

Over-liming: Injury in Relation
to Tannin-containing Materials.

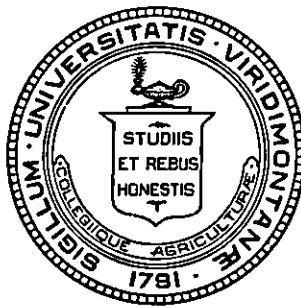
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OVERLIMING INJURY IN RELATION TO
TANNIN-CONTAINING MATERIALS

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Certain acid soils become temporarily toxic to many crop plants when heavily limed, while neutral or basic soils similarly treated do not injure them.

Some soils are much more sensitive to overliming than others and may induce severe toxicity even before they are completely neutralized. This is especially true of the heavily leached A₂ horizon of a podzolized soil.

The type of injury discussed in this bulletin is not due to a deficiency of available nutrients and the problem is differentiated from nutritional disorders reported by other investigators.

The toxin is associated with organic matter and it is very difficult to destroy. Burning the soil to constant weight, boiling it with concentrated sulphuric acid or fusing it with potash proved effective.

Many plant tissues and tree barks, made acid in a manner equivalent to the process of podzolization, caused typical overliming injury when used as a medium for growing flax seedlings. Tannin-bearing materials, such as the barks of hemlock, spruce, and pine, were especially harmful.

The use of soluble tannins, as such, did not bring about the characteristic symptoms whereas many difficultly soluble tannin-like derivatives which become activated with lime did. Work is being continued along this line, using other tannin and natural phenolic resinous materials.

BULLETIN 420: OVERLIMING INJURY IN RELATION TO TANNIN-CONTAINING MATERIALS

A. R. MIDGLEY and D. E. DUNKLEE

For several years investigators at this Station have noted decreased yields and, often, death to seedlings which have resulted when excessive amounts of lime have been applied on acid soils, especially when soil organic matter contents were relatively high. This damage has been particularly serious on certain soils on which alfalfa has been newly seeded, mainly because of the large amount of lime used and because it was calculated to affect about seven inches of soil whereas, as a matter of fact, it was not thoroughly intermingled with the soil to that depth and caused overliming of the surface. County agents and extension workers have reported that legumes have been injured by excessive applications at the time of seeding. Certain phases of this problem have been heretofore discussed by one of us (13, 14), but further work on other phases seemed necessary.

When enough lime is sown theoretically to induce neutrality on very acid soils, plant death often ensues so quickly that the nutrient reserves in the seed are not exhausted; on the other hand, it may be sown in almost unlimited quantities on normal neutral soils without producing this lethal effect. One encounters little trouble in overliming a neutral soil, but may readily overlime an acid soil and severely damage plant growth.

The symptoms exhibited by various crops suffering from this type of injury (p. 6) and the methods and apparatus used in growing plants on several soils and soil-like materials are described (p. 5). A distinct difference has been noted between the type of overliming injury observed at this Station and the nutritional disorders often encountered on overlimed soils by other investigators. Decreased yields usually characterize the latter and seedling death the former. The type of overliming injury now under discussion seems to occur naturally only on podzolized soils such as are frequently found in Vermont forest regions at the higher altitudes. However, it may be induced in the laboratory on almost any soil with a high organic matter content, if made sufficiently acid by leaching.

The success met in the use of certain remedial methods (p. 17) seems to indicate that an organic substance highly resistant to decomposition is the cause. Moreover, toxic substances or materials rich in

tannins have been found in certain plant tissues, such as the barks and leaves of trees. These tannins and allied materials, if made sufficiently acid through leaching or otherwise and used as a soil, may induce overliming injury. In this respect plant tissues behave in much the same manner as does a normal soil which will produce injury if leached with acid.

These observations led the writers to study the chemistry of tannins and their derivatives in order to ascertain the fundamental causes of the observed trauma. Although the exact nature of the toxic agency is not yet fully understood, there seems to be every reason to believe that the damage is caused by toxic substances of plant origin which are associated with tanning materials, presumably not tannin itself but derivatives thereof.

The objective of the present study was to determine what soils and soil-like materials might produce or, after certain treatments, be made to produce overliming injury, as well as to describe the injury itself and the best means of prevention. A distinction is drawn between this type and that described by others as due to nutrient deficiencies. The relation between this type of overliming injury and tannins or tannin derivatives is also described.

