

Degradation Kinetics Study Of Monocrotophos Pesticide (MCP) In Unsterilized Soil in Nigeria

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Abstract— Sorption Kinetics of monocrotophos in unsterilized sandy soil was studied with the aim to establish its degradation in the soil. The soil used was characterized with respect to soil pH, organic carbon, moisture, silt, clay and sand content. The sorption kinetic studies were carried out by observing the disappearance of monocrotophos in solution for several days. The kinetic studies showed that sorption of monocrotophos followed first order kinetics and were measured in terms of two processes namely; fast and slow sorption. The amount of pesticide sorbed by soil was found to increase with time and the values showed that the soil has low capacity to sorbe or retain monocrotophos when applied. During this time, rate constant for the disappearance from solution of monocrotophos for fast and slow sorption processes were studied and the rates for fast sorption and slow sorption were found to be 10.805 s^{-1} and 0.2396 s^{-1}

Keywords— Monocrotophos, Sorption, Kinetic, Soil, Rate, Freundlich Isotherm.

I. INTRODUCTION

DEGRADATION of pesticides refers to the breakdown of pesticides within the environment [1]. The degradation may occur through photodegradation, chemical degradation or biodegradation [2]. All chemicals are susceptible to photodegradation to some extent. The degree of photodegradation will depend on the intensity of the sunlight and the time of exposure [1]. However many pesticides move relatively quickly into the soil and are thus no longer exposed to sunlight and therefore not susceptible to photodegradation [3]. Chemical degradation is due to reactions of the pollutant with e.g. water, oxygen or other chemicals [4], [1]. Biodegradation refers to the degradation of the pesticides by organisms; most often microorganisms like bacteria and fungi, but in some cases plants may be involved in the degradation as well [2].

The term “pesticide” embraces an enormous diversity of products that are used in a number of different activities and are intended for preventing, destroying, repelling or mitigating pests [5]. Their introduction into the environment, whether by application, disposal, or a spill, can be influenced by many processes. They could be translocated, transformed or sorbed.

These processes regulate the ultimate fate of the pesticide by affecting its persistence and movement in the

environment. The optimum life of a pesticides or its persistence is measure by its half-life. Mobility of pesticides is one of the factors that affect the distribution of the pesticides into the soil water phases. The mobility of the pesticide is restricted when associated with solid phase; while on the other hand, the mobility is enhanced when associated with solution [6]. The mobility of pesticides in soil is guided by pH, organic matter, moisture, Clay content, and distribution coefficient (K_d) of pesticide. The hazards of pesticides in soil largely depend on their persistence. The longer they persist, the greater are the chances of contamination of soil. Ideally, pesticides should persist only long enough to complete its intended mission and then degrade to harmless products before it is necessary to apply again [7].

In many developing countries, the pesticides use is not being properly regulated leading to residues in food which poses health hazards to the consumers [8]. Therefore, residues of pesticides could affect the ultimate. Many studies reported that the main pesticide residues were organophosphate [9,10,11, 12].

Monocrotophos (Dimethyl (E)-1-methyl-2 methyl carbamoyl vinyl phosphate) is a broad spectrum organophosphate (OP) insecticide widely used for agricultural and household purposes, which works systemically and on contact [13, 14]. Following concern on its toxicity to non-target species especially birds, monocrotophos was voluntarily withdrawn from sale in the US in 1989. It was also banned in Indonesia, Sri Lanka and Philippines while its use is severely restricted in Kuwait and Malaysia [15]. Monocrotophos is still in use in Nigeria and it is usually applied directly on agricultural land primarily to control pests and to improve crop yield with the aim to meet the high demand for food due to the fast growing population [15]. The long standing practice in which this pesticide was studied intensively on how to be applied to crop and insect pests has been extended to practices such as adsorption and sorption processes in soil environment in different part of the world. This knowledge is essential to make a better use of the wide variety of chemical compounds that are now available for weed, control, and for elucidating possible adverse environmental effects and their control [6]. In Nigeria and elsewhere, there are far-reaching literature on the comparative degradation of MCP by microbial, enzymatic and Photodegradation methods [14,16]. However, despite the abundance of literature on monocrotophos in these aforementioned area, there is scantiness of information on the degradation kinetics of this pesticide in natural soils in Nigeria.

