On the nature of Aitken condensation nuclei

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ABSTRACT

The number of Aitken condensation nuclei in the air is strongly influenced by human activities which increase the natural number manifold through release of combustion products from fires and combustion engines. The natural condensation nuclei near ground level increase during day and decrease during night; there is a general decrease with increasing altitude in the atmosphere. These natural Aitken nuclei are produced in light from volatile products released by the vegetation (mainly terpenes) and therefore are organic macromolecules. They disappear again mainly by agglomeration, or or near the inversion layers, and are then removed by precipitation.

Introduction

Aitken discovered that no fog droplets would form in air supersaturated with watervapor unless preformed nuclei were present. These nuclei were called condensation nuclei (cn) and Aitken developed a cn meter which could measure the concentration of cn in air. He used this meter to make a survey of cn in air in different localities, and found a wide spread, from 1000/cc in pure air to several hundred thousand in polluted city air. Since then a limited amount of research has been done on these Aitken cn by meteorologists (e.g. LANDSBERG, 1938), limited because we believe that only a small fraction of them are involved in actual condensation of moisture in the air. It is also believed that mainly hygroscopic nuclei produce fog droplets. Thus it was commonly accepted that mainly NaCl and $(NH_4)_2SO_4$ particles acted as cn in cloud formation and little was done to ascertain the chemical nature of the great majority of nuclei.

Observations at ground level

My own measurements were done with the very convenient and reliable Rich cn counter (made by Gardner Associates), and for the last two years systematic records were made with the Rich cn recorder (G. E. Condensation Nuclei Counter, Cat. 112L428G1, No. 3264171).

Before a further discussion of the probable source of Aitken cn, we will first present a number of observational facts on the number of cn.

Under most conditions where measurements of cn are made (in or near cities, in the country near highways or habitations), human activities strongly, and in most cases decisively, affect the number of nuclei measured. Any fire, from a match to a burning cigarette to a wood, coal, gas or oil burner, produces cn in concentrations many magnitudes above those occurring in nature. A city charges the air with cn for dozens of kilometers downwind. Any combustion engine, whether car, truck, diesel train or motor generator, charges the air with cn, no matter how efficient its operation. This provides a very serious problem in trying to establish cn concentrations in nature. If one can get far enough away from human activity there is no commercial electric power available, and to operate the Rich cn recorder one has to operate a motor generator with concomitant cn production. And wherever commercial electric power is available, there are roads and/or people nearby.

The most revealing set of records was obtained in an isolated area 20 km WSW of St. Louis, the Tyson Valley Research area of Washington University. The Rich cn recorder, mounted in a trailer as part of a mobile unit, was operated there on commercial electric power. The 700-ha research area is fenced in, and not more than 2–4 motor vehicles are present, of which usually