EXPERIMENTAL METHODS

The writers have grown several crops on soils showing toxic effects from heavy applications of lime. Lettuce, tomatoes, rape, flax, alfalfa, clovers, and mustard in the seedling stage have been seriously damaged under such circumstances. Flax was finally selected as an indicator because of its very characteristic appearance in the seedling stage. The unusual symptoms manifested were of great advantage when many different media were being tested, since injury could be definitely observed in 15 to 20 days after the seed had been sown. No yield data were kept since the injured plants were easily recognized, the abnormality seeming to manifest itself whenever this special toxic condition was produced. Furthermore, the injured seedlings soon died and could not be harvested.

The damaged plants shown in plate 1 are characterized by yellow necrotic terminals which eventually die. The epicotyl as it emerges is often bright yellow in hue in contrast to the green cotyledons. If the plant is severely injured the epicotyl does not emerge beyond the cotyledons; if less severely injured it may come forth and reach the height of the next whorl of leaves before it turns yellow and dies. Some-

times as death approaches the plant makes a futile attempt to branch, although still showing visible signs of injury. The proportion of the plants showing any unusual symptoms could be readily ascertained in all cases. Whereas most toxic substances, other than those present in an overlimed soil, as a rule either entirely inhibited germination or stunted such growth as did occur, flax plants on overlimed soils commonly germinated and grew normally until the epicotyl started to emerge beyond the cotyledons. Furthermore, the roots of injured flax plants were also unable to attain normal proportions. They were knotted and brown and devoid of root hairs. Brown scars were often noticed where roots apparently had attempted to branch and had aborted. Usually they had no branches and never attained a normal spread or size. Plate 1 shows the distinctive root and top growth of flax plants injured by heavy applications of lime, as well as that of normal plants grown on the same soil treated with smaller amounts of lime. Plants grown under conditions of nutrient deficiency do not produce this characteristic development.

The seedlings used in most of the trials were grown at 30° C.¹ in small crucibles immersed in a waterbath holding 35 at a time.² The seeds were more easily germinated in soil materials having a poor physical condition when the containers were covered with a pane of window glass to maintain a high degree of humidity than when not thus protected. During the winter months a 100-watt electric light was turned on each evening to extend the light period. Distilled water was used on the seedlings at the outset but, later, tap water replaced it since a toxic medium when overlimed seemed to produce injury no matter what water or nutrients were added. When the seedlings became sufficiently mature, estimates were made in each case of the percentage of damaged plants and the severity of injury. A plant exhibiting a necrotic terminal bud and knotty, stubby roots of the type previously described was deemed to be injured.

The amount of lime required by the media in which these test plants were grown was calculated as calcium carbonate by the Jones calcium-acetate method (7). This method determines approximately the amount of lime needed to neutralize a definite weight of soil. Multiples of this lime requirement were used to make certain that soils were overlimed, sometimes as much as six times the amount being needed to make

¹ Since these trials were conducted throughout the year it was thought desirable to maintain a constant temperature (30° C.).

² These small containers were used so that many plants could be simultaneously grown and various treatments employed with greater facility. Sometimes only small quantities of material were available and, where certain organic chemicals were used as soil-like media, the cost was materially reduced by the use of small containers which proved to be very satisfactory in all respects but necessitated much care and frequent attention.