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In view of the indiscriminate use intensive and continuous use of MCP in Nigeria, the sorption kinetics of MCP degradation in soils is a need to understand persistence in soil. In this work, the sorption kinetics of MCP in soil was carried out in naturally occurring soil samples; without combination with any microbe or enzyme or sterilization so as to have a clear idea of the behaviour of the pesticide in real life in the field. Sorption processes involve an array of phenomena which can alter the distribution of contaminants between and among the constituents phases and interfaces of subsurface system [17]. Organophosphorus pesticides have been reported to rapidly degraded with less persistence in soil [18]. Monocrotophos has a half-life of 14-21 days at pH 9 and 25°C, with the rate decreasing at lower pH's and increasing at higher temperatures [19]. Degradation on soil exposed to natural sunlight is rapid (half-life less than 7 days) and on dark control samples is slower (half-life approximately 30 days). Monocrotophos is mobile in soil, and although it degrades rapidly it may possess potential for groundwater contamination[19].

The objective of this study is to investigate the degradation of monocrotophos (Dimethyl (E)-1-methyl-2- methyl carbamoyl vinyl phosphate) in neutral

II. MATERIALS AND METHOD

A. Pesticide and Chemicals

All chemicals used were analytical grade reagents and commercial emulsified monocrotophos which was manufactured by: Sabero Organic Gujarat Ltd India. The concentration of the commercial monocrotophos was 400g/L and was used as applied by farmers without further purification. Monocrotophos has a molecular weight of 223.2 g/mol

B. Soil Sampling and Pre-treatment

Soil samples were collected at depths: 0 - 20 cm from university of Agriculture Makurdi farm Land. They were sieved, free from unwanted debris, made lump free and thoroughly mixed before it was used for the sorption study.

C. Soil Characterization

The soil was analyzed for pH, percentage clay content, silt content, sand content, moisture content and total organic carbon.

III. PREPARATION OF VARIOUS MONOCROTOPHOS FROM THE STOCK.

The concentration of the commercial formulation of monocrotophos was 400g/L; distilled water was used to prepare all aqueous solution. A 1.0×10^{-3} -M stock solution of monocrotophos was prepared by diluting 0.285 cm^3 of the commercial formulation to 500 cm^3 with distilled water in a volumetric flask. Separate aliquots of the stock ($0.75 - 4.0 \text{ cm}^3$) were, then serially diluted to 100 cm^3 with distilled water in volumetric flasks to furnish various standards ($7.5 \times 10^{-6} - 4.0 \times 10^{-5} \text{ M}$) which were used to prepare calibration curves for spectrophotometric determination of monocrotophos in aqueous solutions. The absorbance of the solutions of the

various concentrations were measured at 214nm using UV-Visible spectrophotometer (pharamcia Biotech-ultraspect 2000). Absorbance of the supernatant of centrifuged aliquots of the suspensions was measured using distilled water as reference. To ensure the quality of data obtained, the experiment were carried out in duplicate for each sample and the mean data is presented in Table 1

TABLE I
MONOCROTOPHOS CONCENTRATION (MOL/DM³) AND ASORBANCE

Concentration (mol/dm ³)	Absorbance
8.5×10^{-6}	0.176
1.0×10^{-5}	0.217
2.0×10^{-5}	0.300
3.0×10^{-5}	0.487
4.0×10^{-5}	0.577

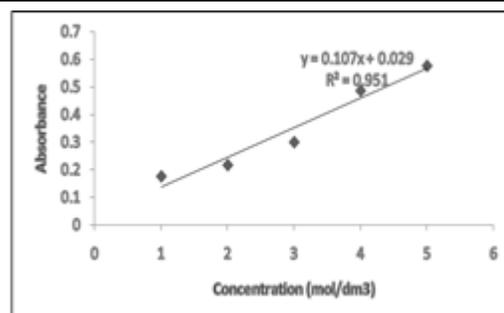


Fig. 3 Calibration curve of monocrotophos at 214 nm.

IV. SORPTION KINETIC STUDIES

To each of the three sample bottles containing 2.5g of soil, 100cm³ of distilled water was added in order to wet the soil surfaces and stirred for 2 hours and allowed to stand for 30 minutes. The Kinetic run was initiated by the addition of 25cm³ of the standard stock solution ($1 \times 10^{-5} \text{ M}$) of monocrotophos into two bottles respectively whereas the third bottle served as the reference. The analysis of the sample commenced ten minutes after addition of monocrotophos (5.0 cm^3) aliquot of the slurry was taken into three 15 cm^3 centrifuge tubes. The tubes were agitated for 3 minutes; the suspension was then centrifuged for a predetermined contact time of 5 minutes without adjusting pH at room temperature. A fixed amount of the supernatant was taken and then filtered using filter paper (Whatmann No. 1). The filtrates were then analyzed in duplicates using UV – Visible Spectrophotometer for quantifying the change of solution concentration with time. The difference between initial and final concentration of monocrotophos was considered as the amount sorbed (Table 2).