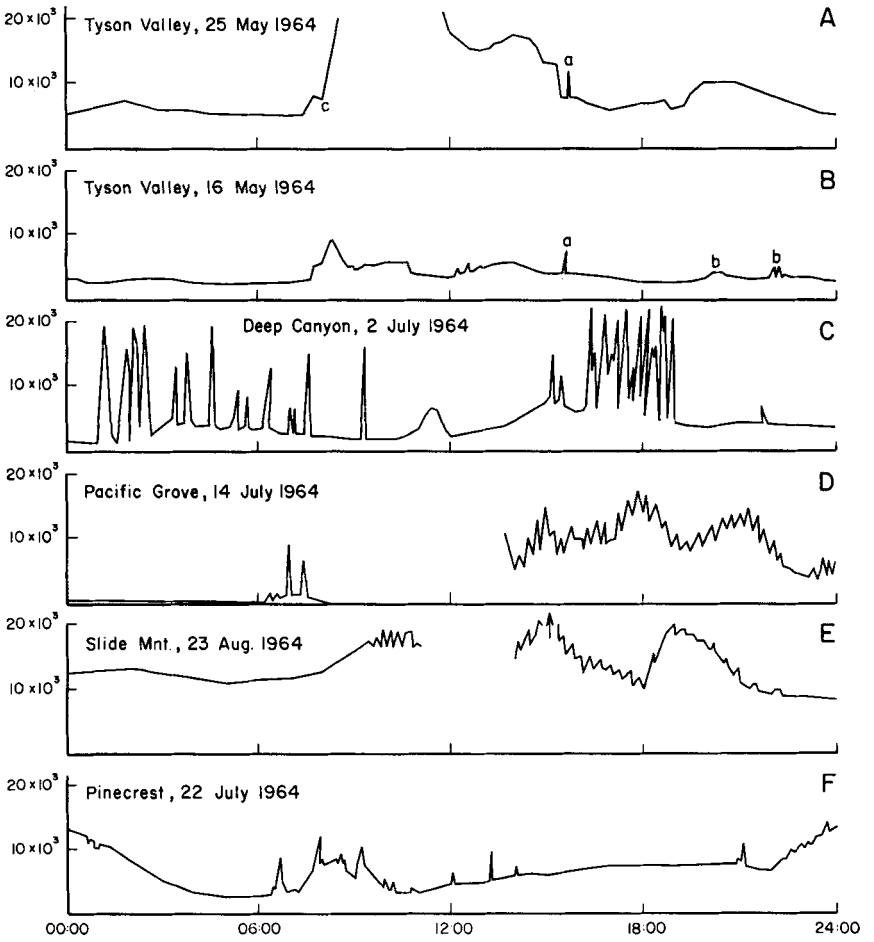

FIG. 1. Concentration of condensation nuclei (ordinate, cn/cc), for 24 hour periods (abscissa, hours local time, in all cases 1 hour ahead of standard time). Locations: *A* and *B*, Tyson Valley, SW of St. Louis; *C*, Deep Canyon, California desert SW of Palm Springs; *D*, Pacific Grove, along California Coast; *E*, Slide Mountain, 3000 m altitude, S of Reno, Nevada; *F*, Pinecrest, 1800 m altitude in Central Sierra Nevada in California.

only one is in operation. There are no fires or burners anywhere in the area. The trailer was located on an isolated, wooded side valley of the Tyson Valley, 2 km N of U.S. Highway 66, ½ km S of railroad tracks, whereas towards the W and NW practically no habitations nor roads were present, the country being covered with woods and traversed by the valley of the Meramec River. On days with Westerly or North-Westerly winds, the cn content of the air was lowest, and remained at a fairly even level, rising somewhat during day and decreasing during night (Figure 1B). Records during such days showed only a few sudden and sharp rises around 9:00 and 16:00, when a watchman in a jeep checked the trailer (marked *a*), and at other times when for some reason a car operated near the trailer. On days with Northerly winds a number of less sharp, but longer lasting peaks of cn appeared five minutes after the passage of diesel-powered trains (marked *b*). Southerly winds produced irregularly rising and falling cn concentrations, depending upon the amount of vehicular traffic on the nearby highway, whereas Easterly winds raised the cn level manyfold due to cn produced in metropolitan St. Louis (point c in Figure 1A). Thus in all cases human activities produced so

many cn that these overshadowed the natural cn content of country air. But country air definitely contained cn, ranging from 1000–5000 cn/cc.

From a dozen places in the U.S. and Costa Rica, day- to month-long records obtained with the Rich cn recorder are now available, obtained either by connecting it with a source of commercial electric power, or by supplying the electricity with a motor generator, 50 m away (and if possible downwind) from the cn recorder. The cn from the motor generator usually are not seriously confusing the record, since when wind brings its combustion products to the cn recorder, the readings immediately are off-scale, to return again to regular low-level values upon a shift in wind.

In all places where commercial electric power was available in the country, there were either roads or fires nearby, interfering more seriously with the record, although often a base-line could be drawn through the lowest values, indicating the likely free-air level. It is obvious that this only can be done with a continuous record, and that the standard Rich cn counter nor the Aitken cn meter, which produce individual measurements, can tell about the instantaneous level of pollution with man-made nuclei.

In St. Louis recordings were made on the campus of Washington University. This was 100 m N of Forsythe Avenue and just N of a parking lot. With winds of a southerly direction the cn record showed the degree of vehicular traffic and the activity on the campus as indicated by the number of cars driving into or leaving the parking lot. Even at night no natural level of cn could be measured.