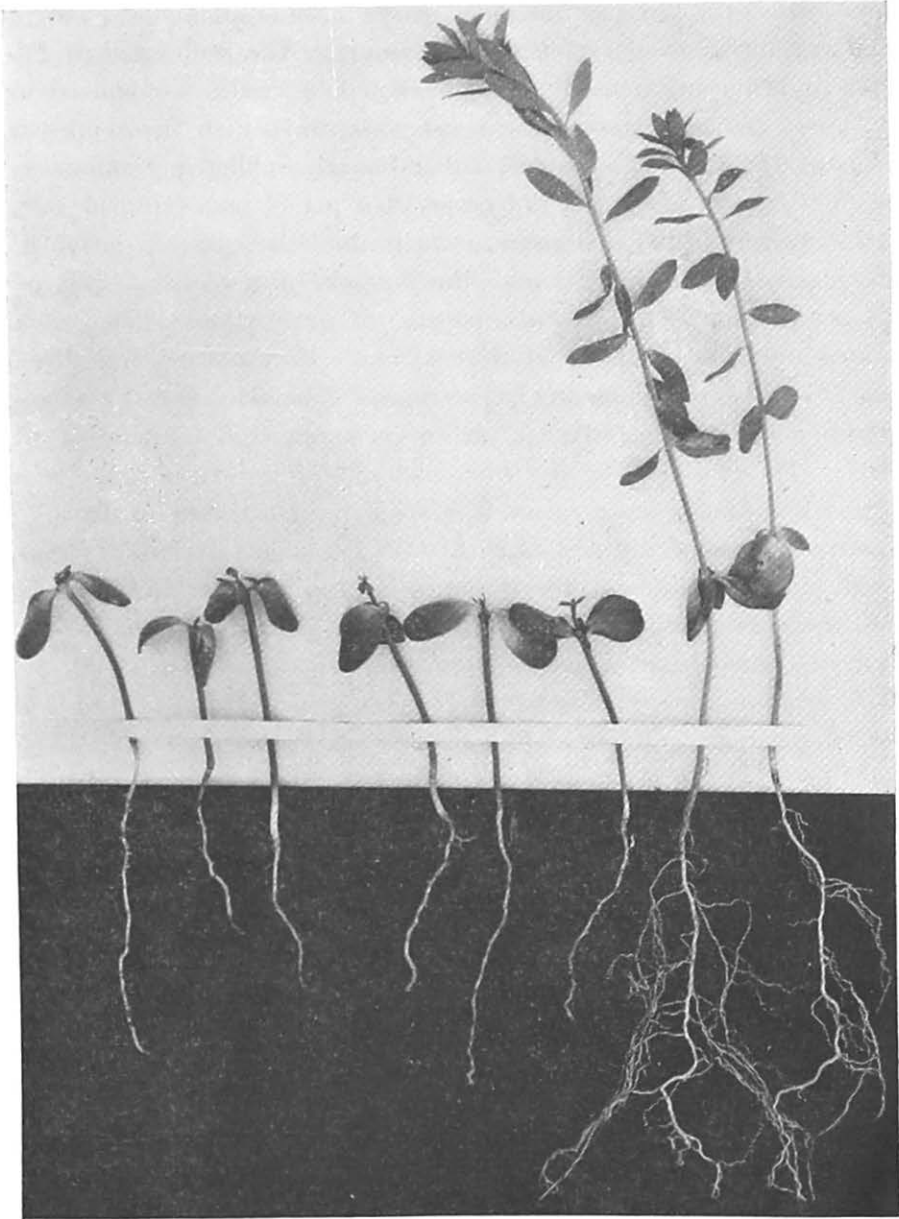


PLATE I.—Flax plants showing typical overliming injury (left) and normal growth (right). The injured plants have short, stubby and somewhat knotty roots practically devoid of branches or root hairs. The cotyledons, while normal in size, soon turn yellow and the epicotyl seldom makes any growth.

absolutely sure that the soil contained enough lime to produce injury if and when toxic agents were present. Sometimes an arbitrary quantity known to be excessive was applied. The same procedure was employed when woody and plant materials were used as media. In order

to avoid confusion all lime requirement data were kept on a weight basis, whether the material employed was of organic or inorganic nature.

The soils were dried and screened to 10-mesh per inch, unless otherwise stated. A good grade of white quartz sand was used as an inert material, to which any amount of lime could be added without injuring the growing seedlings. It was used sometimes to improve the physical nature of certain preparations and sometimes to dilute substances which were so toxic as to prevent seed germination.

OVERLIMING TOXICITY VS. NUTRITIONAL DISORDERS

Many observers have reported injury when heavy applications of lime have been made on certain soils (2, 3, 4, 15, 16, 18, 19) but they do not agree as to its cause. One of us (13, 14) has noted such damage to flax and other seedlings which seemed to be too severe to be ascribed to nutrient deficiencies. Indeed, the plants often died before they were much over an inch high. These heavy applications may decrease the availability of phosphorus, iron, manganese, magnesium, and potash, the lack of which, in turn, may induce nutritional disorders and lessen crop yields, as set forth by Pierre and Browning (15). Some who have wrestled with this problem, notably Truninger (18), Bobko et al. (3), Prianischnikow and Goluber (16), Uspenskii (19), Densch (4), and Arnd (2), do not look upon the plant food situation as crucial in this respect. It is not known to the writers whether or not they were dealing with the type of overliming injury now under discussion, but it is quite likely to be the same. Fortunately enough information is now in hand to enable one to distinguish between overliming injuries due to toxicity, such as are found on highly podzolized soils, and those wherein decrease in the availability of the plant nutrients is involved. Indeed, the phrase "overliming toxicity" better describes the condition now under discussion than does "overliming injury." However, since the latter term is in common usage, it seems best to continue to employ it throughout this article.

