ATTACHMENT E

Virginia Department of Health, Report on "Health Effects Associated with Exposure to Trona – A Review of the Biomedical Literature, June 2007"

Health Effects Associated with Exposure to Trona
A Review of the Biomedical Literature

Virginia Department of Health
Office of Epidemiology
Office of Environmental Health
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EXECUTIVE SUMMARY

The Virginia Department of Environmental Quality (VDEQ) requested that the Virginia Department of Health (VDH) provide a summary report on the possible health effects of trona (sodium sesquicarbonate). The following report discusses the application of trona in flue gas desulfurization, provides a toxicological assessment of trona, examines the available biomedical literature on trona in order to assess any adverse health effects, and identifies research gaps about potential health effects of trona.

In occupational studies reviewed, we can document that trona dust is an alkaline (caustic) substance that can have an irritant effect on respiratory airways, mucous membranes, eyes, and skin. Excessive levels of airborne dust may irritate the mucous membranes and upper respiratory tract. Aside from the irritant effects described, no chronic loss of lung function is attributed to trona in the studies examined and interventions to reduce dust levels improved respiratory and/or skin-related symptoms. As a food substance, refined trona is commonly added to animal feed and double-refined trona is designated by the Food and Drug Administration as a safe product when used in the appropriate context.

There are no published epidemiologic studies of populations living near power plants where trona is used for air pollution control, nor studies examining the health effects as a result of exposure to trona dust among the general population or among special populations that may be at increased susceptibility to airborne irritants. The absence of evidence of adverse health effects in the general population is not the same as evidence that adverse health effects in the general population are absent. Nevertheless, current information available only suggests that trona dust is a transient irritant, especially in the occupational setting.

Further work is needed to assess any impacts trona would have on health and air quality; research gaps to fill include better understanding: (1) the amount of trona dust or trona-related by-products released into air emissions by power plants, if any; (2) the long-term health effects associated with exposure to trona dust; (3) circumstances that increase trona dust levels in ambient air; and (4) the threshold values for occupational and public exposure where risk of

trona's irritant effects are minimized. VDH will continue to assist in addressing public health concerns related to trona utilization in the future.

INTRODUCTION

Mirant Corporation's Potomac River Generating Station (PRGS), located in Alexandria, Virginia, serves the District of Columbia and surrounding states using generating units that burn coal to generate electricity.[1] In an effort to curb the amount of air pollutants created when coal is combusted, PRGS began testing the use of a dry sorbent injection process in the winter of 2005. During the injection process, powdered trona is reacted with the flue gas stream to remove sulfur oxides; most of the solid by-products created are then captured for disposal. Residents in the area surrounding the power station have expressed concerns about the potential environmental and health effects from exposure to by-products emitted from the coal-burning units as well as trona dust that may be released into the air as a result of trona's use in air pollution control measures. The once sparsely populated area in which the power plant originally opened in 1949 is now a densely populated community with the power station at its epicenter.

The Virginia Department of Environmental Quality (VDEQ) requested that the Virginia Department of Health (VDH) provide a summary report on the possible health effects of trona. The following report provides a general overview of trona and its use at PRGS in flue gas desulfurization, in addition to a summary of the toxicologic and health information available on trona. There is limited information reported on the health effects of trona.

TRONA - GENERAL BACKGROUND

Trona is an evaporite mineral also known as sodium sesquicarbonate. Chemically, trona is a hydrated sodium carbonate-sodium bicarbonate compound [$NA_2CO_3 \cdot NAHCO_3 \cdot 2H_2O$]. Unrefined trona ore can contain natural impurities, including clay, silica, and other insoluble material. The types of natural impurities found in the ore will vary and are dependent on how and where the ore was formed. The trona ore is mechanically refined – crushed, screened, and dried – prior to commercial use. Mechanically refined trona is primarily utilized by power plants in air pollution control applications. Trona helps remove sulfur oxides (SO_2 and SO_3), hydrogen sulfide (H_2S), hydrochloric acid (HCl), and hydrofluoric acid (HF) from flue gas emissions.[2]

Coarse trona is commercially used in animal feed products to aid in animal digestion, in cement production to control sulfur emissions, and in other commercial applications. Trona ore also serves as source for soda ash (or sodium carbonate) production when the ore is dissolved to remove impurities and re-crystallized to form soda ash. Soda ash is commercially used in glass manufacturing, chemical products, food additives, detergents, paper mill industries, water treatment, and flue gas desulfurization.[3]

U.S. deposits of trona ore are primarily mined from Wyoming and California, but sources of trona are also located in Colorado, Michigan, Nevada, New Mexico, Utah, and Washington.[4] Industrial use of natural trona as a sorbent in air pollution control measures first began in the mid-1980s.

