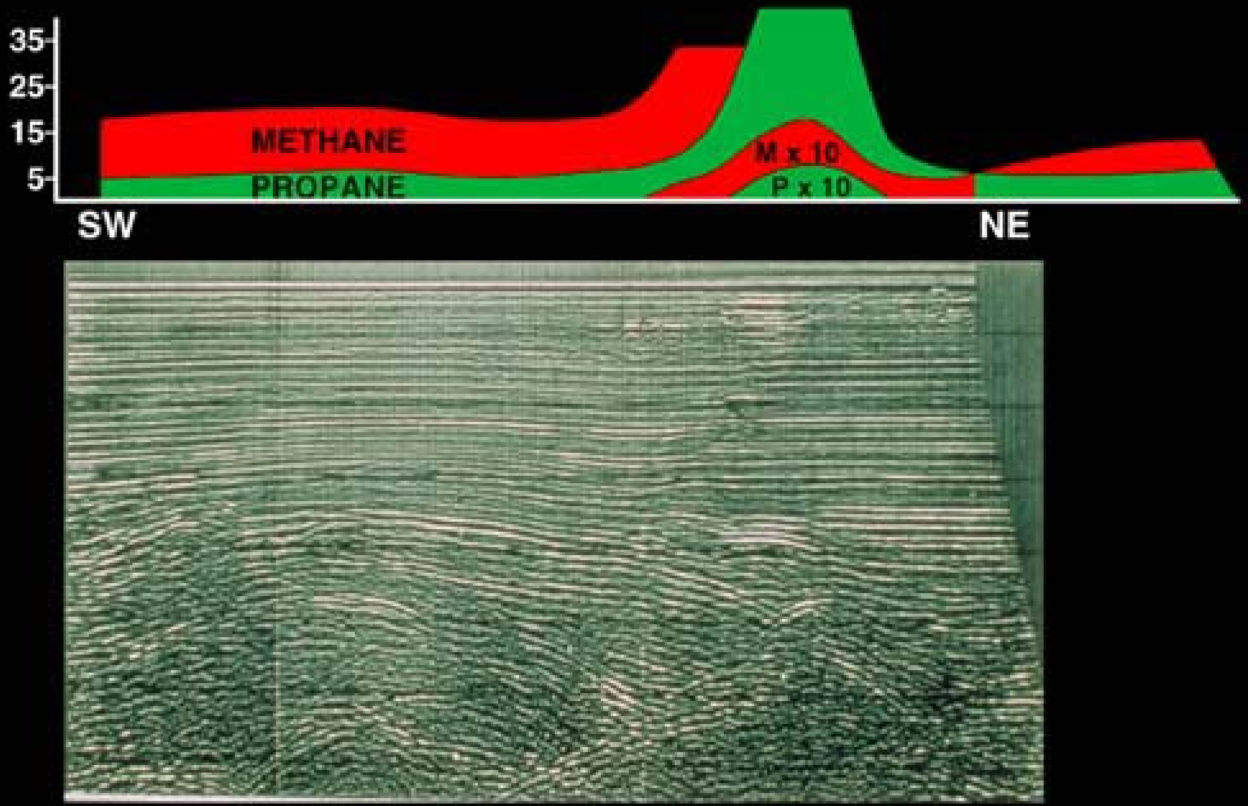
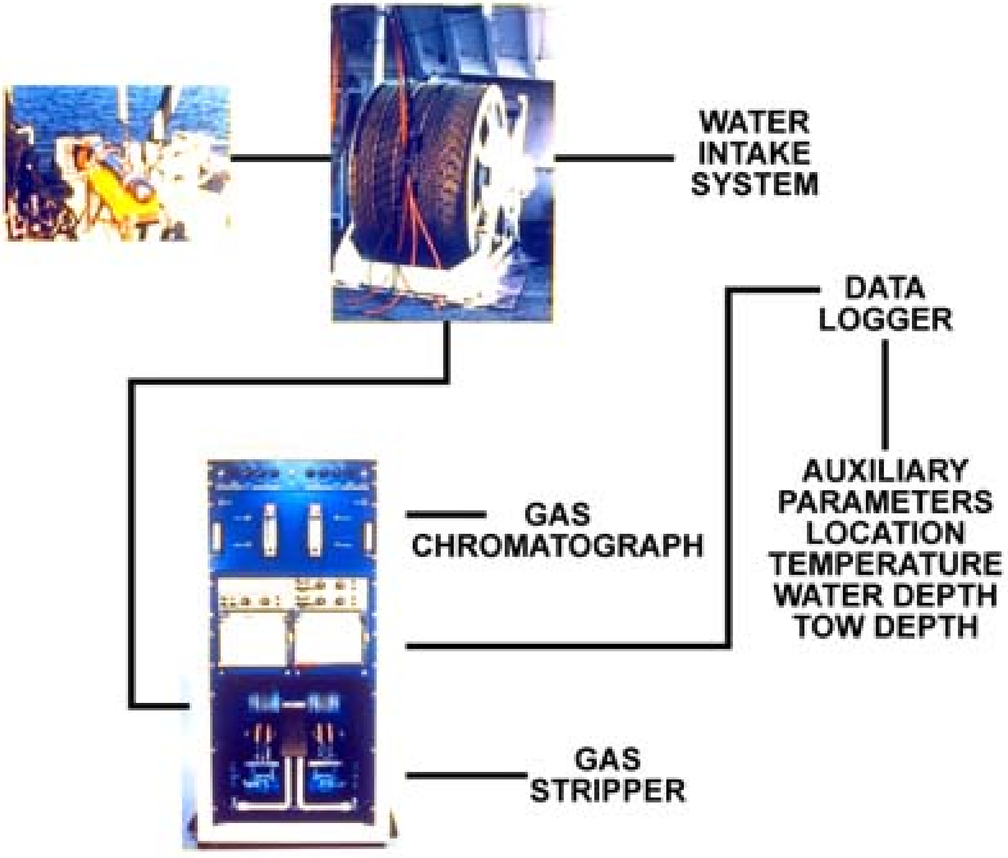
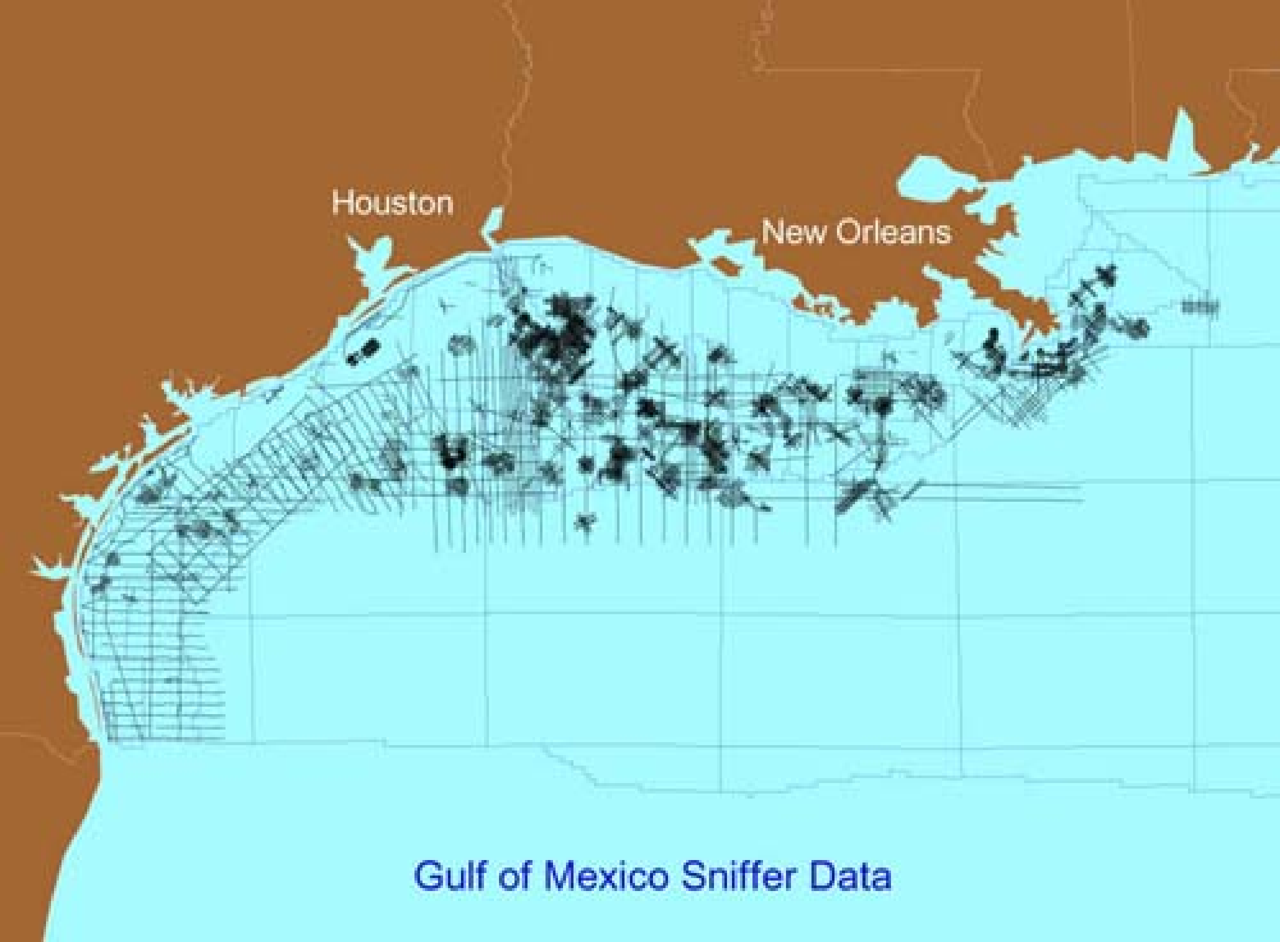
DEEP PROPANE(PPB)
305 DEGREES
CRUISE 53
PANEL 19