That the toxic effects caused by overliming very acid Vermont soils, especially those which are highly podzolized, are not due to available plant nutrient decrements has been quite definitely proven. Plant nutrients have been used by one of the writers (13), singly and in combination on overlimed acid soils, without avail in lessening the extent of damage. While these plant food supplies may have been rendered unavailable with excess lime, theoretically they should be at

least as freely available as those applied to heavily limed neutral soils; yet, similar injuries never occurred there.

In order to secure additional information and to show that lack of available nutrients was not at fault, flax seedlings were grown with and without lime on several inert and plant-food-free media, e.g., distilled water, paraffin, agar, washed cotton, washed white sand, graphite, and C. P. calcium carbonate. They grew in all cases in much the same way as did the normal plants and more vigorously than when grown on a toxic overlimed soil, the nutrients and food reserves in the seed itself being sufficient for seedling development to a point beyond the stage at which overliming injury commonly occurred. These results seem to indicate that the type of overliming injury now being discussed is due to toxicity rather than to nutrient deficiency or nutritional malady.

Further evidence tending to differentiate the cause of damage from phosphatic deficiency was provided by the outcome of a trial, using a soil secured through the courtesy of the agronomist of the West Virginia Station. Decreased crop yields following overliming had been noted there, which were thought to be due to a temporary deficiency of available phosphorus. However, when this soil was overlimed here flax grew well, showing no evidences of the characteristic injury, although yields were lowered. This result seemed to distinguish the injury which Pierre and Browning (15) attributed to lack of available phosphorus from the toxic condition encountered when certain Vermont acid soils were overlimed.

Further evidence along the same line was furnished by the results secured with a normal soil which could be limed to an unlimited extent without injury. It was rendered toxic from heavy applications through electro dialysis. The anions containing phosphorus were then supplied but without avail. Furthermore, no gain was secured when an overlimed podzolized soil was leached with soluble iron phosphates during the whole life of the plant, although the leachate was often tested to make certain that a sufficiency of available phosphorus was always present.

Obviously, the injury caused by an excess of lime applied to certain acid Vermont soils is not due to a deficiency of available nutrients and the problem is differentiated from that of the nutritional disorders reported by other investigators.

OVERLIMING INJURY ON PODZOLIZED SOILS

This type of overliming injury occurs naturally, so far as is known, only on podzolized soils. Ordinarily lime applications are calculated for the depth of the furrow slice and the amendment is often applied on the surface without being thoroughly worked into the soil. The surface soil is then overlimed and apt to become very toxic to many seedlings, in fact so much so that the latter may die. On the other hand, small applications appear to exert no injurious effect upon them. Most Vermont soils are more or less podzolized and those most completely so show the greatest injury from heavy applications.

According to Kellogg (8), podzolization may be expected to occur in humid climates most actively under a coniferous forest cover where enough moisture exists to cause the complete leaching of the soluble salts, including the somewhat less soluble calcium and magnesium carbonates. Trees, especially conifers, feed lightly on bases and do not return enough of them to the surface soil in their leaves to keep it from becoming acid. Hence, the soil constituents become saturated with hydrogen; in other words, the medium becomes acid.

TABLE 1.—ANALYSIS OF AIR-DRIED LEAF MATERIALS*
(Analyses in all cases expressed as percentages of oven-dry weights)

Material	Moisture	Ash	Silica (SiO ₂)	Nitrogen	Calcium oxide (CaO)	Magnesium oxide (MgO)	Potassium oxide (K ₂ O)	Phosphorus pentoxide (P ₂ O ₅)
	%	%	%	%	%	%	%	%
White pine needles (<i>Pinus strobus</i>)	5.75	2.80	0.47	0.55	0.89	0.31	0.17	0.13
Grey birch leaves (<i>Betula populifolia</i>)	6.56	4.29	0.43	0.98	1.82	0.60	0.64†	0.36
Sugar maple leaves (<i>Acer saccharum</i>)	6.72	8.34	3.32	0.85	2.40	0.71	0.51	0.24

* McKibbin and Pugsley, (12).