TABLE II
PHYSICO-CHEMICAL PROPERTIES OF SOIL.

Properties	Mean
pH in aqueous CaCl ₂	5.10
pH in H ₂ O	6.50
Silt content	5.30%
Clay content	2.0%
Sand content	92.0%
Soil type	Sandy soil
Moisture content	0.40%
Total organic carbon	4.10%

V. SORPTION KINETICS PARAMETERS

The interaction between the pesticide and the soil is represented by the following.



Where ‘‘Pap’’ represents the solution phase concentration of the pesticide, ‘S’ represents the solution phase concentration of the pesticide bound to the soil surface by reversible labile processes, then

$$X_c = X_{LS} + X_0 \tag{2}$$

Where, Xc is a measure of the total sorption sites (molg⁻¹) which is called the labile sorption capacity, X_{LS} is the concentration (molg⁻¹) of active sites occupied by pesticides and X₀ is the concentration (molg⁻¹) of active sites that are unoccupied. When equilibrium between the soil pesticide and aqueous slurry is reached, the law of mass action may be applied and the weighted average equilibrium constant, K₁ is determined as [6]

$$K_1 = X_{LS} / C_p X_0 \tag{3}$$

Where C_p is the equilibrium concentration of the percentage of the pesticide on the soil solution. The distribution coefficient (K_d) is an empirical constant that described the affinity of the pesticides molecule for the solid phase relative to the solution.

$$K_D = X_{LS} / C_p \tag{4}$$

Combing equation (1) (2) and (3) gives equation (4)

$$K_D = K_1 (X_c - X_{LS}) \tag{5}$$

Equation (4) implies that K_d is not a constant but depends inversely on the surface loading of the pesticide (i.e X_{LS}). The rate of loss of the pesticide from solution to labil surface site can be defined by the formula.

$$- \frac{dC_p}{dt} = K_f C_p X - K_{des} X_{LS} \tag{6}$$

Where, K_f is the second order rate constant describing the absorption process. That is, sorption of pesticide to soil surfaces depends on the concentration of the pesticide sites on the soil surface, where a desorption is a first order reaction whose rate constant, K_{des}, depends only on concentration of pesticide molecule on the occupied sites. In case where there is low coverage of sorption sites, then X_{LS} << X_c, and therefore, X₀ ≈ X_c = constant, and the values of K_{des} K_{LS} is very small. Under this condition, equation (6) reduces to equation (7)

$$- \frac{dC_p}{dt} = K_f C_p \tag{7}$$

K_f is now a pseudo-first order rate constant integrating, we have

$$2.3031 \log C_p / C_{p0} = K'f \tag{8}$$

A plot of log (C_{p0} – C_{pt}) vs time is expected to be a straight line for the pseudo-first order processes with a slop equal to K’f /2.303. The pseudo-first order rate constant (K’f = -2.30 x slop).

VI. RESULTS AND DISCUSSION

A. Soil Properties

Before the kinetic experiment was carried out, the soil was characterized. Some of the physicochemical properties are shown in table 2. The pH range of the soil shows that it is moderately acidic. These properties are likely to influence the fate of monocrotophos in soil to varying extents [20, 21]. It usually follows the trend the higher the pH, the higher the base saturation. It is generally observed that for most soils at a pH of 7 or above, the base saturation approaches 100% [6]. From the texture triangle, the soil was found to be sandy soil, low in clay, silt and organic carbon. The small size fraction that contains clay minerals and organic carbon are those that are particularly active in terms of interaction with the pesticide. The small amount of organic matter and the nature of the clay minerals of this may lead to smaller degree of sorption of the pesticide soil interaction. The amount of organic carbon content determined by the wet oxidation method is a measure of the total organic carbon of the soil but may be partial due to other component that may be present and was found to be 4.12%. The moisture content was found to be 0.45% after drying at 105°C.

