The Questionable Practice of Slash Burning

Slash burning is commonly practiced in Pacific Northwest forests to remove wood and brush from clearcut sites in preparation for planting commercial tree seedlings. In this article, a geochemist presents the information that is beginning to emerge regarding chemicals released and formed by slash burning and the hazards these chemicals pose to nearby residents and the environment. Some of these chemicals are formed because wood is being burned; others may be present because the slash and brush have been sprayed with herbicides prior to burning.

A second article on additional environmental effects of and alternatives to clear cut/slash burn practices will appear in the December issue of NCAP NEWS, a special on manual alternatives to vegetation management.

by Roger Hart

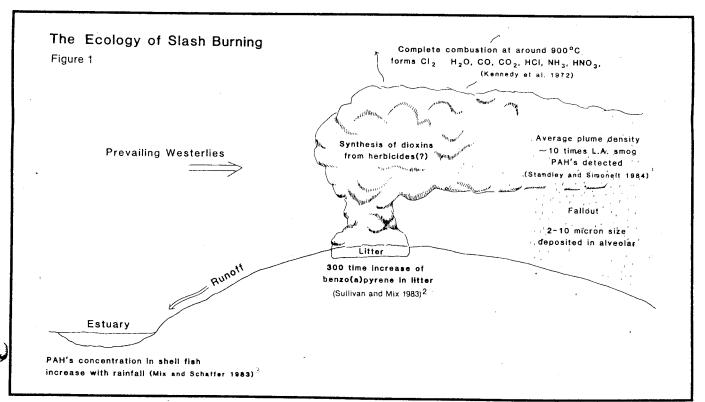
"Don't worry, the smoke simply dissipates and all the toxic chemicals degrade to harmless substances." How many times have we been given this reassurance about slash burns? As a professional geochemist, I am trained to trace the life cycle of various chemical substances in geological processes. Members of my profession realize no chemical dissipates, degrades or disappears. For example, in 1982, El Chichon, a volcano in Mexico, erupted. The ash from the eruption did dissipate into

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the atmosphere, but the ash cut down on the sun's energy reaching earth and dropped the temperature of the earth a fraction of a degree in the last two years. Eventually ash from volcanic eruptions settles to the bottom of the ocean where it is found below sediment layers typical of glacial epochs. Thus, we know particulate matter in the atmosphere affects earth's climate. Eventually over the period of millions of years, ocean sediments are subducted into the earth-at colliding plate margins, melted to produce magma, and rise once again to the surface in volcanic eruptions. This is an example of a geochemical cycle that takes millions of years to complete. With the viewpoint of geochemical cycles as background, I reviewed recent studies of slash burn smoke and found it contains potent carcinogens that may be collecting in our estuaries and that burning of herbicide slash can potentially form dangerous compounds of chlorine similar to war gases banned since World War I. In this article, I first discuss the carcinogens produced in any slash burn, then consider the chlorine compounds produced in herbicide-treated slash, and conclude with some observations on possible legal actions that can regulate slash burning.

Carcinogens in Slash Burn Smoke

Carcinogenic substances known as polynuclear aromatic hydrocarbons (PNAHs) have been detected in slash burn smoke¹ and the ash and litter left after a slash burn,² and are known to increase in shellfish in Yaquina Bay (OR) during periods of high rainfall, perhaps as a result of runoff from slash burn sites³ (Fig. 1).



Scientists believe PNAHs are formed only by the heating of organic substances. This happens in natural fires, human-caused fires, and burial of organic matter deep in the earth by natural geologic processes. PNAHs have been found in a fossil sea lily 150 million years old. How are PNAHs formed and why are they carcinogenic even if the precursor organic matter is not?