† K₂O in birch leaves, single determination only.

Table 1 shows the relative mineral content of pine, birch, and maple leaves. Only about one-third as much basic material occurs in white pine needles as is found in maple leaves. The obvious inference is that the quantity of bases returned to the surface of the soil by pine needles in comparison to maple leaves is so small that podzolization develops more rapidly on the former.

The decomposition of organic matter produces acids which dissolve and leach out soluble bases, the iron and aluminum precipitating in the B horizon. Indeed, the bases are practically all removed from the soils in the leached horizons.

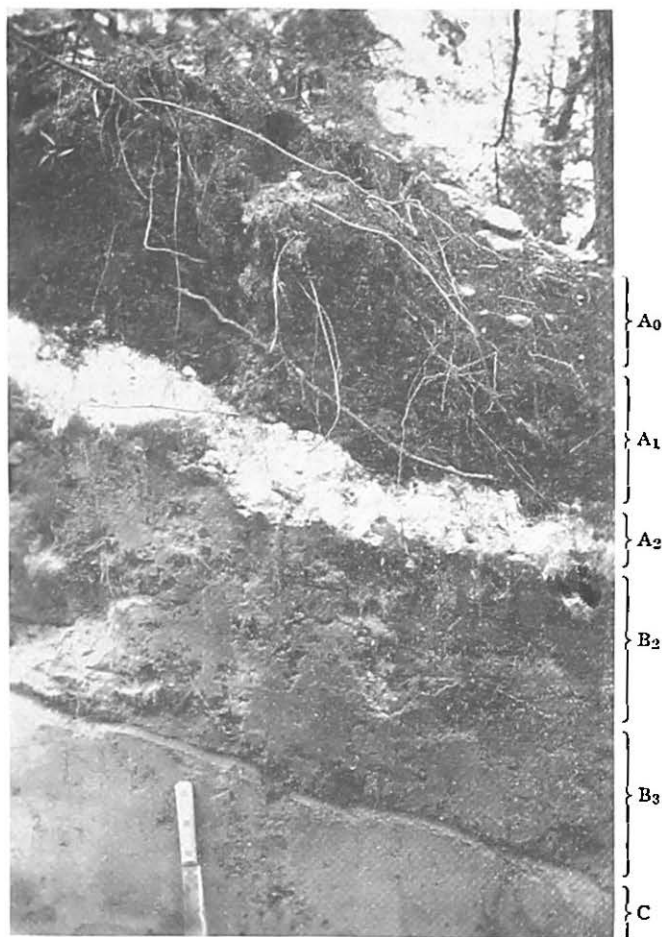


PLATE II.—A well defined podzol profile from Ripton, Vt. Sufficient quantities of each horizon were obtained for liming studies in the greenhouse. The B₁ horizon is not well developed in this picture but a large quantity was found in the immediate vicinity. It is a reddish-black material high in iron humates and often highly cemented (ortstein).

From top downwards: A₀, organic debris; A₁ (H), black raw humus; A₂, grey siliceous layer; B₂, reddish area, high in iron; B₃, yellowish area, high in iron; C, unweathered parent material.

Plate 2 shows a typical podzol profile of a soil used in these studies. A well-developed podzolized soil of the Hermon fine sandy loam type was obtained on Breadloaf Mountain near Middlebury, much care being taken to separate the individual horizons. The forest cover in this region was hemlock, spruce, balsam fir, and yellow birch, with conifers pre-

dominating. The lime requirements of the several horizons were computed and the results reported in tons of calcium carbonate per 2,000,000 pounds of soil. The soil representing each horizon was then overlimed on this basis and flax grown thereon with a view of attempting to determine the nature and extent of injury.