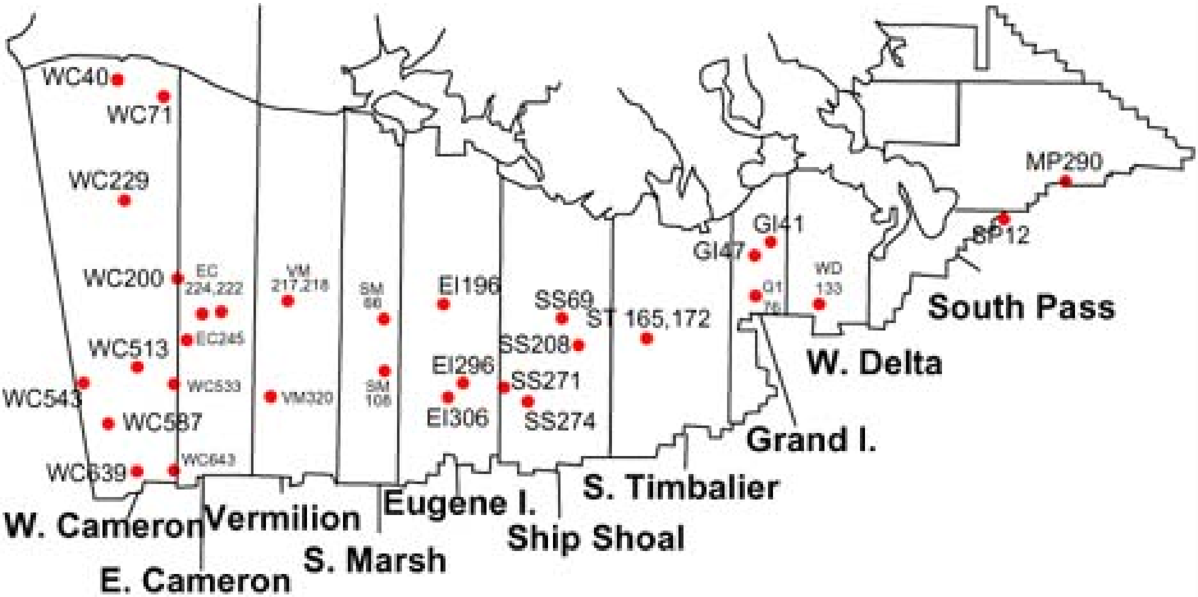

35
25
15
5
METHANE
PROPANE
M x 10
P x 10
SW
NE



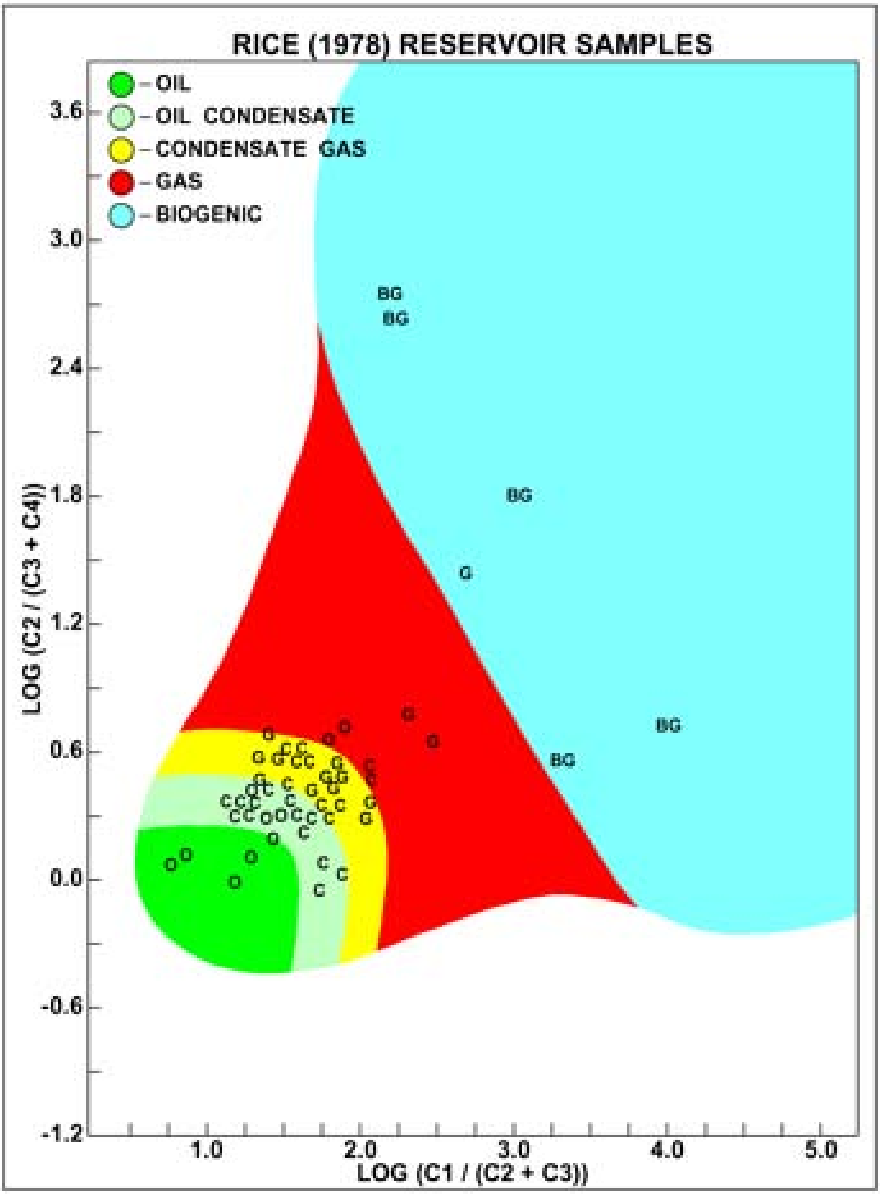
WATER
INTAKE
SYSTEM
DATA
LOGGER
AUXILIARY
PARAMETERS
