the (001) plane is made possible by the linkage of the octahedra to the tetrahedra of the 6f type by the general position tetrahedra. It should be kept in mind that the distances (see Table 2) between the equilibrium sites for the Ag+ ions put constraints on the motions of the Ag+ ions. This is more fully described in (5).

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References and Notes

- 1. H. Wiedersich and S. Geller, in The Chemistry of Extended Defects in Non-Metallic Solids, L. Eyring and M. O'Keeffe, Eds. (North-Holland, Amsterdam, 1970), pp. 629-650
- 2. S. Geller, Science 157, 310 (1967). 3. _____ and M. D. Lind, J. Chem. Phys. 52, 5854 (1970).
- 4. The first report of compound formation in the pyridine-silver iodide system was made by B. B. Owens (138th national meeting of he Electrochemical Society, Atlantic City, N.J., October 1970, abstract 24, p. 65).
- 5. For the Ag+ ion site distribution, structure,

Environmental Applications of the Weibull Distribution Function: Oil Pollution

Abstract. The Weibull distribution function appears to be a powerful tool for the statistical analysis and interpretation of environmental pollution data. To illustrate its potential, the method is applied to a variety of oil pollution topics. Other applications are suggested.

applicability.

 $\ln \ln [1 - F(x)]^{-1} =$

data from (3).

Beach

а

b с

d

f

as (1)

Most forms of environmental pollution cannot be quantified by a single or unique numerical value. Rather, a complicated and interactive set of physical, chemical, biological, and human processes act in concert to yield a spectrum of measured values. In order to establish meaningful and representative concentrations of pollutants, it is thus customary to collect field data from several sampling stations, at different times, and under a variety of sampling conditions. The individual measurements are then combined to yield an average, a median, a mean, a geometric mean, or some other statistical expression of pollutant concentration.

My purpose here is to report some preliminary results of a new method for statistically analyzing environmental pollution data. In this method the Weibull distribution function is used as a correlating model, and the method appears to have considerable potential for interpreting ambient pollutant concentrations. In the following paragraphs, pertinent features of the Weibull distribution function are summarized and then several examples and conductivity of $(C_{8}H_{5}NH)Ag_{5}I_{6}$ between -30° and 125°C see S. Geller and B. B. Owens (*J. Phys. Chem. Solids*, in press).

- 6. The density was measured by compacting some of the polycrystalline material at a pressure of 5500 bars and measuring and
- weighing the resulting pellet. P. B. Crandall, *Rev. Sci. Instrum.* **41**, 1895 7. P. (1970).
- 8. A. Schuyff and J. B. Hulscher, ibid. 36, 957 (1968).
- (1968).
 9. B. Post, R. S. Schwartz, I. Frankuchen, *ibid.* 22, 218 (1951).
 10. W. L. Bond, *Acta Crystallogr.* 12, 375 (1959).
 11. W. R. Busing, K. O. Martin, H. A. Levy, *Report ORNL-TM-305* (Oak Ridge National Content of Conte 11. Laboratory, Oak Ridge, Tenn., 1962). 12. D. T. Cromer and J. T. Waber, Acta
- Crystallogr. 18, 104 (1965).

- Crystallogr. 18, 104 (1965).
 13. D. T. Cromer, *ibid.*, p. 17.
 14. M. V. King and W. N. Lipscomb, *ibid.* 3, 318 (1950).
 15. Calculated with the crystallographic function and error program of W. R. Busing, K. O. Martin, and H. A. Levy [Report ORNL-TM-306 (Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964)].
 16. I wish to thank H. Wiedersich and B. B. Owen for discussion, G. P. Espinosa for growing the crystals used in this study, M. D. Lind for use of some of his computer programs, and P. B. Crandall for technical assistance. assistance.
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dealing with oil pollution are given

to illustrate the method's versatility and

The Weibull equation is an empirical three-parameter distribution function

 $-\ln \alpha + \beta \ln (x - \gamma) \quad (1)$

в

Median

 (g/m^2)