TABLE 2.—OVERLIMING INJURY ON THE HORIZONS OF A HIGHLY PODZOLIZED SOIL
(Calcium carbonate applied at rates of 1 to 12 times the lime requirement)

Horizon used	Lime requirement per 2,000,000 pounds of material (CaCO ₃)	Overliming injury (flax plants used as indicators)
A ₁ (H layer) ..	Tons 65.	With two or more times the lime requirement, severe injury to tops and roots, inducing death.
A ₂	1.6	At or beyond the lime requirement very severe injury to tops and roots, inducing death. Roots were branchless.
B ₁ Black	8.3	No injury—good growth.
B ₂ Red	5.	No injury—good growth.
B ₃ Yellow	3.	No injury—good growth.
C Original ...	1.6	No injury—good growth.

Overliming injury occurred only on the highly leached A horizons of the podzolized soil, none whatever being observed on the heavily limed B and C horizons, notwithstanding the fact that the lime requirements of the B and A₁ (or H) horizons were greater than that of the A₂ horizon. However, the A₁ (or H) soil on a volume basis actually needed only about one-fourth of the 65-ton lime requirement because it contained so much organic matter that the furrow slices of an acre weighed only about 500,000 instead of the customary 2,000,000 pounds.

The injury noted on the flax grown on the A₂ horizon wrought by a comparatively light application of lime, was surprisingly severe, because the soil on this horizon looks so much like sand. The same sort of injury has also been observed on the leached horizons of many other podzolized soils.

MORE DETAILED STUDIES ON THE A₂ HORIZON (ELUVIATED)

More work was done on the A₂ horizon than on the A₁ (or H) layer because the ashy grey layer of a podzol soil has been found to be an excellent test medium. Physically it resembles sand and actually contains much silica. Seeds germinate on it very easily, yet eventually die soon after developing cotyledons if sufficient lime is present. Very small applications are without injurious effect.

pH at which injury occurs. The A₂ horizon was limed at increasing rates in order to determine the point—expressed as pH—at which injury began to appear (table 3).

TABLE 3.—pH STUDIES ON THE A₂ HORIZONS OF A PODZOL SOIL

Rate of liming using C.P. CaCO ₃	pH of the limed soil	Notes on injury, with flax plants as indicators
1/3 lime requirement...	4.7	No injury to roots or tops.
1/2 lime requirement...	5.1	No injury to roots or tops.
2/3 lime requirement...	5.2	8% of seedlings injured.
Full lime requirement..	6.4	All seedlings injured; severe injury to tops and roots.
1 1/3 lime requirement..	6.9	All seedlings injured and dead.

Injury began to appear on the ashy grey A₂ horizon at pH 5.2 and was severe at 6.4. All seedlings exhibited such severe injury at pH 7 that they quickly died. Those grown on the A₁ (or H) horizon also were found to die if enough lime was added to reach pH 7 or neutrality.

The A₂ horizon, in spite of its low lime requirement of 1.6 tons per acre, induced very severe injury and ultimate death when lime was applied in amounts less than enough to bring about neutrality. The extremely sensitive character of this sand-like material is apparent in contrast to sand itself, which may be limed to any degree desired without injury (p. 8). The A₁ (or H) layer seems to be less sensitive, and usually more lime had to be applied to cause a similar injury, perhaps because the lime requirement is not sufficient to bring this highly buffered material to neutrality.

Organic matter. The ignition loss of the soil on this A₂ horizon was 2.5 percent by weight, a figure which checks well with that secured by Lunt (10), who reports from 0.2 to 3.9 percent ignition losses on similar horizons. The organic matter content of this soil is very small by weight but, since its bulk is relatively large, this ignition loss is more significant than would at first appear. The organic matter content of such a soil, as will be shown later, seems to be of vital importance in relation to overliming injury. In comparison, the A₁ (or H) layer seems to be composed largely of organic matter, although no ignition loss was determined.

Mechanical analysis. The ashy grey sand-like layer was fractionated mechanically to determine the location of the injurious substances. Analyses and statements of injury are recorded in table 4.