In the Petrified Forest National Park we were probably as far away from human habitations as anywhere else. But a lightly traveled road to the E and the Santa Fe Railroad tracks to the N provided irregularities whenever cars or trains passed (during our stay we had mainly N–E winds). At an altitude of 1800 m in the center of the Sierra Nevada we were parked less than 100 m away from a few houses, and about 0.5 km from a camping site and 1.5 km from a small settlement, Strawberry. Every morning cooking activity in the nearby houses and in afternoon and evening campfires seriously interfered with our measurements (Figure 1F). In a very isolated spot in the Northern Coast Range in California campfires made by hunters would send the cn count up manyfold during morning and evening. In the desert cn produced by a motor generator seriously interfered with the cn recordings (Figure 1C).

When all this human interference was discounted, a very consistent picture emerged of the naturally occurring cn concentration at ground level. This picture could not be derived from weekly or monthly averages, from which the human interference could not be excluded.

In every case a gradual decrease in cn occurred during night. This decrease reversed itself after sunrise, when there was a less regular, but very consistent, increase in cn. Wind played a large part in the cn level. When upper air, low in nuclei, was brought in, very low values alternated with higher values, when locally produced nuclei reached the recorder. This was particularly pronounced on Slide Mountain, a 2900 m mountain SW of Reno, Nevada, rising 500–1500 m above the surrounding country (Figure 1E). And it was also strongly developed in Pacific Grove, California, where during day extreme fluctuations occurred even with constant W or NW wind, bringing only sea air towards the Rich cn recorder (Figure 1D). To check whether this was a result of human activities, the cn recorder was taken out to sea on a Navy boat with 110 v–60 cycle power. It was found that 10 km out to sea, with a sea breeze and no possibility of contamination with man-made nuclei, there was a continuously fluctuating number of cn, while there were no white-caps. During night the number of cn decreased rapidly, until by early morning (all the time with a sea breeze, W or NW of about 10 km/hour) the number of cn reached an extreme low of a few hundred per cc.

Observations above ground level

All measurements at ground level of cn can give us only a very incomplete picture of cn distribution in the atmosphere. To supplement the ground measurements, many observations were made in airplanes, in August, 1963, over the Ozarks plateau in SW Missouri, and in 1964 and 1965 over NW and S Nevada, Central California and N Arizona, the latter mostly with the Rich cn recorder, mounted in the Beechcraft plane of the Desert Research Institute, which had a 110 v–60 cycle power

supply installed for the cn recorder. Commercial airlines cannot be used for such measurements, since all air entering the cabin is filtered through filter bags which very effectively remove cn. But in the research planes the air intake was unfiltered and extended ahead of the engines. Only when circling around we once picked up our own exhaust air from the previous lap. In the neighborhood of airports we also occasionally picked up the exhaust from another plane, but these were only short periods, lasting a few seconds, and if one deliberately tries to follow the slipstream of a nearby plane, it is hard to pick up its cn at a distance of more than 1 km.

With the few exceptions to be mentioned later, the number of cn is highest near ground level and decreases to less than 1000 cn/cc above the main inversion layer. During night this decrease is gradual, as in a diffusion gradient, but during day the cn concentration is fluctuating between ground level and upper air level, apparently being high in the ascending air cells and low in the descending, which brings upper air down to the ground. In flying, one encounters the adjacent Benard cells in succession.

In the air above the inversion there are occasional clear layers, which have accordingly lower cn counts, but on the average the cn concentration does not change much above the main inversion layer. The latter layer occasionally has a higher cn content, correlated with an abrupt temperature increase of one to a few degrees, compared both with the air below and above it.

To explain the vertical distribution of cn, two possibilities exist. The first is that they originate in the upper troposphere or above. Then they might be concentrated by gravitational action in the lower troposphere, but this would result in precipitation on the ground surface. Besides, the gradient should still be in the opposite direction as observed. The second possibility is that the cn are produced at ground level, then disappearing at higher altitudes. The naturally occurring gradient upper air supports this possibility. But then there must be a mechanism by which they are removed in the upper air, and specifically in the inversion layer. It has already been mentioned that occasionally the cn are more concentrated in the inversion layer. There the particles not only accumulate but also increase in size as the transition from blue haze to gray or yellow layers suggests.

