



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

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Dear Sir:

Enclosed is a summary of the vinyl chloride ambient monitoring programs conducted by EPA. These programs included preliminary monitoring by the regional offices around vinyl chloride (VC) and polyvinyl chloride plants (PVC) in the spring of 1974, more extensive monitoring around VC and PVC plants during November 1974 to June 1975, and monitoring around five polyvinyl chloride fabrication plants. These data are not new; they have been made available before to interested parties and are summarized in the Scientific and Technical Assessment Report (STAR) for vinyl chloride which we sent you previously. The enclosed summary provides more detail than the STAR document on the more extensive monitoring program around VC and PVC plants and the monitoring program around fabrication plants, and is intended only to supplement the information you already have.

Sincerely yours,



Don R. Godwin
Director
Emission Standards and
Engineering Division

Enclosure

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EPA PROGRAMS OF MONITORING
VINYL CHLORIDE
IN
AMBIENT AIR

MAY, 1974

NOV 1974 - May 1975

FEB - JUNE 1975

ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF AIR QUALITY PLANNING AND STANDARDS
Research Triangle Park, N.C. 27711
- Feb 2, 1976 -

GENC 013612

EPA PROGRAMS OF VINYL CHLORIDE
MONITORING IN AMBIENT AIR

EPA has conducted three programs to measure the vinyl chloride concentration in air around plants which either manufacture the material or use it. The first was a quick survey designed to estimate the magnitude of the airborne vinyl chloride (VC) problem. The second was a carefully planned program to measure VC around one plant which manufactures VC and around two plants which polymerize the monomer to form polyvinyl chloride (PVC). The third program was designed to measure VC around 5 plants which form the PVC into consumer products. The first and third of these programs have been completed, the data analyzed, and reports made public. Data from the second program - that concerning the single VC plant and the 2 PVC plants - are still being analyzed, but copies of the complete raw data have been provided to the monitored plants. Following, is a brief description of these three programs.

In early 1974, EPA Administrator, Russell E. Train, established a task force to determine what action EPA should take to protect the public from inadvertent exposure to VC, a compound which only recently had been shown to cause cancer in man. A major objective of the task force was to collect information on the concentration of VC in

air, waste water, sludges, etc., from VC and PVC plants. Because of the apparent urgency of the problem, it was decided that each of the EPA Regional Offices should conduct a brief sampling program around one or more plants in their region. Accordingly, on very short notice and with little equipment and planning, the seven Regional Offices which have such plants carried out a monitoring program. Table I lists the plants monitored.

TABLE 1
PVC Plants Monitored in May, 1974

<u>EPA Region</u>	<u>Company</u>	<u>Location</u>
I	Borden, Inc.	Leominster, Mass.
II	Tenneco Chemicals, Inc.	Flemington, N.J.
III	Diamond Shamrock Corp.	Delaware City, Md
	Stauffer Chemical Co.	Delaware City, Md
	Firestone Tire Co.	Perryville, Md
IV	B F Goodrich Co.	Louisville, Ky
V	Uniroyal, Inc.	Painesville, Ohio
	Robintech, Inc.	
VI	Goodyear Tire Co.	Plaquemine, La
IX	American Chemical Corp.	Long Beach, Ca
	B F Goodrich Co.	Long Beach, Ca

The sampling and analytical procedures used for this monitoring program had not been rigorously tested at the time, but because of the urgent need for data, all Regional Offices attempted to follow them carefully. Some were more successful than others. Both the sample collection procedures and the analytical procedure have subsequently been shown to be satisfactory.

Sampling was done in two ways: "grab samples" (glass syringes, glass tubes, vacuum containers, or Tedlar bags) and integrated samples (a known flow-rate of air passed through a charcoal adsorption column for 24-hours). The

samples were taken to the laboratory and analyzed by gas chromatography. Any vinyl chloride found in the samples could then be expressed as "instantaneous" concentrations (micrograms per cubic meter, $\mu\text{g}/\text{m}^3$), if the sample were a grab sample, or as 24 hour average concentration, if it were an integrated sample. Because the ambient concentrations of VC are usually small, the integrated sample collection procedure is usually the one which shows any VC. Only if a grab sample is taken at the very time a puff of VC passes the sampling point will there be any indication of VC in the ambient air.

The results from this brief monitoring program were perforce less than satisfactory. Lack of equipment, unskilled personnel, and unusual weather patterns combined to produce many blank samples or data of unknown accuracy. The most important conclusion from the experiment was that VC could be found in ambient air near PVC plants and that a much better monitoring program was needed. Table II summarizes the data gathered around each plant. It must be remembered that the analytical accuracy is unknown, and that low values could mean either low emissions from the plant, adverse meteorology, or inappropriate sampling times. The detailed reports have been made public for those who want to examine them, but it is felt that Table II summarizes the data as completely as is justified.