0.10

.12

.07

.03

11.0

0.23

A/B

0.18

.15

.01

.03

.33

.35

which is expressed in linearized form

In this equation, F(x) is the cumula-

tive probability that a variable will have

a value of x equal to or less than a

Table 1. Weibull parameters obtained from

the analysis of beach tar deposits along the

southern California coastline. Beach locations

are shown in Fig. 1A; Table 1 is based on

Α

Threshold

 (g/m^2)

0.018

.018

.001

.001

3.6

0.080

18 October 1971; revised 20 March 1972

given value, α is a scale parameter, β is a shape parameter (which varies with the skewness of the distribution), and γ is a threshold parameter. The parameter of greatest interest in the present application is γ . In its broadest sense, γ may be interpreted as the minimum value that the variable x is likely to attain; that is, the probability of x being less than γ is essentially zero.

The Weibull distribution function (which, in modified form, is known by several other names) has been applied to a wide variety of topics including fatigue (life) testing, quality control, particle size analysis, and odor threshold (1). Although it is basically an empirical model, these applications have suggested that a physical interpretation can be made of its parameters—particularly γ . To my knowledge the Weibull distribution function has not been previously applied to pollution monitoring problems.

The first example deals with beach contamination from natural oil seeps along the southern California coastline (2) (see Fig. 1A). Data used in this analysis were collected at 12 monthly intervals in 1959 and 1960 (3). The ambient amounts of contaminating beach tar deposited at four of the six sampling stations are shown in Fig. 1C (the amounts at stations b and c are very nearly the same as that at station a and are not shown for reasons of clarity). Table 1 summarizes the important Weibull parameters (4).

Although a detailed interpretation of these results is beyond the scope of this report, one observation can be made immediately. The data in Table 1 show that the threshold and median concentration of tar found on beach e is considerably heavier than that on any other sampling station. However, the ratio of the threshold to median values for this beach is essentially the same as for beach f (see Fig. 1A). In the same vein, similar threshold to median ratios exist for beaches a and b in Santa Monica Bay and for beaches c and d in the eastern Santa Barbara Channel. These observations suggest the possibility that the tar deposition process may be governed by several spatially distinct mechanisms of oil transport. Knowledge of the threshold values has thus opened new doors for the interpretation of these data.

The second example deals with the more conventional topic of oil spills. Curve 1 in Fig. 1D shows a Weibull plot for minor and moderate spills, that is, less than 80,000 liters, during the period January through June 1971. The data used in this analysis were reported by the Environmental Protection Agency and involved 296 spills of known size (5). The analysis indicates a median value of 2300 liters and a threshold value of 600 liters. One possible interpretation of this threshold value is that spills of less than 600 liters are either not reported or are dissipated too quickly to be detected.

At the other end of the spectrum are major oil spills, those greater than 80,000 liters. Figure 1D shows the Weibull analysis of two sets of data on major spills: curve 2 for 24 spills



Fig. 1. (A) Map of the southern California coastline showing (\bullet) major regions of active natural oil seepage and (\bigcirc) locations of beach sampling stations. The beaches shown are as follows: *a*, Sunset; *b*, Torrance; *c*, Mussel Shoals; *d*, Summerland; *e*, Coal Oil Point; and *f*, Gaviota. (B) Weibull plots from major oil spills for the period 1956–1969. Curve 1 shows the extent of coastline contamination; $\gamma = 7$ km. Curve 2 shows the spill duration; $\gamma = 1.3$ days. (C) Weibull plot of the amounts of beach tar deposited along the southern California coastline. Weibull parameters are summarized in Table 1. (D) Weibull plot of oil spill volumes; curve 1 for minor and moderate spills, January–June 1971: $\gamma = 600$ liters; curve 2 for major spills, January–June 1971: $\gamma = 150,000$ liters; curve 3 for major spills, 1956–1969: $\gamma = 140,000$ liters.

occurring during the first half of 1971 (5) and curve 3 for 27 spills occurring from 1956 through 1969 (6). The difference in median values $(3.1 \times$ 10^5 liters for 1971 compared to 3.6 \times 10⁶ liters for 1956 through 1969) presumably reflects the large difference in time span. However, despite these large differences, both sets of data yield comparable threshold values: 150,000 liters for curve 2 and 140,000 liters for curve 3. It would thus appear that little if any progress has been made in minimizing the amount of oil released in a major spill. This type of data interpretation should be of particular value to organizations involved in contingency planning. For example, sufficient equipment should be stockpiled at any given staging area to deal with a spill of at least 150.000 liters.