Not only in the inversion layer itself there may be a higher level of cn, but especially cloud edges are high in cn. This was first measured with the Rich cn counter (WENT, 1964); it has now been confirmed with the Rich cn recorder. Whereas with the Rich cn counter only every half minute a sample could be taken, the higher cn content of the cloud edges could only be established by statistical treatment of all data: averaging cn concentrations for all cn determinations made in cloud edges, and comparing them with all determinations made either inside or outside the clouds. This gave statistically a highly significant doubling of the cn concentration in the lateral edges of clouds, with a 15–30 fold increase in the upper edge of larger expanding cumulus.

With the Rich cn recorder the cn level in the clear air outside the cloud was found to be reasonably constant. Upon entering a cumulus there was a sharp peak in cn, leveling off inside the cloud, with a second peak upon leaving the cloud. A delay of a few seconds was due to the lag between air intake and the sample reaching the expansion chamber. There is very little likelihood that this increase in cn in the cloud edge is an artifact, for the supersaturation in the expansion chamber is so many times higher than that in the cloud edge or cloud interior that it should offset any differences between outside and cloud air. Besides this should not make any difference specifically in the cloud edge compared with the cloud interior.

Some information was obtained about a thunderstorm with large hail pellets of about 1 cm diameter, through which the plane inadvertently flew on a flight plan on March 24, 1965. It was at 4500 m altitude over the Amargosa desert in S Nevada. We had been flying above the inversion layer (at 3700 m) when we entered a large towering cumulus. The cn count immediately went up to 2–3 times the 800 cn/cc level in the clear air. When we reached the hail pocket this number increased another five fold, presumably much higher than anywhere at ground level over the desert. Also measurements were obtained in the dark-colored rain curtains dropping out of dark-edged clouds over the NW Arizona area near Hoover Dam. Each time the plane passed through such a rain cur-

tain the number of cn increased several-fold, fluctuating violently, and returning to the original value once the rain was passed. How do these observations relate to experimental information we have about condensation nuclei?

Facts about the nature of CN

Work done in Japan (KUROIWA, 1956) with the electron microscope threw doubt upon the universal and exclusive role of salt nuclei in water vapor condensation in nature, since 50 per cent of all snowflakes has "combustion" nuclei. When it occurred to me that volatile plant products might be a source of cn in nature (WENT, 1960), very much like olefins in the air can produce cn noticable as a blue smog haze, a number of measurements of volatile plant products (RASMUSSEN & WENT, 1965) and of cn in nature (WENT, 1964) were initiated. The present paper summarizes and augments the previously published information.

Aitken cn have a size distribution with a peak around 5×10^{-6} cm diameter (JUNGE, 1963). Occasionally there may be large numbers of smaller ones but they disappear rather rapidly through agglomeration and adsorption, resulting in the formation of particles in the range of 10×10^{-6} cm diameter. There is no physical possibility of such sub-microscopic particles arising through diminution of larger nuclei: it is a one-way reaction from small to larger nuclei. Since we know that the half-life of the smallest nuclei is a matter of minutes, it follows that Aitken nuclei are continuously formed anew. And from that it follows that they cannot be dust particles nor that (at least over land areas) they can be salt nuclei.

Admitting that Aitken nuclei can only arise from still smaller source materials, there are only two mechanisms by which they can form:

1) Condensation of molecules once they have reached supersaturation. In nature this is only possible for water molecules, and an enormous degree of supersaturation is required before they nucleate spontaneously. And then they grow immediately to 5 μ droplets which are white and not blue. No other compounds ever approach supersaturation: CO_2, NO_2, CH_4, H_2S, SO_2, or any organic compounds such as esters, terpenes, ethylene, skatol.

2) Development (from molecularly disperse—volatile—substances in the air) of products with such low volatility that they cannot remain individual molecules. They either must condense on surfaces or on each other (this has the same effect as if a high degree of supersaturation had developed).

It is obvious that only the second mechanism is feasible. Let us examine what is involved in this and whether the facts support an explanation of cn formation along these lines.

Measurements have been made of organic volatile materials in country air with a gas chromatograph using a hydrogen flame detector (RASMUSSEN & WENT 1965). This detector measures only reduced organic substances such as hydrocarbons and terpenes. This has shown that in a dozen localities in the United States, and one locality each in the Netherlands and in a tropical rain forest in Costa Rica, there are always measurable amounts of terpenes in the air, amounting to 2–20 parts per 1000 million. The concentration is low during winter, intermediate during summer and highest in autumn. This material can be shown to originate in the vegetation and to be given off especially upon death of the cell. Not only land plants but also algae and plankton produce terpenes, giving rise to the pine smell of coniferous forests, the sweet odors of meadows, the pungent smell of chaparral and other dryland vegetation, and the "salty" odor of the sea.