B. Sorption and Speiation of Monocrotophos in the Soil – Solution Matrix

The experiment was carried out using slurries maintained over a period of approximately three days from commencement. The method enables separation of the various loci of pesticide molecules in the entire slurry. The effects of the pesticide initial concentration with contact time are shown in Figure 4 and 5. The sorption can be viewed in here as a two phase process, with a rapid initial decrease in concentration of monocrotophos in solution, followed subsequently by a much slower rate. The rapid adsorption occurred at the beginning since there was only physical affinity between the soil and pesticide, and there was a difference in concentration gradient between bulk solution and surface of soil [22], thereby representing a significant motivating force for monocrotophos transfer between the solution and the soil surface. However, after the initial period, slow sorption may be due to slower diffusion of solute into the interior of the soil. The figure 4 shows a rapid initial decrease in concentration of the pesticide in solution within the first day and then slowly until no appreciable change in concentration was observed, while the amount monocrotophos sorbed by the soil was found to increase with increase in time (Figure 4).

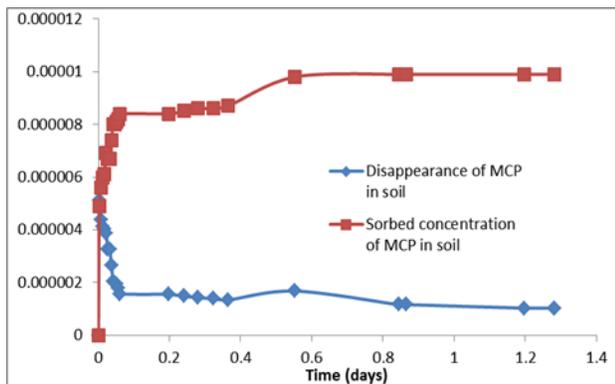


Fig. 4 Effect of contact time , sorbed concentration and initial Monocrotophos disappearance in Soil

VII. KINETIC EVALUATION

Kinetics analysis is required to get an insight of the rate of sorption and the rate-limiting step of the transport mechanism, which are primarily used in the modeling, and design of the process [23]. Several adsorption kinetics models have been developed to understand the adsorption kinetics and rate limiting step [24]. In this work however, Lagergren pseudo-first order kinetic model was considered to investigate the mechanism of monocrotophos absorption in soil. This is because pseudo first order kinetic model is better for predicting the kinetic process in the experimental conditions than the pseudo second order kinetic model [5,12]. Usually, the pseudo first order kinetic correlation coefficients, r^2 and sorption values are calculated from the plot of $\log (C_{p,o} - C_{p,t})$ vs. time. Nevertheless, in this work, we plotted $14 + 1 \ln (C_{p,o} - C_{p,t})$ against time as shown in Figure 6 and 7. The values for the fast sorption rate and slow sorption rate were found to be 10.805 s^{-1} and 0.2396 s^{-1} respectively (Figure 6 and 7). The result revealed that the soil has low capacity to sorb or retain monocrotophos when applied. Within this period of time for the sorption study, a number of processes occur: the monocrotophos distribute itself between the solution phase and the solid phase, and in the later phase, the amount of pesticide that diffused irreversibly, into soil voids or is otherwise irreversibly bond to the soil surface which is called bound residue (BR). The phenomenon of BR is more associated with soils of high organic carbon, it is expected that the occurrence of bound residues of the pesticide in this soil will be low judging by the amount present in this soil.

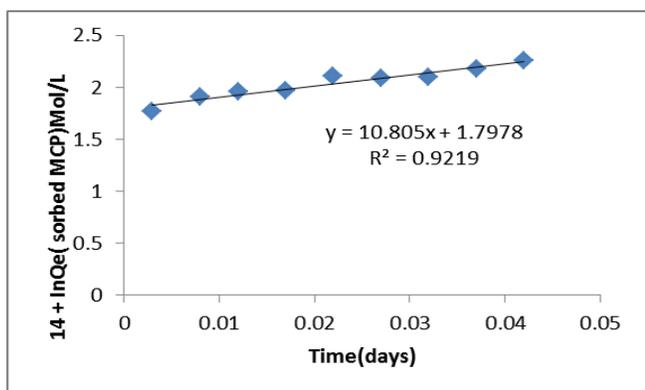


Fig. 6 Sorption Kinetics of monocrotophos on soil (Fast)