TRONA IN AIR POLLUTION CONTROL

Coal combustion results in the formation of acid gases, such as sulfur dioxide, among other air pollutants. The environmental and health effects linked to sulfur dioxide are well documented. In order to reduce and control acid gases emitted during coal-burning processes, trona is used as an acid neutralizer and sorbent to remove pollutants from flue stack emissions. As air emission standards have tightened for coal-burning power plants, the use of trona in air pollution control strategies has steadily increased.

PRGS employs a dry sorbent injection process that involves pressurized injection of powdered trona (trona dust) into a duct containing flue gasses. When trona is heated above 275°F, it is calcined to sodium carbonate and becomes a reactive reagent that can achieve a range of efficiencies in acid neutralization. The heated trona provides a large, reactive surface area for sulfur oxide gases to bond, creating solid sodium salt by-products that can then be removed from the exhaust stream and collected for disposal. Trona also reacts with other acid gases [hydrogen sulfide (H_2S), hydrochloric acid (HCl), and hydrofluoric acid (HF)], if present; the solid by-products can be similarly removed and disposed. The reaction of trona with acids also creates carbon dioxide gas and water vapor.

The use of dry sorbent injection systems do have advantages over other flue gas desulfurization systems, including lower capital costs to retrofit the system to existing plant operations, and less corrosive by-products relative to wet-scrubber systems. Additionally, sodium-based sorbents, such as trona, in dry injection systems have been shown to have high removal efficiencies over a wide range of temperatures.[5, 6]

The control of waste by-products relies on the capability and efficiency of electrostatic precipitators (ESP) to capture the dry particulate waste. One concern expressed by the City of Alexandria is the ability of the ESP to effectively handle the large quantities of waste products produced during operations. Large amounts of trona are added to the system to remove sulfur dioxide; the trade-off for reducing sulfur dioxide gas emissions is to create substantial increases in ash loading relative to burning coal alone. If the quantities of trona used overwhelm the ESP, increased levels of particulate matter could be released into the air. However, trona has been shown to reduce sulfur dioxide gas levels and particulate matter emissions. Mirant reports that during trial injection tests conducted at PRGS, substantial sulfur dioxide removal could be achieved while maintaining particulate emissions and opacity performance within limits.[7]

To date, estimates of the quantity of trona dust escaping flue stacks or being released during the transportation/unloading stages have not been reported by regulatory agencies. No information exists in the literature related to potential human health effects due to exposure to trona during or following these pressure injection treatments at power plants. Although the use of trona to remove sulfur oxides from air emissions should reduce particulate matter in air emissions, it is possible that trona and its by-products may inadvertently be released as particulate matter.

TRONA CHEMISTRY & EXAMPLE BY-PRODUCTS

Trona Decomposition
(heat calcines trona into sodium carbonate at temperatures above 275°F)

$Na_2CO_3 \cdot NaHCO_3 \cdot 2\,H_2O \rightarrow Na_2CO_3 + NaHCO_3 + 2\,H_2O$
Trona — Sodium Carbonate — Sodium Bicarbonate — Water

$NaHCO_3 \rightarrow \frac{1}{2}\,CO_2 + \frac{1}{2}\,H_2O + \frac{1}{2}\,Na_2CO_3$
Sodium Bicarbonate — Carbon Dioxide — Water — Sodium Carbonate