The oil spill data for 1956 through 1969 provide yet other examples of the applicability of the Weibull method of analysis. Curve 1 in Fig. 1B shows the analysis of coastline contamination from 21 major oil spill incidents (7). These data indicate that, should a major oil spill occur, it is likely to affect at least 7 km of coastline. This result is clearly of value to contingency planners. Furthermore, this threshold level of coastline contamination reflects on the effectiveness of open-sea combatant techniques and the rapidity of oil spill response measures. In other words, a "perfect" response capability could be interpreted to mean that, even if a major spill occurred, the oil would be contained and treated at sea and none would reach neighboring beaches. If this were the case, the threshold level of coastal contamination would be expected to be zero.

As a final example, the oil spill data for 1956 through 1969 also provide information on the expected duration of a given incident. Somewhat surprisingly, the data shown in curve 2 of Fig. 1B, which are based on 23 incidents, indicate a threshold value of only 1.3 days and a median value of 13 days. Loosely interpreted, the duration of a spill is a measure of the length of time during which combatant procedures are either required or effective. It would thus appear that the dissipative action of the marine environment is a significant deterrent (or, depending on one's point of view, a powerful ally) in combating a major oil spill.

At this point I wish to reemphasize that the main purpose of this report has been to focus attention on the Weibull distribution function as a means of correlating environmental pollution data. In this regard, the preceding analyses of oil pollution data attest both to the method's versatility and to its correlational ability. The interpretations that have been offered for these Weibull analyses are by no means conclusive; rather, they are merely intended to illustrate the interpretative potential of the Weibull threshold parameter.

I believe that the Weibull distribution may well be applicable to such diverse environmental problems as automotive emissions, pesticide and trace metal contaminant concentrations, marine fauna mortality, and a host of others. It may also provide new insight in evaluating the effectiveness of pollution control measures. Hopefully, investigators from other disciplines and fields of interest will explore these possibilities.

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References and Notes

- Excellent reviews and bibliographies of the Weibull distribution function are presented by F. H. Steiger [*Chem. Technol.* 1, 255 (1971)] and C. C. Harris [*ibid.*, p. 446].
 Details of the natural oil seeps in the Santa
- Details of the natural oil seeps in the Santa Barbara Channel have been presented by A. A. Allen, R. S. Schlueter, and P. G. Mikolaj [Science 170, 974 (1970)]; seeps in the Santa

Monica Bay have been discussed by A. A. Allen, L. E. Fausak, V. N. Sutherland, P. G. Mikolaj, and R. S. Schlueter ("Santa Monica Bay natural oil seep investigation," final report to the El Segundo Refinery, Standard Oil Company of California, by Marconsult, Inc., Santa Monica, December 1971).

- Santa Monica, December 1971).
 H. F. Ludwig and R. Carter, "Analytical characteristics of oily substances found on Southern California beaches," report prepared for the Western Oil and Gas Association by Engineering-Science, Inc., Arcadia, Calif., 1960; J. Water Pollut. Contr. Fed. 33, 1123 (1961).
- 55, 1125 (1901).
 4. The data points shown in Fig. 1, B–D, were obtained by arbitrarily grouping the actual field measurements. In all cases, the highest level of pollution shown coincides with the maximum field observation. Although grouping the data tends to introduce some variability into the resultant parameters, it simplifies considerably the task of obtaining a visual straight line. Other more sophisticated methods are also available (*I*).
- "Oil Pollution Research Newsletter" (Environmental Protection Agency, Edison Water Quality Laboratory, Edison, N.J., July 1971), vol. 4.
- 6. G. A. Gilmore, D. B. Smith, A. H. Rice, E. H. Shenton, W. H. Moser, "Systems study of oil spill cleanup procedures; vol. 1, Analysis of oil spills and control measures," report prepared for the American Petroleum Institute by the Dillingham Corporation, La Jolla, Calif., February 1970).
- 7. This analysis does not include the *Torrey Canyon* spill which contaminated a reported 390 km of coastline. The remaining data included 12 incidents with a shoreline contamination ranging from 3 to 45 miles (4.8 to 72 km); in addition to these, two incidents were reported as minor and seven were reported as moderate. These latter incidents were assumed to involve less than 5 miles, and 5 to 10 miles of shoreline, respectively.
- 8. This work is a result of research sponsored by the National Science Foundation under grants GH 43 and GH 95, and by the National Oceanic and Atmospheric Administration Office of Sea Grant, Department of Commerce, under grant USDC 2-35208-5.