LOCATION
TEMPERATURE
WATER DEPTH
TOW DEPTH
GAS
CHROMATOGRAPH
GAS
STRIPPER



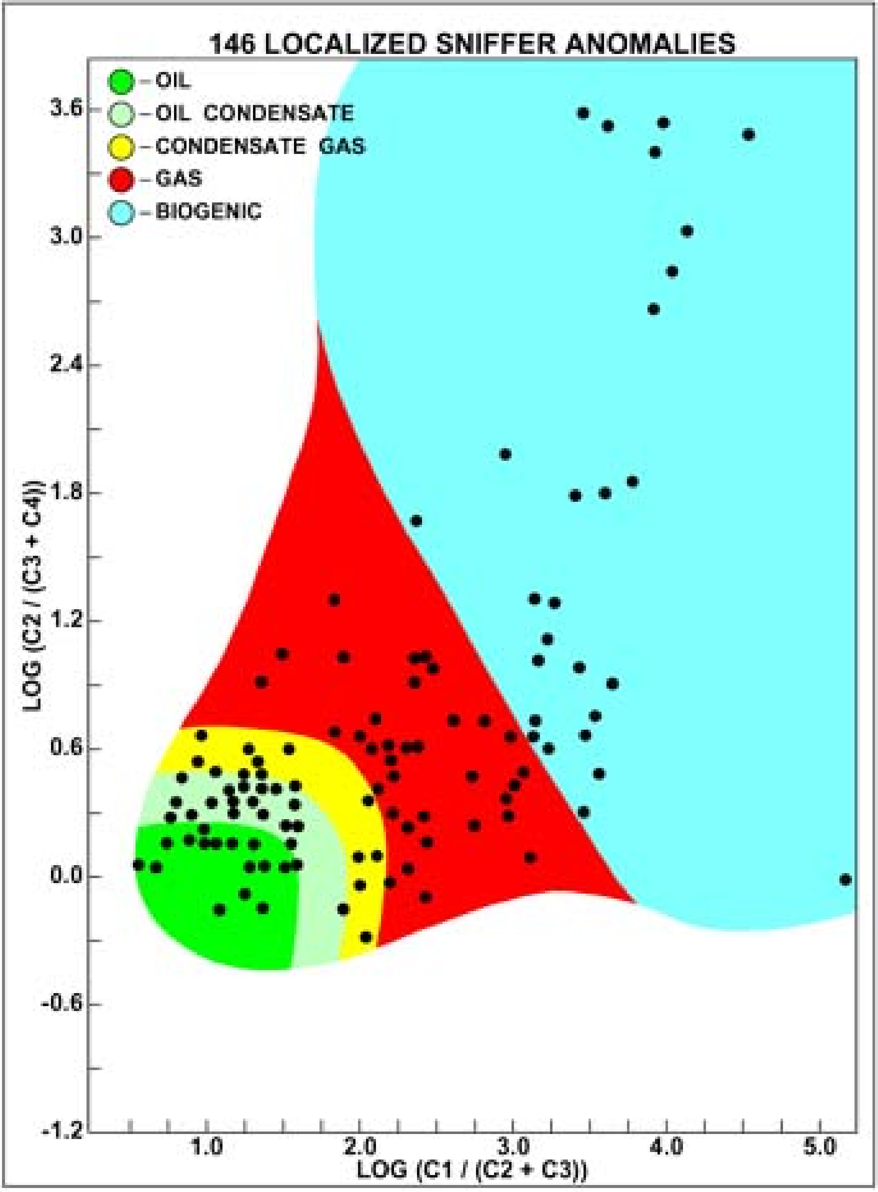
Gulf of Mexico Sniffer Data



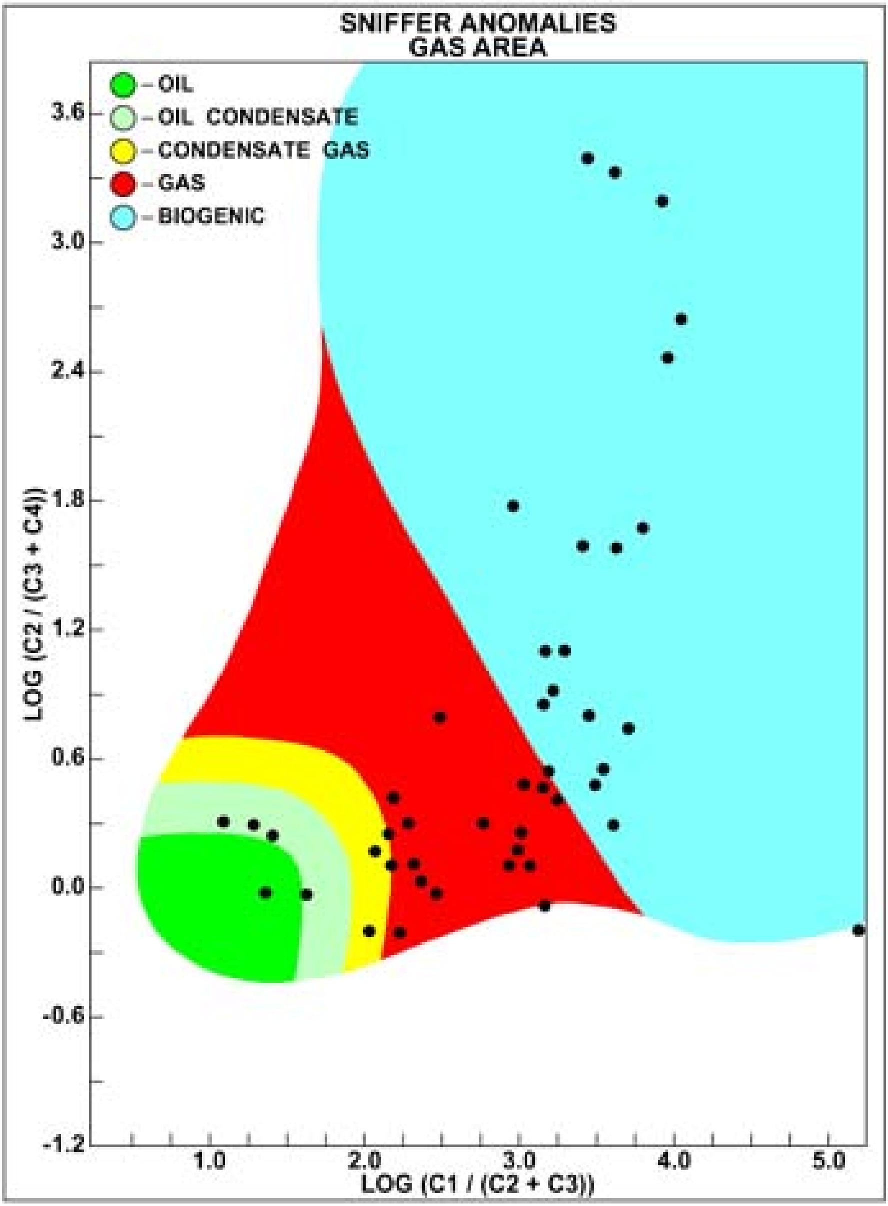