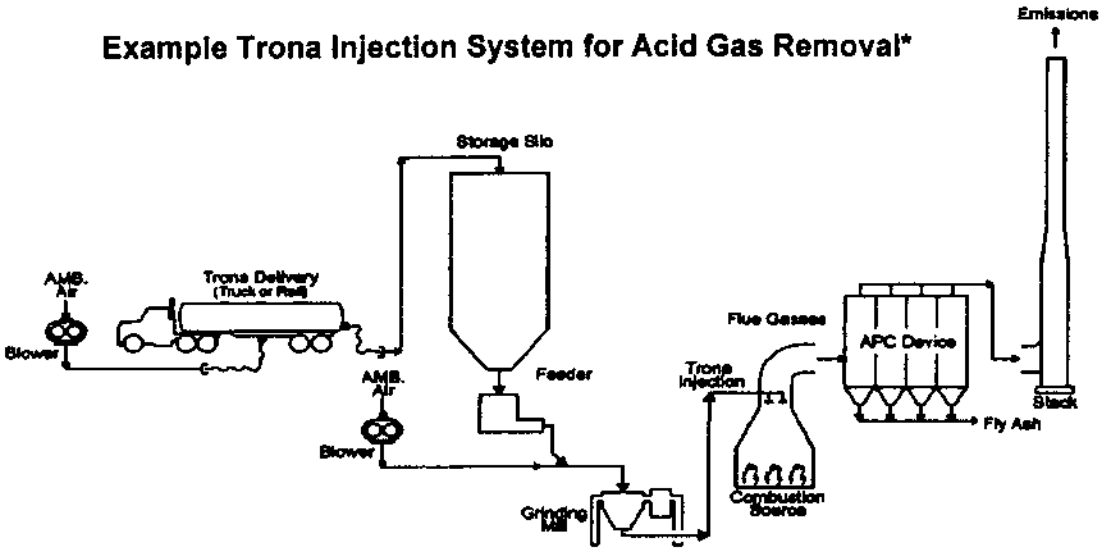
Trona Reactions with HCl and SO_2 flue gas pollutants

$Na_2CO_3 \cdot NaHCO_3 \cdot 2\,H_2O + HCl \rightarrow 3\,NaCl + 4\,CO_2 + 2\,H_2O$
Trona — Hydrochloric Acid — Salt — Carbon Dioxide — Water

$2(Na_2CO_3 \cdot NaHCO_3 \cdot 2\,H_2O) + 3\,SO_2 \rightarrow 3\,Na_2SO_3 + 4\,CO_2 + 5\,H_2O$
Trona — Sulfur Dioxide — Sodium Sulphite — Carbon Dioxide — Water

$3\,Na_2SO_3 + O_2 \rightarrow 3\,Na_2SO_4$
Sodium Sulphite — Oxygen — Sodium Sulphate

Example Trona Injection System for Acid Gas Removal*



*Mazluk, John. 10 March 2005. Trona Injection Above 700 to Remove Sulfur Oxides from Flue Gas. Solvay Chemicals Presentation. http://www.solvaychemicals.us/static/wma/pdf/6/8/5/2/Trona_injection.pdf.

HEALTH EFFECTS - EPIDEMIOLOGIC AND CLINICAL STUDIES

There are few studies examining the human health effects of trona. A literature search revealed two occupational studies on trona dust exposure. A third occupational study examined port workers exposed to sodium carbonate, a compound derived from trona. Following exposure-response principles, we anticipate that any health effects associated with trona will more readily be observed in occupational settings due to the increased likelihood of airborne or dermal contact with the substance. Examining occupational exposures to varying levels of trona dust may provide insight on the effects of trona to human health.

Trona Miners and Millers

In 1981, epidemiologic and clinical studies of trona ore miners and millers in Wyoming described the respiratory and dermatologic health effects associated with trona dust exposure.[8, 9] The studies were conducted following a union group request to the National Institute for Occupational Safety and Health (NIOSH) for a health hazard evaluation. The evaluation involved a structured interview, a standardized questionnaire about respiratory and dermatological effects, a lung function test, and a skin patch test for sensitivity. Prior to this evaluation, NIOSH had completed a lung function survey among a subset of the same workers in 1976.[10]

Respiratory Effects

NIOSH examined the impact of occupational exposures to trona dust on respiratory function. The study involved 142 underground miners and 88 surface workers who volunteered to participate in a cross-sectional study that included a questionnaire about respiratory symptoms, pre- and post- work shift lung function evaluation, and a five-year follow-up. Exposure determinations included total work-years, self-reported categorical exposure (high, medium, low) to different types of dust, and an exposure-index based on a mean score of all dust exposures. Area and personal exposure dust samples were also collected for total and respirable dust levels. Outcomes of interest included various pulmonary function measures, including forced expiratory volume at 1 second (FEV_1), and reported respiratory symptoms.