TABLE II

Summary of VC Monitoring Data - May, 1974

<u>Region</u>	<u>Plant</u>	<u>Sampling Period</u>	<u>No. of Samples</u>	<u>Max VC (ppm v/v)</u>
I	Borden, Inc.	May 9,10,13	45 bag 112 syringe 12 integrated (128 samples had no detectable VC)	0.9 6.0 1.05
II	Tenneco Chem.			
III	Diamond Shamrock Stauffer Chem Firestone Tire	May 16, 20, 22 May 21,29	5 bag bag	0.7 ppm none detected
IV	BF Goodrich	May 8-16	121 bag 67 syringe 35 integrated 21 helicopter syringe (65 samples had no detectable VC)	33 11 1.5 0.25
V	Uniroyal Inc Robintech Inc	May 8-10	13 bag 58 can 36 syringe 29 tube (37 samples had no detectable VC)	0.11 1.16 0.35 2.26
VI	Goodyear Tire Co.	May 7-9	31 bag 12 syringe	2.07 5.76
IX	American Chem Corp. BF Goodrich Co	May 7-9	180 bag 16 integrated continuous instrument (on plant property)	3.4 0.65 75 ¹ (instant. peak)

¹Due to a ruptured pipe.

From this brief survey it was apparent that vinyl chloride could be found in the ambient air around PVC plants and a more rigorous monitoring program was warranted. Accordingly, a major effort went into setting up and carrying out a study of the VC around two PVC plants and one plant which produces the VC monomer. Simultaneously, a more modest study was begun to measure the VC around plants which fabricate PVC into consumer products, since the fabricating operations can liberate occluded BC from the PVC raw material. This latter program will be described first, because it is simpler, completed, and the results published. (The bigger program is more complex to describe and the data are still being analyzed.)

PVC is formed into thousands of user-products, but the majority of the material goes into a relatively few basic products. It was decided that the PVC fabrication plant study should concentrate on 5 of these large use products and that the largest plants producing these products should be monitored, if at all possible. Table III lists the pertinent information about these plants.

TABLE III
Plants Monitored During the PVC Fabricator Study

<u>Company</u> <u>(Principal Product)</u>	<u>Location</u>	<u>Dates of Sampling</u>
Ford Motor Co. (Upholstery Products)	Mt. Clemens, Mich	Feb 12-26, 1975
Congoleum Industries (Floor Coverings)	Marcus Hook, Pa	Feb 15-March 1
Reynolds Metals Co. (Packaging Materials)	Grottoes, Va	March 12-26
Charlotte Pipe and Foundry (Pipe & Fittings)	Monroe, N.C.	April 10-24
ITT Co. (Cable Coverings)	Pawtucket, R.I.	May 22-June 5

The monitoring program consisted of collecting 24 hour integrated samples daily on each of the four sides of the plants, as close to the fence line as possible, for two week periods. A minimum of 56 samples were thus collected at each plant. The samples were returned to the laboratory and analyzed by gaschromatography. A rigorous quality control program was instituted at the beginning of the program, so that the analytical data are considered reliable. In addition, some duplicate samples were collected and analyzed by independent laboratories, thus adding to the confidence in the data. The minimum detectable concentration of VC by the methods used is 0.5 parts per billion ($0.5 \text{ in } 10^9$, v/v). Table VI summarizes the data from this program.

TABLE IV
Data Summary From the PVC Fabricators Study

<u>Plant</u>	<u>Location</u>	<u>No. of Samples Collected</u>	<u>Max VC Found (ppb)</u>	<u>No. of Samples With no VC</u>
Ford Motor Co.	Mt Clemens, Mich	64	7.0	55
Congoleum Ind.	Marcus Hook, Pa	63	4.0	26
Reynolds Metals	Grottoes, Va	61	2.0	18
Charlotte Pipe & Foundry	Monroe, N.C.	62	0	62
ITT Co.	Pawtucket, R.I.	63	0	63

Thus, the data show that very little, if any, VC escapes from PVC fabricating plants into the surrounding air.

The major monitoring program carried out by EPA has one designed to validate a mathematical model which attempts to simulate emissions from any VC or PVC plant. The Shell Chemical Co. plant at Norco, Louisiana was the vinyl chloride manufacturing facility chosen, and the Conoco Chemicals plant at Aberdeen, Miss. and the B F Goodrich Chemical Co. plant at Louisville, Ky both of which produce PVC, were selected.