Nearly one-half of the soil of this horizon passed a 100-mesh sieve. It is unusual for a sand-like material to exhibit so fine a texture. Overliming injury occurred in all cases, being more pronounced on the fine

TABLE 4.—OVERLIMING INJURY ON MECHANICAL FRACTIONS OF THE A₂ HORIZON OF A PODZOL SOIL

Fractions	Mechanical analysis	Percentage and degree of injury from full lime requirement
	%	
Passes 10- stays on 20-mesh	5.	61 slight
Passes 20- stays on 40-mesh	8.	44 slight
Passes 40- stays on 60-mesh	11.3	100 moderate
Passes 60- stays on 80-mesh	15.3	100 moderate
Passes 80- stays on 100-mesh	16.8	100 severe
Passes 100- stays on 150-mesh	12.3	94 severe
Passes 150- stays on 200-mesh	15.4	100 severe
Passes 200-mesh	15.9	100 severe

separates. That any injury whatever should be produced on the coarser fractions is an interesting observation. Obviously the substances causing the toxic effect are distributed through all the mechanical fractions of the soil representing this horizon.

Plant behavior. Many crop plants in the seedling stage other than flax have been grown on the A₂ horizon of an overlimed podzolized soil. Lettuce, tomatoes, mustard, rape, cabbage, sweet, white, and red clovers, alfalfa, and vetch were severely hurt, while soy beans, wheat, oats, and timothy seemed uninjured. Practically all of the damaged seedlings germinated normally but later developed unusual traumatic symptoms. Lettuce died slowly, soon after its first two leaves appeared. The other leaves were red, withered at the edges, and soon ceased to function. The initial two outlived their successors. The first two tomato leaves also survived longer than the newer ones, which died as fast as they appeared. A similar situation obtained with rape, cabbage, red clover, and alfalfa seedlings, all of which died after the first two leaves were developed. The alfalfa seedling roots lacked nodules. The sweet clover seedlings did somewhat better, but growth ceased when the plants were two inches high and the plants were characterized by a reddish tinge. They remained alive for some time. The growth of hairy vetch seedlings was much retarded but they seemed otherwise entirely normal. When less than half the specified lime requirement was applied on podzol A horizons, all these seedlings developed normally and grew well.

The aspects of overliming injury on podzolized soils have been described with special reference to the natural formation and properties of different horizons. A toxic condition from heavy applications of lime has been found when the A horizons have been limed approximately up to neutrality or higher. Such a condition, while highly injurious to many kinds of seedlings like flax, does not seem to harm grasses or soy beans. In practice, where clover is desired, lime sown on acid soils in

Vermont at any one time should be applied in relatively small amounts lest more harm than good result. This is most important on newly cultivated soils still showing traces of the ashy grey horizon.

METHODS OF PRODUCING OVERLIMING INJURY ON OTHER SOILS

Attention has been called to the leaching process by which a podzol soil is formed (pp. 9, 10). The writers have devised several laboratory methods whereby normal soils relatively high in organic matter may be converted into a form very similar to, although perhaps not identical in behavior with, a podzol soil. Such soils, normally unaffected by heavy liming, if made sufficiently acid, become very toxic when excessive applications are made. Flax seedlings grown on soils so treated and heavily limed are injured in apparently the same fashion as when grown on a podzol soil similarly limed.

Leaching with dilute acids. Garden soils, preferably loams, were leached on a filter with dilute hydrochloric, sulphuric, phosphoric, or acetic acid (0.05 normal or somewhat stronger) until the filtrate was calcium free and washed with water until the filtrate gave no test for the anion. A heavy application of lime on such a soil proved fatal to flax seedlings, the injury resembling that produced on podzol soils. This procedure, insofar as its effects are measured by the response of the flax plant, differs profoundly from that which involves the simple addition of an acid to the soil prior to overliming. The plants succumb in the one case but do not exhibit the toxic symptoms in the other.

Overliming injury of the type now under discussion has been produced on many soils, on mucks, peats, garden and field soils, after they have been made sufficiently acid by leaching. North Dakota and Minnesota prairie soils, as well as a West Virginia loam, not naturally injurious in the toxic sense after having been leached with dilute acid, caused severe overliming injury. This procedure seems applicable to any neutral or slightly acid soil which is relatively rich in organic matter, converting it into a form very toxic to seedlings when excessively limed.

Boiling with dilute acids. This procedure was as effective as leaching with dilute acid, provided enough was used and all the soluble acid was removed by washing. Fifty grams of soil, slowly boiled for 30 minutes in an open beaker with 250 cc of 0.5 N HCl were converted into an injurious form. When a material was used which was highly buffered and which contained a large supply of bases, more acid was used and repeated treatments were necessary. Certain mucks and some

of the soil of the Hollis, Woodbridge, Calais, Blandford, Merrimac, Mohawk, Hermon, Pittsfield, and Dutchess series, not naturally toxic on overliming, were thus converted into toxic forms which induced severe overliming injury of the type now under discussion. Since this procedure was rapid and results quickly attained, it was commonly used by the writers.