While it has thus been settled that over any vegetated area there always is volatile organic material around, we now will consider whether such volatiles can produce cn. There are actually five sets of facts which support this conclusion.

1) The original Tyndall experiment. When through a tube filled with air plus organic vapors (such as amyl nitrite or allyl iodide) a strong beam of light is passed, a "blue cloud" develops, consisting of submicroscopic particles. This "Tyndall effect" is due to Aitken nuclei, and the blue color can only be detected when the nuclei are numerous and relatively large (0.01–0.2 μ in diameter).

2) Repeating the Tyndall experiment with terpenes, no blue cloud is formed unless light-absorbing catalysts such as nitrogen oxide or iodine vapors are added. This is in line with what is known about photochemical smog formation, which requires the presence of olefins, nitrogen oxide and sunlight.

3) Instead of using the appearance of a visible "blue cloud", an Aitken condensation nuclei

counter will indicate the formation of particles. In this way cn production at much lower concentrations of terpene vapors and catalysts can be demonstrated. Thus the reaction mechanics of the photochemical process can be followed. When e.g. in a 40-liter clear plastic bag 1 p.p.m. NO_2 was injected in a few p.p.m. terpene vapor atmosphere, and the bag was then exposed to full sunlight, it took 10–15 minutes for a measurable increase in the number of cn; ten minutes later the maximum number was produced, after which there was a steady decline in cn; the concentration decreasing each ten minutes by one-half.

4) Using a 35 amp. carbon arc lamp, cn production could be demonstrated too in an α-pinene–NO_2 mixture, the number of cn being a function of the NO_2 concentration (WENT, 1964).

5) Observation and measurements in nature in the hot springs area of Yellowstone National Park has shown that on cold winter days the number of cn is exceptionally low. When α-pinene vapors were released into the air, a great increase in cn nuclei could be observed when simultaneously NO_2 vapors were released while the sun was shining. This increase was observed using a condensation nuclei counter and watching steam-cloud formation in the supersaturated air over the hot pools.

Summarizing these data, we can conclude that organic vapors in the air will give rise to the formation of condensation nuclei as measured with a cn counter, as observed through cloud formation in very pure supersaturated air, and visibly as a blue haze. This is a photochemical process, requiring much light of at least full sunlight intensity. Since terpenes and most other organic vapors do not absorb in the visible range, a colored catalyst, such as NO_2 or I_2 vapor, is essential. With the information mentioned earlier, that all air over vegetated land contains organic vapors, we have now in hand all essential facts to explain cn and blue haze formation.

Conclusions

All these observations are entirely consistant with the hypothesis that the great majority of cn have their source in photochemically transformed organic molecules of plant origin. It was found that the quantity of volatile organic material present in the air at any one time may be as high as 10^6 ton over the whole world. The rapid changes in concentration, the lack of odor at some distance of a pine forest or other strong smelling type of vegetation suggests a rapid decomposition and a turnover rate at least five times per day. This occurring at least 200 days of the year suggests a total yearly production of volatile organic substances of 10^9 tons over the whole world.

Filtering solid materials out of the air with a Staplex Hi-Volume Air Sampler, at ground level quantities of less than 0.1 mg/m³, and at cloud level 0.1–0.3 mg/m³ were found (in summer over the Ozarks). The latter figure agrees with an average cn diameter of 30×10^{-6} cm, which is about what is found in the distribution over the weight classes. This amounts to 2×10^7 tons of cn over the vegetated parts of the world. At a turn-over rate of once per week this gives us a yearly production of 10^9 tons per year over the whole world. This is the same figure as derived (by an entirely different method, the gas chromatograph) for all volatile organic matter produced.

The distribution of cn in the atmosphere as a function of height conclusively shows that they are being formed at ground level. Their number distribution over a 24-hour period also proves that they are formed during day, and disappear during night, partly by an agglomeration process, because the number of small nuclei decreases, with perhaps a slight increase in the larger nuclei.

There is no special increase in cn as one nears the ocean, suggesting that at most a small part of all cn can be of marine origin. This is also shown by the very low number of cn in oceanic air measured at Pacific Grove coming from beyond the 100 km coastal zone, rich in plankton.