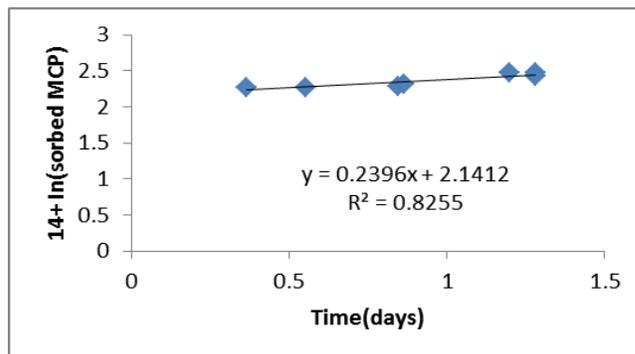


Fig. 7 Sorption Kinetics of monocrotophos on soil (Slow rate)

VIII. ADSORPTION ISOTHERM

A more general method of static determination of distribution coefficients (KD or KF) encompasses gauging and numerical or graphical analysis of a sorption isotherm, which describes the equilibrium sorbate distribution between the phases of the tested system, solid sorbent (s) – water (w), at constant temperature and in conveniently chosen intervals of overall solute concentrations in the system.

1. Langmuir isotherm

The Langmuir [25] model assumes that uptake of monocrotophos occur on a homogenous surface by monolayer adsorption without any interaction between adsorbed ions. The Langmuir equation may be written as:

$$q_s = \frac{q_m K_L C_e}{1 + K_L C_e}$$

Transforming the Langmuir equation into liner form, you have

$$\frac{C_e}{q_s} = \frac{1}{q_m K_L} + \frac{C_e}{q_m}$$

Where C_e is the equilibrium concentration of the adsorbate (mg / L)

q_e is the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg/L)

q_m is the maximum monolayer coverage capacity (mg / g)

K_L is the Langmuir isotherm constant (mL / mg)

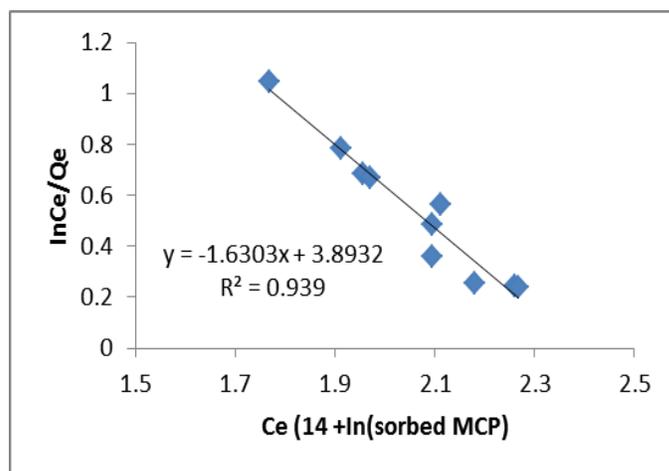


Fig. 8 Linear Langmuir Isotherm for the sorption of monocrotophos by soil

2. Freundlich isotherm

The course of experimentally obtained real isotherms can often be fitted by the equation of a model Freundlich isotherm (Toul et al., 2003)

$$C_s = K_F \cdot C_w^{1/n}$$

where C_s and C_w stand for equilibrium sorbate concentrations in both phases of the system in question, K_F is an empirical coefficient of the Freundlich equation, and the exponent $1/n$ is a measure of non-linearity of the investigated dependence for a given sorbent and a given sorbate. The distribution coefficient (K_d) was computed by taking the ratio of adsorption concentration in soil (C_s) and equilibrium concentration in solution (C_e). The results were summarized in Table 1. The values of $K_F \approx K_d$ and $1/n$ are gained from the equation in a logarithmic shape (Toul et al., 2003)

$\ln C_s = \ln K_F + (1/n) \ln C_w$ as a slope $1/n$ and an intercept $\ln K_F$ of such linear dependence $\ln C_s = K_f (\ln C_w)$.

Linear Freundlich Isotherm for the sorption of monocrotophos by soil is presented in Figure 9 with a correlation coefficient (r^2) of the line 0.8323 while that for Langmuir isotherm is shown in Figure 8 with coefficient (r^2) 0.939. These suggested that the data is fitted well with Langmuir model than Freundlich isotherm proving monolayer surface of adsorption of monocrotophos on soil.