PNAHs were discovered in 1865 by Friedrich Kekule. Organic matter normally contains hydrocarbons, long molecules like a centipede in which the body of the centipede is made of carbon atoms and the legs are hydrogen atoms. For example, the hydrocarbon hexane has six carbon atoms in a straight chain with fourteen "legs" of hydrogen atoms. When hexane is heated in the presence of oxygen in air, some of the hydrogen "legs" burn off and combine with the oxygen to form H₂O, leaving an unsatisfied chemical charge on the body of the centipede (Fig. 2). As a result of this charge discrepancy, the body of the centipede curls around and the head attaches to the tail like negative and positive poles of two magnets. The new ring molecule is known as benzene and Kekule first solved the riddle of its structure after having a dream in which dancing snakes bit their own tails.

Benzene is the simpest of the PNAHs, and is known to cause leukemia. The reason PNAHs cause cancer is simple. The hydrogen "legs" prevent hydrocarbons from entering the DNA molecule. Once some of the "legs" have been scorched off, the probability that the flat ring molecule of benzene will enter DNA and other organic molecules increases. This destroys normal cell growth (Fig. 2).

While benzene was the first of the PNAHs documented to be carcinogenic, it is not the most dangerous. That distinction belongs to benzo[a]pyrene, a planar grouping of five benzene rings fitting together like six-sided Cheezit crackers. According to Drs. Timothy Sullivan and Michael Mix of Oregon State University, who first documented PNAHs at slash burn sites, "PNAHs were the first chemical compounds shown to be carcinogenic; some are classified among the most potent procarcinogens known." Drs. Mix and Sullivan measured a 300-fold increase in benzo[a]pyrene in the forest litter following a slash burn at the Camp Chilcote site in Benton County (OR) and estimate almost three tons of benzo[a]pyrene and almost fifty tons of total PNAHs are produced every year

Combustion
CYCLE
Figure 2

Benzo(a)pyrene

during slash burning in western Oregon. A 1972 study by the National Academy of Sciences estimated a total of 127 tons/year of benzo[a]pyrene—about one fourth of the total US open combustion production—is from forest and agrifultural fires in the Western US.4

Where does the benzo[a]pyrene go? Does it simply degrade and disappear? The presence of PNAHs in the 150 million year old sea lily fossil suggests they can be stable over long periods of time. Significant levels of PNAHs were detected in smoke collected by high volume air samples at the site of a Boise Cascade burn in Lincoln County (OR) in July of 1983. The PNAHs are probably absorbed into fine charcoal grains. Charcoal in the gas masks used during World War I absorbs gases and volatile compounds. Breathing of these charcoal particles with absorbed toxic substances can be hazardous because the finer particles (less than 10 microns) are deposited and trapped in the alveoli of the lower lungs. Significant quantities, resulting in black lung, can be accumulated by repeated exposure.

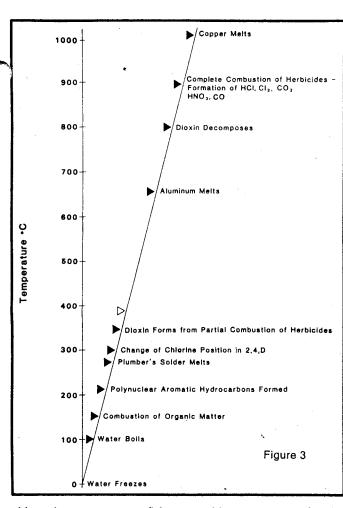
Eventually the airborne charcoal particles settle back to earth, the large ones closest to the burn site. Along with non-airborne litter, the particles can be washed into the estuaries and accumulate in the sediment coating the bottom. As of yet, no studies have been made of PNAHs in estuary sediments. However, in 1983 Drs. Michael Mix and Randy Schaffer of Oregon State University reported the results of a PNAH study of Yaquina Bay mussels.³ They found a dramatic increase of PNAH levels during the rainy season, leading Dr. Timothy Sullivan to speculate, "a significant potential source of PNAH within these watersheds, and throughout western Oregon, is slash burning, the burning of residual materials that remain after logging operations."