The major monitoring program carried out by EPA was one designed to validate a mathematical model which attempts to simulate emissions from any VC or PVC plant. The Shell Chemical Co. plant at Norco, Louisiana was the VC manufacturing facility chosen, and the Conoco Chemicals plant at Aberdeen, Miss. and the B. F. Goodrich Chemical Co. plant at Louisville, Kentucky, both of which produce PVC, were selected.

Twenty-four hour integrated samplers were set up around each of these plants at various directions and distances after a study of the meteorology of the area. In general, two samples were collected per week at each sampling site and returned to the laboratory for gas chromatographic analysis. The majority of the stations were in the predicted downwind direction, while a smaller number was distributed in upwind directions in order to establish background levels of VC in the incoming air. Partway through the program, when it became clear that the prevailing meteorological patterns were different from the predicted ones, it was decided to concentrate all samplers for one-month periods at two of the plants in sequence. Table V summarizes the sampling periods.

Table V
Sampling at VC and PVC Plants

<u>Company</u>	<u>Location</u>	<u>No of 24-Hour Integrated Samplers</u>	<u>Dates</u>
Shell Chem. Co.	Norco, La	15 30	Nov 19-Apr 8, 1975 Apr 8-May 5, 1975
Conoco Chem.	Aberdeen, Miss	15	Nov 6-Mar 27, 1975
B. F. Goodrich	Louisville, Ky	17 38	Nov 6-May 15, 1975 May 15-June 12, 1975

In addition, one continuous sampler was used during the sampling program at Aberdeen and two and three continuous samplers were used during the second parts of the sampling programs at Norco and Louisville, respectively. The purpose of these samplers was to evaluate the instrument's reliability and to observe any rapid excursions of vinyl chloride, should they occur. Information from these samplers is of limited value because on many days they did not operate due to malfunctions.

Information on wind direction and wind speed were collected at each plant during the sampling program. Also the plants submitted to EPA records of unusual occurrences which would be expected to affect emission rates from the plants. These included such things as relief discharges, plant shut-down or start-up, changes in operating rate, and installation or adoption of control measures.

For several reasons it is difficult to summarize the data from this sampling program. A frequency distribution of all the data, for example, is not warranted because the samplers were not sited at the proper distances nor in the optimum directions. Neither are average values significant, because the prevailing wind speeds and directions produced many non-detectable concentrations in many of the samples. Even the frequency distribution and averages for single samplers are of limited value for the same reasons. The data have been summarized to the extent possible in Table VI.

TABLE VI
Results From Sampling Program Around
VC and PVC Plants

	<u>Norco</u>	<u>Aberdeen</u>	<u>Louisville</u>
Total No. Samples	807	530	1156
No. of Zero's	128	53	170
No. < 25 ug/m ³ (0.01 ppm)	533	205	702
No. > 250 ug/m ³ (0.1 ppm)	84	153	65
Max. Value Found (24-hour average)	27046 ug/m ³ (10.6 ppm)	23430 ug/m ³ (9.2 ppm)	976 ug/m ³ (0.38 ppm)

Interpretation of the data would be useful in two respects. First, it would be useful to evaluate the significance of the results in terms of health effects. This is not possible for a couple of reasons. Since the purpose of the sampling program was to validate a diffusion model, a large proportion of the samplers were located on plant property rather than in residential areas. Even if there were more data from the residential areas, EPA knows of no threshold level of health effects to compare these values with.

Second, it would be useful to determine if there are any relationships between peak concentrations and specific emission sources or plant operations, and if so, to define these relationships. This is difficult, especially at PVC plants, for several reasons. During the sampling program, due to economic conditions, VC and PVC plants in general were not operating at their normal capacities. The VC plant used in the program was operating between 50 and 110 percent of capacity,

averaging at about 70 percent. One of the PVC plants operated at about 50 percent of capacity during the first part of the program and 60 to 70 percent during the second part of the program. The operating rate at the second PVC plant varied widely from 0 to 80 percent of capacity. It operated at below 50 percent of capacity during most of the program. Also, particularly in PVC plants there are a large number of emission sources and a fluctuation in emissions. PVC production unlike VC production is largely a batch rather than a continuous process. Since only abnormal plant occurrences were requested to be reported to EPA, normal fluctuations in emissions cannot be compared with ambient concentrations. Furthermore, the placement of samplers and the meteorological conditions at the time of an emission excursion are important in determining which samplers, if any, are affected. Obviously, enough samplers cannot be placed around a plant to pick up all emission excursions. Also, the degree of variability in meteorological conditions during the 24-hour period that an integrated sample is collected affects the amount of vinyl chloride collected in that sample.