Louisiana Well Location Map



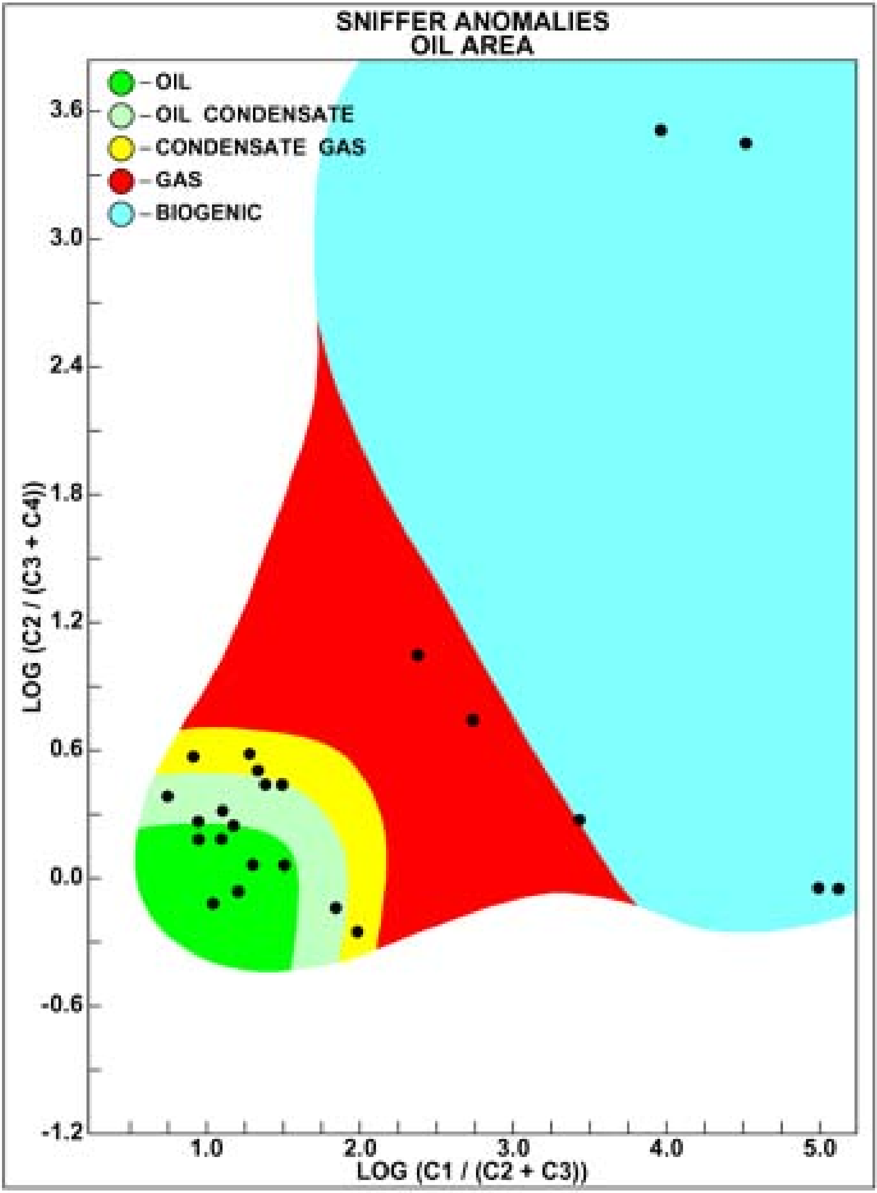
RICE (1978) RESERVOIR SAMPLES
– OIL
– OIL CONDENSATE
– CONDENSATE GAS
– GAS
– BIOGENIC
LOG (C2 / (C3 + C4))