Burning Herbicide-Treated Slash

Most clearcuts are sprayed with herbicides prior to burning. This kills and dries out grasses, shrubs, and bushes and enhances the likelihood of a successful burn. Herbicides such as 2,4-D, picloram, Garlon (triclopyr), dichloroprop, and dicamba are applied to salmonberry, red alder and salal at bud break in the spring. The burning season begins in early July after slash and forest litter have sufficiently dried. In addition, a general toxicant such as Dinoseb is often applied a few days prior to burning. Dinoseb, a nitrophenolic compound, rapidly kills foliage (as well as insects and fungi) and desiccates the clearcut.

In September 1981, 0.7 acres of slash on a Bonneville Power Administration right-of-way were sprayed with 2,4-D and burned. Several fire fighters exposed to the smoke suffered respiratory illness after the burn. Incidents such as this raise the question: does burning of herbicides produce toxic substances?

Experimental burning of herbicides and other chlorinated hydrocarbons in the laboratory has produced dioxin,6 chlorine gas,7 cyanide,8 and phosgene.9 What are the symptoms of exposure to these substances and are they likely to occur in toxic concentrations during slash burning? In order to answer these questions let's quickly review some chemistry of herbicides. The nucleus of most herbicide molecules is similar to the benzene ring of polynuclear aromatic hydrocarbons; in addition, however, herbicides commonly have legs of chlorine atoms radiating from the nucleus like the legs of a crab. The number of chlorine atoms is different for each herbicide. For example, 2,4-D (2,4-di-



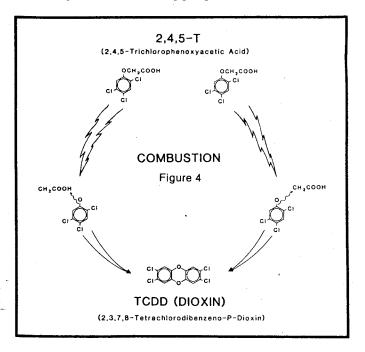
chlorophenoxyacetic acid) has two chlorine atoms and picloram (4-amino-3,5,6-trichloropicolinic acid) has three chlorine atoms. In addition, most herbicides have an acid molecule "tail" connected to the benzene ring by an oxygen molecule. 2,4,5-T and 2,4-D both have acetic acid molecules attached to the benzene. It is this "tail" jutting out like the tail scaffolding on the starship Enterprise that cuts down on the probability of the herbicide molecule entering the DNA molecule. Numerous laboratory experiments have shown that burning herbicides cleaves off the acid molecules as well as the chlorine atoms at much lower temperatures than that required for total degradation of the herbicide (Fig. 3). The cleaving of the acetic acid radical from 2,4,5-T leaves a negative charge balance that is compensated by the combination of two molecules to form TCDD, a toxic variety of dioxin (2,3,7,8-tetrachlorodibenzo-p-dioxin; Fig. 4). In a laboratory experiment conducted at the analytical laboratories of Dow Chemical at Midland, Michigan, Drs. R.H. Stehl and L.L. Lamparski found, "Under these experimental conditions [temperature 350-800°C] we observed a small amount of TCDD was produced in addition to that present as a trace contaminant in the 2,4,5-trichlorophenoxy species."6 TCDD levels in the soil surrounding the Dow Midland Michigan Laboratory are five times higher than the highest concentration measured anywhere else. Other types of herbicides will form other, presumably less toxic, dioxins. For example, 2, 4-D probably converts to 2,7 dichloro-pdibenzo dioxin. No attempts have yet been made to measure dioxin concentrations at slash burn sites. At about the same temperature as that of dioxin formation, chlorine atoms are

cleaved off during burning of herbicides. 2,4-D converts to ortho- and para-monochlorophenoxyacetic acids with the loss of one chlorine atom in the temperature range 210-300 °C. ¹⁰ At temperatures above 800 °C, considerable chlorine gas has been measured. No attempt has been made to analyze the form or concentration the chlorine atom takes as it cleaves off from herbicides during slash burning. Experiments conducted by Russian and Japanese scientists show burning of polyvinyl chloride (PVC), another chlorinated hydrocarbon, releases chlorine in the form of hydrochloric acid and phosgene, a war gas that causes respiratory illness.