Although definitive conclusions cannot be made about the results from the sampling program, observations can be made by selecting out the relatively high data, looking at the wind speed and direction, and thereby determining the probable source of emissions. "Relatively high" as used here means high with respect to other data obtained from the plant and not necessarily high with respect to levels which cause health effects.

For example, Table VI indicates that the maximum 24-hour average value reported at the VCM plant was 10.6 ppm. It should be noted that this is an unusually high value obtained for this plant. The next to

highest value was approximately 1.66 ppm. The maximum concentration was obtained on plant property between two VC storage tanks in the area where tank cars are loaded with VC. A leaky valve could possibly have caused this high concentration. This sampler location continued to be the source of the majority of the relatively high 24-hour average values obtained during the sampling program at this plant. There was a reduction in the number of relatively high values from this sampler as the program continued. This can probably be attributed to the plant's efforts to detect and eliminate major sources of leaks in the storage and shipping area. Another plant operation which appeared to cause relatively high results in the 24-hour average samples was plant start-up. The relatively high concentrations ($> 500 \mu\text{g}/\text{m}^3$ or .198 ppm) were found that day at three samplers located on plant property downwind of the stack.

The maximum one-hour average reading from the continuous monitors located at the VC plant was 1.40 ppm. This reading occurred three times at a monitor located on plant property and 650 feet from the main stack. The 24-hour samplers were not operating the days these readings occurred. Two of the maximum readings occurred consecutively on one day. The plant was not operating that day. No abnormal plant operations occurred at the time of the third maximum reading. The cause of these peaks is unknown. Interference is a possibility, however, because this plant is located in a large petroleum complex.

The maximum 24-hour value observed at the PVC plant in Aberdeen was in a sample collected on plant property downwind from the reactor buildings. Another sample collected at a nearby sampling site and also on plant property showed an average concentration of 3.0 ppm

for the same 24-hour period. The reason for the high values is not readily apparent. The plant was operating at about one-sixth of its capacity, which was lower than average during the sampling period. According to plant records, there were two nonroutine occurrences in the plant operation that day. A vinyl chloride filter in the reactor area (100 feet west of the reactors) was cleaned and a blowdown tank was drained and flushed. It is not known for sure whether these operations contributed to the high values. However, on another day when two vinyl chloride filters were cleaned and the wind direction was approximately the same, relatively high VC values were observed from the same and additional samplers. It should be noted that most of the relatively high 24-hour average readings ($>500 \mu\text{g}/\text{m}^3$ or .198 ppm) obtained during the sampling period at Aberdeen occurred in the area where vinyl chloride monomer is unloaded from tank cars and stored.

There were several reactor relief discharges at the Aberdeen plant during the sampling program. The 24-hour integrated samples would not necessarily reflect these discharges due to the short time of the release and the long averaging time of the sample. These discharges were not reflected in the continuous monitor readings either. This is probably because the wind on these days was not moving in the direction from the plant to the continuous monitor. On the day when a power failure occurred and one of the large reactors was vented, the wind was moving in the opposite direction from the continuous monitor. The peak one-hour average concentration detected by the continuous monitor during the sampling program at Aberdeen was 1.40 ppm. The cause of this peak is unknown.

The maximum 24-hour average value observed at the Louisville PVC plant occurred on a day when a relatively large number of the samplers both on and off plant property (9 out of 38) had relatively high readings ($>500 \mu\text{g}/\text{m}^3$ or .198 ppm) compared with the other days samples were taken at this plant. The only nonroutine operation recorded by the plant that day was a reactor relief discharge. This is not necessarily the cause of the higher values obtained by the 24-hour samplers due to their long averaging time. There were 3 peak one-hour average values on the continuous monitor that day (2.00 ppm, 2.00 ppm, and 2.44 ppm). Two of these occurred about the time of the relief discharge. The wind was blowing in the direction of the continuous monitor at that time. There were several other days during the sampling program on which there were relief discharges. On all of these days except one, the continuous monitors were not operating. On that day, one monitor was operating and the wind was not blowing in the direction of the monitor from the plant.

In conclusion, some relatively high readings were obtained during the sampling program. The majority of these were on plant property. Sufficient information is not available to draw definitive conclusions concerning the relationship between these values and health effects in the residential areas around these plants. Also, it appears that emission excursions are reflected in the concentrations measured at the plants. EPA's proposed standard for vinyl chloride will reduce emission excursions through regulation of relief discharges and fugitive emissions.