LOG (C1 / (C2 + C3))
3.6
3.0
2.4
1.8
1.2
0.6
0.0
-0.6
-1.2
1.0
2.0
3.0
4.0
5.0
BG
G
C
O

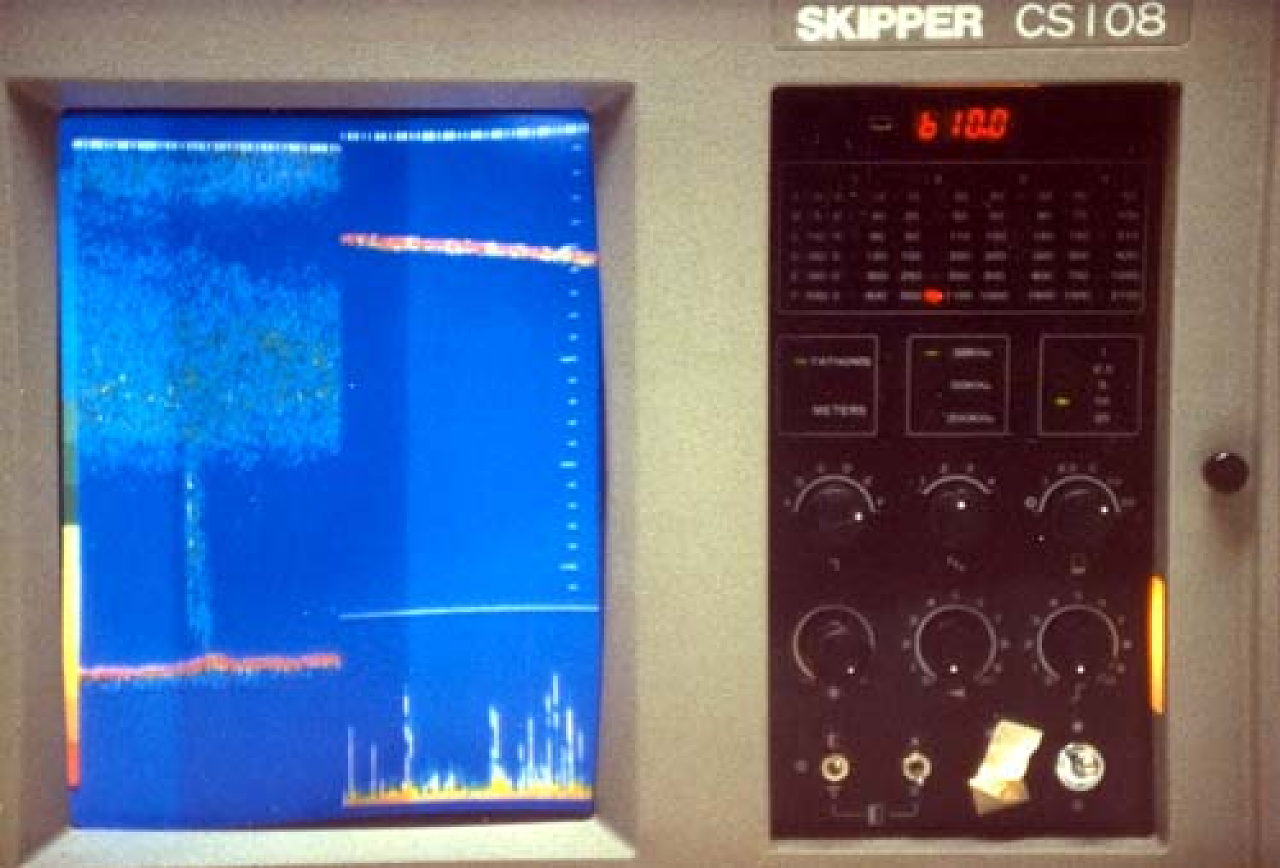


146 LOCALIZED SNIFFER ANOMALIES
– OIL
– OIL CONDENSATE
– CONDENSATE GAS
– GAS
– BIOGENIC
3.6
3.0
2.4
1.8
1.2
0.6
0.0
-0.6
-1.2
LOG (C2 / (C3 + C4))
1.0
2.0
3.0
4.0
5.0
LOG (C1 / (C2 + C3))



SNIFFER ANOMALIES
GAS AREA
– OIL
– OIL CONDENSATE
– CONDENSATE GAS
– GAS
– BIOGENIC
3.6
3.0
2.4
1.8
1.2
0.6
0.0
-0.6
-1.2
LOG (C2 / (C3 + C4))
1.0
2.0
3.0
4.0
5.0
LOG (C1 / (C2 + C3))


SNIFFER ANOMALIES
OIL AREA
– OIL
– OIL CONDENSATE
– CONDENSATE GAS
– GAS
– BIOGENIC
3.6
3.0
2.4
1.8
1.2
0.6
0.0
-0.6
-1.2
1.0
2.0
3.0
4.0
5.0
LOG (C2 / (C3 + C4))
LOG (C1 / (C2 + C3))


SKIPPER CS108