The formation of hydrochloric acid and phosgene during burning of PVC suggests they can also be formed during burning of herbicides. The actual chlorine compounds produced during slash burning depends on the type and availability of free ions (charged atoms and molecules) with which the chlorine ion can react. If the released chlorine ions encounter other chlorine ions most frequently, then chlorine gas (Cl2) is produced. If the chlorine encounters free hydrogen ions most frequently, hydrochloric acid (HCl) will form. If carbon monoxide ions are encountered, phosgene (COCl2) is formed. If oxygen ions are encountered, chlorine dioxide (ClO₂) forms. In a slash burn, oxygen (which comprises about 20 % of air) is readily available and combines with carbon released during burning of organic matter to form carbon monoxide and carbon dioxide. Hydrogen released from the hydrocarbon by burning combines with oxygen to form water (H2O). Thus the availability of oxygen to form chlorine dioxide depends on the proportion of air to slash and the speed at which the air is replenished. It seems likely all these compounds can be produced in different proportions under variable conditions of temperature, organic matter-to-air ratios, and position in the smoke column.

Until more accurate information is available concerning the presence of these chlorine compounds in herbicidetreated slash burn smoke, we should become aware of their various characteristics and the symptoms induced by exposure to them:

Hydrogen chloride (HCl; anhydrous hydrochloric acid) is a colorless gas with an irritating pungent odor that irritates the



eyes, mucous membranes and skin. Exposure of rabbits and guinea pigs to 4290 parts per million (ppm) hydrogen chloride for thirty minutes has caused death from pulmonary edema (swelling of lung tissue); exposure to 300 ppm for six hours caused corneal and upper respiratory irritation. In humans, exposure immediately results in a cough, burning of the throat, and choking. Exposure to 50-100 ppm is barely tolerable for one hour and extreme exposure can cause pulmonary edema in humans. The Occupational Safety and Health Administration (OSHA) has set a standard ceiling for exposure to hydrogen chloride at 5 ppm.

Chlorine (Cl2) is a poisonous greenish-yellow gas with a

The Individual & Slash Burning

Concern over slash burn smoke has been voiced by Oregon coastal residents for years because, as Newport (OR) resident Susan Parker notes, "Slash burning is allowed only when wind conditions will keep smoke out of the Willamette Valley, which is to say that slash burning is only allowed when the smoke will fall on coastal residents. When the smoke stays in your valley for three to six days, and then everyone, literally everyone exposed to the smoke gets sore throats, lung inflammation and congestion, and total body aches, you have to feel like you're being poisoned. Many residents believe that breathing the smoke is direct exposure, like right into the lungs and into the blood stream. The numbers of pneumonias reported in hospitals have seemed to increase every winter for the past three years, but someone has yet to really look into the prob-

As a member of the Coastal Coalition for Alternatives to Pesticides (CCAP), an NCAP member group concerned with the loss of fish and wildlife, the health effects, and the air pollution resulting from management practices on the forest lands surrounding them, Susan notes that, "We've questioned for years what chemicals are produced when sprayed slash is burned, but no one was looking. The EPA told me that they contracted in 1975 with Logan Norris of the Pacific Northwest Research Station to look for dioxin in smoke from slash burns, but we were the first people to take samples in 1983."

With a high volume air sampler and the help of scientists, CCAP itself began testing for the total particulates and certain chemicals in slash burn smoke. The air sampler takes in air at 50 cubic feet per second and collects the air's particulates and chemicals on filter paper. These chemicals can later be identified and quantified in a laboratory. Arrangements can be made by other citizen groups to use CCAP's air sampler, although one of the CCAP members, trained to use the sampler correctly, would need to introduce its use to the group.