A significant fall in FEV_1 was found among non-smokers and surface workers in the shift study comparing pre- and post-shift FEV_1 values; the decrease in FEV_1 among the highest exposure group approached statistical significance. Processing stages that involve higher levels of trona dust (i.e., crushing, roasting, calcining, and filtering) appeared to have an acute effect on lung function, regardless of smoking habit. Some correlations between dust exposure and decreased FEV_1 were found among smokers, in relation to age and possibly work-years. The five-year follow-up did not reveal any chronic loss of lung function, which investigators hypothesized could be related to dust control improvements, decreases in smoking, and high worker turnover, among other factors.

Personal exposure dust samples (eight-hour, time-weighted average) ranged from 0.6 to 99 mg/m^3 for total dust and 0.1 to 11 mg/m^3 for respirable dust. The average total dust levels were 32 mg/m^3 for underground workers and 27 mg/m^3 for surface workers; the average respirable dust levels were 2.2 and 1.4 mg/m^3, respectively. Although some areas had high levels of total trona dust, the respirable fraction was much lower, accounting for only about 5% to 7% of the total dust. Free silica in the dust samples was not detectable.

Chronic cough and phlegm production was reported in 23% of the participants; both symptoms were more common among smokers than nonsmokers. Thirty-three percent of the workers complained of dyspnea (breathing difficulty) when hurrying on level ground or walking up a slight hill. There were significant exposure-response associations between reported upper respiratory symptoms (nasal and throat irritation) and trona dust exposure. Nasal drainage was reported among 48% of the respondents, and symptoms of eye and nose irritations occurred in nearly 60% of workers. Upper respiratory irritation commonly reported among workers coincided with air sampling data indicating dust particles of larger size.

Dermatologic Effects

A companion study examined the dermatologic effects of trona dust exposure. Exposure measures were determined as noted above, and outcome measures of interest included a list of skin irritations – redness, itching, scaling, skin sores, and dry, cracked skin.

Each of the 230 study participants (i.e., 142 underground miners and 88 surface workers) was interviewed to assess dermatologic signs and symptoms both before and after beginning work in the trona industry; participants were also given a skin examination by a physician. Skin patch tests were conducted on 67 of the study participants; 10% solutions of raw trona, sodium carbonate, and a saline control were applied on the upper arm. Additionally, all employees (n=1300) were given a self-administered questionnaire inquiring about health problems related to trona.

Among the group of 230 study participants, the incidence of skin signs and symptoms was from 2 to 15 times greater after beginning work in the trona industry. There was an exposure-response relationship between skin irritations and dust exposure among participants working in underground mines, but not for surface workers who reported higher rates of skin symptoms relative to underground miners. Skin irritations on exposed areas of the arms, hands, and legs were commonly reported. Twenty-five percent of the workers examined showed signs of inflammation to the mouth, nose, pharynx and eyes. One-half of the workers showing signs of mucous membrane inflammation also had conjunctivitis. Patch tests with the 10% aqueous solutions of raw trona and sodium carbonate were negative, which suggested the dermatitis occurring among workers was due to irritation, not allergy.

The self administered questionnaire provided to all employees was returned by 50% (648/1300). Of those that responded, 47% (305/648) reported a physical ailment caused or exacerbated by occupational exposure to trona dust. Sixty nine percent of those reporting ailments caused by trona dust cited skin irritations. Personal hygiene, protective clothing, dust control, and barrier creams were recommended interventions for curbing the occupational-related dermatitis.

Study Limitations

The studies have a number of limitations, which include:

- low participation rates [24% (142/600) of the underground miners and 44% (88/200) of the surface workers] and voluntary self-selection into the study. This may have created an unrepresentative sample of the population of concern.

- short employment duration (average length 10 years). The effects of trona exposure over a longer period of time are unknown. Additionally, those reporting low exposure tended to be older, to have worked longer in the industry, and may have been transferred to lower exposure duties over time. This may have lessened the exposure-response relationships under study.
- lack of an unexposed comparison group, which makes it difficult to assess and interpret exposure-response rates for respiratory and dermal measures.
- exposure to other dust, such as sodium carbonate. Although the dust may have predominantly been trona, it is difficult to know whether the health effects observed are attributable to trona versus sodium carbonate exposure.