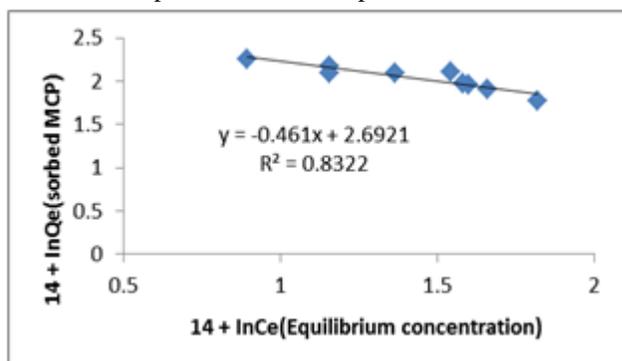


Fig. 9 Linear Freundlich Isotherm for the sorption of monocrotophos by soil

This is an indication that adsorption mechanism of monocrotophos was not related to non-ideal, reversible and multilayer adsorption with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface. The Freundlich adsorption exponent ($1/n = -2.169$) and Langmuir constant (-2.16 mLmg^{-1}) were obtained from slope of this lines which were less than unity (<1.0) indicating a relative decrease in concentration with increase in time with fixed initial concentrations of monocrotophos. At the beginning of the absorption process, the trend line is almost linear; suggesting that competition for pesticide between soil and aqueous phase was almost the same or increasing at the same rate (at this point K_f could also be named as soil-water partition coefficient K_D). However, as sorption process proceeds with time, the $1/n$ value deviated from unity indicating the nonlinear relationship between Q_e and C_e with relatively strong adsorption of pesticide on soil as compared to that of water. This is a common feature for adsorption of organic chemicals in soils with low organic matter [26].

Although isotherm does not give confirmations about adsorbate-adsorbent interaction [26,27], but its shape helps in understanding the adsorption mechanism [26]. The Freundlich adsorption exponent values obtained in this work are comparable to those reported by [22,26,28,29]. The extent of adsorption K_F from the intercept of the line which was 3.0673 mg/kg .

IX. CONCLUSION AND RECOMMENDATION

This work was geared towards investigation pesticide – soil interaction. The soil used was characterized with respect to soil pH, organic carbon, moisture content, silt, clay and sand content. The sorption kinetic studies were determined by observing the disappearance of monocrotophos in solution for several days.

The sorption could be described by two distinct kinetic processes, namely, fast sorption (occurs within few hours after spiking the soil) and slow (for the remaining days). The first order plot showed that the concentration of monocrotophos decrease with time (days). Inversely, the amount sorbed was found to increase with increase in time and the values showed that the soil has low capacity to sorbed or retain monocrotophos when applied. This could be probably due to low organic content, abiotic and biotic factors since the soil was not sterilized before used. It was also assumed that the sorption of monocrotophos in the soil could result in low “bound residues” since it is associated with soil reach in organic matter.

In order to have comparable data on the sorption of monocrotophos, more work should be carried out on different classes of pesticide using different agro – environmental zones. This will also enable us to predict their fate in different environment. To avoid microbial degradation, work should be done using sterilized soil. Attempt should also be made to account for hydrolytic degradation since soil surfaces could act as catalyst for pesticide hydrolysis.

TABLE II
SORPTION IN SOIL

Days (Days)	Absorbance	Monocrotophos mol/L at Time(t)	Sorbed Conc.(Q_e)	Ln(Sorbed Concentration)
0.000	0.000	0.00000	0.0000	0.0000
0.003	0.393	0.0000051295	0.0000049	-12.2323
0.008	0.336	0.0000043782	0.0000056	-12.0889
0.012	0.329	0.0000041192	0.000006	-12.0438
0.017	0.302	0.0000040415	0.0000061	-12.0307
0.022	0.250	0.0000038860	0.0000069	-11.8890
0.027	0.214	0.0000032642	0.0000067	-11.9081
0.032	0.151	0.0000032513	0.0000067	-11.9062
0.037	0.136	0.0000026425	0.0000074	-11.8198
0.042	0.105	0.0000020337	0.000008	-11.7403
0.047	0.047	0.0000019689	0.000008	-11.7322
0.051	0.041	0.0000019430	0.0000081	-11.7290
0.056	0.040	0.0000018005	0.0000082	-11.7114
0.061	0.039	0.0000015803	0.0000084	-11.6849
0.198	0.038	0.00000155440.00	0.00000840.	-11.681
1.281	0.001	0.0000010363	0.0000099	-11.5233
1.281	0.001	0.0000010363	0.0000099	-11.5233

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