CCAP will be continuing its efforts to get slash burn smoke analyzed, to compare the chemicals in smoke from sprayed and non-sprayed slash, and to provide public education about slash burning and alternative forestry practices. For more information, contact Susan Parker; 825 NE Grant; Newport OR 97365; (503) 265-9648.

characteristic irritating odor. Nasal irritation, coughing, choking and chest pain occurs at about 0.5 ppm. These symptoms are frequently accompanied by nausea, headache, and dizziness. Chronic exposure may increase susceptibility trespiratory infections. At higher concentrations pulmonary edema, pneumonia and death may result. The current OSHA standard for chlorine is a ceiling level of 1 ppm averaged over a fifteen minute period.¹¹

Phosgene (COCl2) is a colorless gas with a sweet odor like hay at low concentrations and a sharp pungent odor at high concentrations. The gas at concentrations of 1-2 ppm causes eye irritation, at 5 ppm, cough with discomfort in the chest and irritation of the nose and throat. At concentrations of 50 ppm phosgene is rapidly fatal as a result of pulmonary edema characterized by frothy sputum. The current OSHA standard for phosgene is .1 ppm averaged over eight hours."

Chlorine Dioxide (ClO₂) is a yellow-green to orange gas with a pungent sharp odor. The symptoms for chlorine dioxide are similar to those for phosgene with respiratory irritation followed by pulmonary edema. Exposure to 19 ppm for an unspecified time has resulted in fatality. Rats repeatedly exposed to 10 ppm died after ten days of exposure, Repeated exposure may cause chronic bronchitis. The OSHA standard is the same as that for phosgene, 1 ppm averaged over an eight hour period.¹¹

Two significant generalizations are derived from these observations. First of all, possible chlorine compounds released by thermal degradation of herbicides all cause respiratory problems ranging from coughing to chronic bronchitis, to pulmonary edema and pneumonia. Secondly, the gaseous chlorine compounds are toxic at concentrations as much as 800 times lower than the herbicide from which they are derived. For example, the concentration for loss by death of fifty-percent of laboratory animals for picloram is 8,200 ppm. Potentially, 84% of the picloram could be converted to chlorine dioxide, which is lethal to rats at 10 ppm.

Concentrations of Chemicals in Slash Burn Smoke

What is the likely concentration of chlorine compounds in slash burn smoke? An accurate estimate cannot be made without actual measurements. Rough calculations presented below suggest the chlorine compounds produced by thermal degradation of herbicides during slash burning should not be neglected. The concentration of released chlorine compounds in slash depends on the nature and amount of herbicide, the temperature of the burn, and the amount of air into which the chlorine compounds are released. The chlorinated herbicides 2,4,-D, 2,4-DP, atrazine, picloram, Silvex, dicamba, triclopyr, dalapon and pronamide contain from 32 to 49 percent chlorine by weight. Recommended herbicide application rates for conifer release vary from 1 to 15 lbs/acre (455 to 6,825 gm/acre). Higher concentrations are known to damage conifers or reduce growth rate, especially if applied after bud break. There is no established upper limit for rate of herbicide application prior to slash burning for dessication purposes. In addition to the rate of application, the degree to which it persists between time of application and the slash burn must be considered. Atrazine, diacamba, pronamide, and triclopyr are known to persist for at least one month. Picloram exists for more than a year and a half. In the case of the short term herbicides such as 2,4-D and dichloroprop, consideration must be given to the nature of the degradation products. Degradation is believed to take place by microbe

activity. Are the herbicides absorbed into the cells of woody plants and microbes without significant chemical change? If so, herbicide concentration may build up in organic matter with repeated application. Of particular interest is the fate of the chlorine in the degradation processes. Does it remain bonded to a partially degraded benzene hydrocarbon or is it released as ClO₂ and absorbed in the forest litter? At the 70th annual meeting of the Air Pollution Control Association in Toronto, Drs. R.A. Karnes, D.S. Duvall and W.A. Rubey, who conducted herbicide thermal degradation experiments concluded, "Decomposition products should remain a concern in all thermal degradation studies of any compound such as those investigated." Does the same warning apply to microbial degradation? Does the chlorine simply disappear?