The determinations also show that most cn become trapped in the inversion layer, either in the layer itself, or in the cumulus clouds forming in them. The trapping mechanism is unknown, although in the cloud it might be suggested that it is connected with droplet formation and droplet movement within the cloud, comparable to the mechanism suggested for charge separation.

There are several ways in which the chemical nature of the cn in the atmosphere can be ascertained.

1. *By direct sampling.* To this end enormous quantities of air must be filtered, for per m^3 only 0.1 mg of solid material can be collected. To get one gram of cn, 10^4 m^3 air must pass the filter membrane. It would be advantageous to collect all of this at higher altitudes (from an airplane). The water filter bags used by commercial ariliners to filter all cabin air would be ideal, but for 15 per cent of the time (just before take-off and after landing) they filter airfield air. Fig. 6 from Went 1964 shows that this contributes about 5 per cent of all solids filtered by the air sampler or water filter bags, yet for scientific satisfaction all sampling should be done at or just below the inversion layer.

A number of water filter bags from piston-driven airliners (TWA) were analyzed, and it was found that the filter retained fairly large amounts of black carbon, infiltrated with oils. The latter were a complicated mixture of highboiling materials without resolution in a gas chromatograph. Elementary analysis indicated a multi-ring carbon compound, low in hydrogen. When first received the filters also had a strong aromatic odor, suggesting phenolic compounds or terpenes; upon inquiry I was informed that no chemicals had been added to these water filter bags.

2. *Precipitation.* Thus far little attention has been paid to the organic content of residues in rainwater or melted snow. Soluble and radioactive materials are well investigated. The insoluble material consists of

(*a*) Dust, soil and other inorganic particles, under the microscope partly identifiable as silica, mica and montmorillonite.

(*b*) Organized particles, such as lint (fibers), pollen, spores, insect wing scales, bacteria. These are particularly numerous in summer rain and thunderstorm residues, but are largely absent in snow melt water.

(*c*) Irregular masses of usually highly colored material, yellow, brown, or black, producing porous aggregations. In addition one may see deep-yellow or brown spots on the soil particles. These soil particles do not show Brownian movement when suspended in water between slide and coverglass, apparently because they stick to the glass surface.

(*d*) Upon further aggregation we can see tar-like droplets, semiliquid, black, attaching themselves to the fibers of filter paper. This was found also in snow melt water, from snow fallen in midwinter in Yellowstone, NW Wyoming, far from industrial areas, with hardly any human activities during winter.

Eriksson and others have found that more than 50 per cent of the non-volatile material in rainwater collected in Sweden is organic in nature, and I have also published evidence that the solids in snow from the Greenland Icecap and from an ice island floating in the Arctic region consist of 3–7 per cent organic material (WENT, 1960, 1964).

The later fate of this organic material, brought back to earth by precipitation, need not concern us here, but it is conceivable that it is the source material for petroleum and oil (WENT, 1960) and coal, that it is an important component of humus, that it is the material which gives clay its sticky consistency.

Summary

Measurements of condensation nuclei (cn) with a Rich cn counter and a cn recorder have shown, that they are formed in the atmosphere during day at ground level, and decrease in number during night, and with increasing height above the ground. Over the land areas investigated volatile plant emanations (mainly terpenes) are the source materials for cn production. Under the influence of sunligt, with the aid of a catalyst such as nitrogen dioxide, these terpenes are condensed to macromolecular aggregates, which appear as a blue haze. They disappear again from the atmosphere through collection in the inversion layer and in convective clouds and return to the earth as impurities in precipitation.

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О ПРИРОДЕ ЯДЕР КОНДЕНСАЦИИ Aitken'a

На число ядер конденсации Aitken'a сильно влияет деятельность человека, которая увеличивает природное количество этих ядер посредством разложения продуктов сгорания из печей и двигателей внутреннего сгорания. Естественная концентрация ядер в приземном слое увеличивается в течении дня и уменьшается ночью, кроме того, она уменьшается с высотой. Естественные ядра Aitken'a образуются на свету из летучих продуктов, выделяемых растениями (в основном терпен), и поэтому являются органическими макромолекулами. Они исчезают в основном посредством слипания внутри или около инверсионных слоев и вымывания оттуда осадками.