Sodium Carbonate Port Workers

Clinical examinations of shipping workers exposed to high levels of sodium carbonate, or soda ash, showed many workers developed skin conditions (e.g., ulcers, erosion, and eczema), soda ash burns, and inflamed mucous membranes of the nose, pharynx and eyes.[11] Dust levels over 300 mg/m^3 in the ship holds and freight cars were reported. When interventions were employed to reduce dust levels by tenfold, 2/3 of the skin conditions were eliminated and upper respiratory tract symptoms were reduced by 1/3.

Additional Studies

Other studies examining the human health effects of trona focus on the use of trona as a food additive.[12-14] In parts of Tanzania, local sources of high-fluoride content trona is used as a food tenderizer and implicated as a major source of dental fluorosis in those communities. However, the source and application of high fluoride trona used in these communities are outside the scope of our discussion and will not be examined.

From the relevant studies reviewed, we can document that trona dust is a caustic substance that can have an irritant effect. Direct contact with trona dust causes irritation of the eyes and continuous or prolonged contact may cause skin irritation (red, dry, cracked skin). Excessive levels of airborne dust may irritate the mucous membranes and upper respiratory tract. Aside

from the irritant effects described, no chronic loss of lung function was noted and interventions to reduce dust levels improved respiratory and/or skin-related symptoms.

All effects in the studies examined have been reported among those occupationally exposed to high levels of dust, either acutely or over prolonged periods of time. There are no published epidemiologic studies of populations living near power plants where trona is used for air pollution control.

HEALTH EFFECTS - TOXICOLOGICAL SUMMARY

There are no animal toxicity studies of in-vitro toxicity for trona. Several studies do reference the use of trona in animal feed to help buffer the acidity in the rumen and duodenum[15] of farm animals, such as cattle and dairy cows. Trona helps to enhance the digestibility of grain diets in cattle[16] and increase milk production in dairy cows.[17]

Toxicological information for trona often reference toxicity data for sodium carbonate, a compound related to trona.[18] Laboratory studies involving rodents exposed to sodium carbonate indicate that the acute oral toxicity[i] in rats is 4,090 mg/kg (milligrams of substance per kilogram of animal weight), and the acute inhalation toxicity[ii] in rats is 2,300 mg/m^3 over a 2-hour period. Dermal exposure to sodium carbonate produces mild irritation at levels in excess of 2,000 mg/kg in rabbits. In rabbits, trona is a severe eye irritant at 50 mg. This parallels the acute effects reported with trona overexposure in humans which causes severe irritation of the eyes, and can lead to corneal opacities. Dusts and mists may be irritating to the skin, mucous membranes and upper respiratory tract and ingestion may cause nausea, vomiting, stomachache, and diarrhea. Chronic, excessive exposure or contact with trona may produce "soda ulcers" on the skin and perforation of the nasal septum.

Trona is not considered to be a probable or suspected human carcinogen. However, trona ore may contain trace amounts of silica (crystalline quartz). Silica[iii] is a suspected carcinogen that

[i] LD_{50} - lethal dose that will kill 50% of the experimental animals
[ii] LC_{50} – lethal concentration that will kill 50% of the experimental animals
[iii] ACGIH set their TLV for silica at 0.025 mg/m^3 for an 8-hour time weighted average. The OSHA PEL for crystalline silica is [(10 mg/m^3)/(%Silica +2)].

has been shown to cause silicosis (a lung disease) in humans when present in concentrations greater than 1%. Material safety data sheets (MSDS) on natural trona (unprocessed) indicate the presence of silica at less than 2%;[19] commercially processed trona used by Mirant (Solvay T-200®) indicates the presence of silica at less than 0.4%.[20]

REGULATIONS AND ADVISORIES

Food Safety

Double-refined trona ore (i.e., purified sodium sesquicarbonate) is "generally recognized as safe" (GRAS) by the Food and Drug Administration for use as a food ingredient within the context of good manufacturing practices.[21] Health-related literature on trona primarily focuses the use of processed trona, such as refined trona, sodium carbonate and sodium bicarbonate, as pH control agents in animal feed, human food products, and in various chemical industries.