For the purposes of making a demonstrated calculation, I will assume 5 lbs/acre of herbicide is present at the time of burning. This roughly corresponds to 1,000 gm/acre of chlorine. The net concentration in air depends on how fast the herbicide is degraded and the chlorine is released. Herbicides are more volatile than wood and litter. For this reason they will be burned and emitted in the early stages of the burn. It is possible to consider two extremes. In the worst case, all the chlorine is quickly released into a column of air one meter high. This corresponds to 4,000 cubic meters or 5.36 million gms of air. The concentrations of gas in this case are 187 ppm for chlorine, 192 for hydrogen chloride, 283 ppm for phosgene and 358 ppm for chlorine dioxide. While the worst case is highly unlikely, the concentrations are alarmingly high; 187 times the OSHA standard for chlorine. 2,830 times for phosgene and 3,580 times for chlorine dioxide. The phosgene concentration is 6 times that known to cause fatalities and the chlorine dioxide concentration 18 times the concentration that can cause fatality. These extreme concentrations could occur only under bizarre conditions of herbicide build-up in plant and microbe cells or blatant disregard of recommended rates of application.

Now consider the other extreme. If the assumption is made that the chlorine is released at the same rate as wood is burned, it is possible to estimate the total volume of air the chlorine is released into by calculating the amount of particulate matter required to obscure vision. This assumption allows an estimation of minimum concentrations because the chlorine is volatilized much faster than the particulates are released from thick logs and litter. Dr. Frank Dost of the Department of Agriculture Chemistry at Oregon State University, in a report written for the Bonneville Power Administration, estimates a visibility of 100 meters in smoke corresponds to a particulate density of 5 mg/m³. He suggests 6,955,000 mg of particulates are released per acre of slash burned and that to reduce visibility to 100 m, the particulates must be released into 1,391,000 m³ of air.13 If chlorine is released into the same amount of air from 1000 gm/acre, then the concentrations are: .54 ppm for chlorine, .55 ppm for hydrogen chloride, .81 for phosgene and 1.02 ppm for chlorine dioxide. The concentrations of phosgene and chlorine dioxide are still 8 and 10 times, respectively, the OSHA standard. These calculations suggest the respiratory problems suffered by the BPA firefighters could have been from exposure to chlorine compounds produced during burning of herbicides. It also seems likely that residents of the Coast and Cascade ranges of Oregon may suffer from chronic bronchitis, pulmonary edema, and pneumonia after exposure to slash burn smoke.

Litigation

Litigation against slash burning has been attempted on the grounds of encroachment on private property. To date, the courts regard slash burn smoke as non-hazardous despite published evidence to the contrary. In the case of Parker, et al. v. Boise Cascade heard last January in Oregon Federal district court, Judge Owen Panner ruled that the burden of proof that slash burn smoke is hazardous is on the plaintiffs in each specific instance of infraction. 14 Thus, private individuals pursuing litigation are forced to support the costs of sampling and analyzing slash burn smoke and presenting the evidence in a fashion that is credible in court. This includes documentation of wind direction to avoid "Act of God" arguments on the part of defendants. The complete evidence in a successful court case would require documentation of: total particulate density, quantitative analysis of benzolalpyrene and other carcinogenic PNAHs, the presence of chlorine substances such as chlorine dioxide which is noticeable because of its orange color, the possibility of relict and degraded herbicides as well as dioxin, and 24 hr data on wind velocity and direc-

Summary

Slash burning forms carcinogenic polynuclear aromatic hydrocarbons (PNAHs) which are apparently released into the atmosphere via smoke and into aquatic networks via runoff. Dioxins and other chlorinated compounds may be similarly released if the slash has been treated with chlorinated herbicides. The known effects of these compounds on human respiratory systems warrant concern for citizens subjected to the smoke from slash burning incidents. Litigation based on careful analysis of slash burn smoke may prove helpful in spurring consideration of alternatives to slash burning.

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