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Statistical Thermodynamic Model for the Distribution of Crustal Heat Sources

Abstract. The observed linear correlation of surface heat flux in continental regions with the radioactive heat release in the surface rocks is consistent with an exponential depth dependence of the concentration of the heat sources. We suggest that this depth dependence can be explained as an equilibrium distribution of the heat-producing elements in a gravitational field. The effective mean mass range of the elemental assemblies being differentiated is predicted, and it appears that potassium, uranium, and thorium diffuse upward in ionic complexes with other elements. Similar considerations should apply to the distribution of other elements in the crust and mantle.

Quantitative evidence for the upward concentration of heat-producing elements within the continental crust in general and large plutonic bodies in particular has come from geochemical studies (1, 2), from measurements of surface heat flow coupled with measurements of heat production in nearsurface igneous bodies at the sites of the heat-flow measurements (3-5), and from direct measurements (6). It has been shown (3-5) that surface heat flow, q_s , in continental regions has a

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linear correlation with the radioactive heat release, $H_{\rm s}$, in the near-surface rocks. This correlation is shown in Fig. 1 for the Sierra Nevada, Basin and Range, and tectonically inactive regions of the United States. Lachenbruch (7) has shown that these results are consistent with an exponential dependence of the radioactive heat release on depth.

So far no adequate explanation has been advanced for this exponential depth dependence, which is of fundamental significance in understanding the evolution of the continental crust and which is not readily understood in terms of conventional igneous differentiation processes. We have approached this problem by considering the equilibrium distribution of large ionic complexes in a high-temperature medium in a gravitational field. This technique has been used successfully to treat such problems as the distribution of gas molecules or particulates in the atmosphere. The applicability of this differentiation process to the crust has been suggested by Ramberg (8).

For the differentiation process to have resulted in the observed upward concentration of heat production it must have, to a greater or lesser extent, affected all three of the principal heatproducing elements, uranium, thorium, and potassium. This has been confirmed by the concentrations measured in borehole samples by Lachenbruch and Bunker (6).

Lachenbruch (7) shows that observations are consistent with an exponential fall in radioactivity with depth of the form

$$H \equiv H_{\rm s} \exp(-y/h) \tag{1}$$

where y is the depth and h is the scale depth for the radioactive heat sources. Integration of Eq. 1 gives

$$q_{\rm s} \equiv H_{\rm s} \, h + q_{\rm z} \tag{2}$$

where q_{∞} is the heat flow from the lower crust and upper mantle. The linear correlation from Eq. 2 is given in Fig. 1 with h = 10 km. Within the experimental scatter the scale depth is the same for these very different geological provinces.

The exponential depth dependence and the nearly constant scale depth can be explained by equilibrium statistical thermodynamics, that is, the Boltzmann factor. In thermodynamic equilibrium the distribution of any group of particles is proportional to $\exp(-\epsilon_i/kT)$, where ϵ_i is the energy of the particle *i*, *k* is Boltzmann's constant, and *T* is the absolute temperature. Taking the energy to be the gravitational potential energy we may write

$$H = H_s \exp\left(-\frac{\Delta \rho Mgy}{\rho RT}\right) \qquad (3)$$

where M is the molecular mass of the assembly that is being differentiated, $\Delta \rho$ is the density difference between the molecular assembly and the surrounding medium, ρ is the density of that medium, R is the universal gas con-