Occupational Exposure

The American Conference of Governmental Industrial Hygienists (ACGIH) has not established a specific Threshold Limit Value (TLV) for trona.[iv] Federal guidelines treat trona as particulate matter not otherwise regulated; OSHA lists the Permissible Exposure Limit (PEL) for particulates not otherwise regulated at 5 mg/m^3 (milligrams of substance per cubic meter of air) for the respirable fraction, and 15 mg/m^3 for total dust over an 8-hour time-weighted average.

Air Quality

There are no specific regulations for trona set by the U.S. Environmental Protection Agency (EPA). However, EPA does set air emission standards for coarse particulate matter (PM_{10}) and fine particulate matter ($PM_{2.5}$) in the National Ambient Air Quality Standards (NAAQS).

The 2006 NAAQS for coarse particulate matter, PM_{10}, is limited to 150 $\mu g/m^3$ for a 24-hour exposure period, not to be exceeded more than once per year on average over a three-year period. For fine particulate matter, $PM_{2.5}$, the annual exposure standard is limited to 15 ug/m^3 and the 24-hour average is limited to 35 $\mu g/m^3$, averaged over three years.[22]

[iv] ACGIH proposed in 1999 a TLV of 0.5mg/m^3 for respirable trona, but subsequently abandoned this effort.

Waste Disposal

Trona discarded or disposed of as purchased it is not listed hazardous waste according to U.S. Federal Resource Conservation and Recovery Act (RCRA) regulations (40 CFR 261). As a non-hazardous waste, the material may be disposed of in a landfill in accordance with local and state government regulations.

CURRENT EVALUATIONS

At the request of the Alexandria Health Department, the Agency for Toxic Substances and Disease Registry (ATSDR) reviewed existing air quality and environmental data related to the operations at PRGS to assess any potential health hazards to nearby residents. In a January 2007 response letter, ATSDR discussed the uncertainty of the available air dispersal models that estimate SO_2 exposures and the need to collect additional monitoring data, including monitoring data to evaluate model estimates; data on the intensity, duration, and frequency of emissions; and data on indoor/outdoor contaminant ratios.[23]

Mirant began collecting monitoring data in June of 2006 for a Model Evaluation Study that will include a comparison between modeling and monitoring data for PRGS. The data will help to assess the accuracy of the modeled concentrations. Additionally, ATSDR has proposed conducting an exposure investigation to better assess the potential human exposure to airborne concentrations of sulfur dioxide, particulate matter, and selected metals. The proposed investigation would measure ambient and limited indoor air for contaminants and is designed to fill data gaps in evaluating community exposure pathways. Although not trona-specific, the investigation would help provide further information to determine if health hazards exist (from sulfur dioxide, particulate matter, and selected metals) in areas not currently monitored. Additionally, the Alexandria Health Department (AHD) developed a complaint form for residents living within a one-mile radius of the power station. Residents are encouraged to report health events believed to be related to the operation of the plant. AHD will review the collected data to determine if further studies are warranted.[24]

Assessment and Discussion

There is limited medical, toxicological, and public health literature on the direct health effects attributable to trona dust. Occupational exposures provide evidence that trona, at some threshold level, is an irritant to skin, the upper respiratory tract, and mucous membranes. However, no specific occupational exposure limits have been developed for trona either by ACGIH or OSHA. Additionally, there are no studies examining the health effects resulting from exposure to trona dust among the general population or in special populations that may be at increased susceptibility to airborne irritants. The absence of evidence of adverse health effects in the general population is not the same as evidence that adverse health effects in the general population are absent. Nevertheless, current information available only suggests that trona dust is a transient irritant, especially in the occupational setting.

More research and ambient air monitoring data are needed to assess exposure levels and better understand fully whether or not trona has any significant, negative, short- or long-term human health effects. There are no studies of the human health impacts of trona used in the context of air pollution control and flue gas de-sulfurization processes. Further work is needed to assess any impacts trona would have on health and air quality; research gaps to fill include better understanding: (1) the amount of trona dust or trona-related by-products released into air emissions from power plants, if any; (2) the long-term health effects associated with exposure to trona dust; (3) circumstances that increase trona dust levels in ambient air; and (4) the threshold values for occupational and public exposure where risk of trona's irritant effects are minimized. VDH will continue to assist in addressing public health concerns related to trona utilization in the future.

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