Boiling with acid salts. The results secured by the use of the salt of a strong acid and a weak base in many respects paralleled those obtained by boiling with a dilute acid. Muck soils which were not toxic with excess lime were converted into a toxic lime-sensitive form by boiling with such salts as the chlorides and sulphates of iron and aluminum, the soils being freed of the soluble anion on a filter before overliming. It was sometimes necessary to boil the soil with one-third of its weight of the salt, wash the soluble anion out, and repeat the treatment to be certain that the desired result had been secured. When susceptible soils were sufficiently treated in this manner, very severe overliming injuries of the type under investigation were induced.

Electrodialysis. This is another method of making soils acid; in fact, Mattson (11) considers that dialyzing a soil according to his directions is equivalent to podzolization. In this process the active bases are removed from the soil and hydrogen takes their place. When the soil is devoid of active bases it becomes very acid.

In order to determine whether or not it was possible to make a normal soil exhibit an injurious condition if made acid in this way and then overlimed, a large storage battery case was cut into three pieces and fitted together to make a suitable cell for electro dialyzing a relatively large quantity of soil. It closely resembled the Mattson cell except for its large central soil compartment. It was connected to a 110-volt direct current with suitable resistance and cooling coils to keep the soil from overheating. A 100-gram sample of sandy loam, known to react to leaching with acid, was electro dialyzed for 10 days. A mechanical stirring device was used in the central compartment to keep the water-soil suspension in motion.

In determining what degree of dialyzing might be necessary before injury could be produced with an excess of lime, samples were removed after various intervals of time, dried, and tested on a small scale with flax plants. The first three samples of dialyzed soil thus tested were not injurious when heavily limed. The fourth sample, having been dialyzed for 10 days, manifested a slight toxic condition. It was thought that greater injury might have been produced had different mem-

branes been used so that iron and aluminum silicate removal might have been facilitated. Hence, the rest of the soil was transferred to a single dialyzing cell, as described by Lea and Midgley (9), and further dialyzed for three days, during which time large quantities of iron and aluminum silicates and other basic materials were removed and readily passed through the filter-paper membrane. When this soil was overlimed, severe injury resulted. Thus a normal soil which previously did not show an injurious condition with excess lime had been converted into an injurious one with heavy applications thereof.

Since the soil was able to exert its injurious effects only after certain bases had been removed, the question arose as to what would happen if the fractions of the several cations obtained by electro dialysis were separately replaced on a comparable quantity of soil which was known to be toxic after heavy applications of lime. This was done. The cations were removed from the cathode chamber every time the soil was sampled or removed from the dialyzer, evaporated to dryness, and added to a comparable quantity of podzolized and injury-inducing soil. The replacement of the cations removed during the first four intervals did not serve to overcome the injury due to excessive liming, but the replacement of those removed from the last fraction was helpful. Those drawn off at first consisted of such strong bases as calcium, magnesium, sodium, and potassium, while the last fraction contained rather large quantities of complex iron and aluminum silicates.¹ It has been previously shown by one of us (13, 14) that such silicates have a beneficial effect in reducing overliming injury, an observation which is now further substantiated.

Another trial was planned to determine whether the removed anions could overcome injury caused by excessive liming. Since the amount removed from a normal soil is very small in comparison to that of the displaceable cation, no attempt was made to abstract them at regular intervals. After dialyzing for 10 days, the contents of the anode were removed, partly evaporated, and added to an equivalent amount of a podzolized soil previous to a heavy application of lime. The anions did not prevent overliming injury. This observation lends added support to the assertion that this type of injury is not due to phosphorus deficiency since the anode contained much soluble phosphorus.

These trials showed that a normal soil could be converted into a form exhibiting overliming injury by electro dialyzing it sufficiently to remove iron and aluminum silicates. When these abstracted silicates were rein-

¹Since silica is an anion it might be expected that it would migrate to the anode chamber along with phosphorus, sulphur, etc.

roduced therein in comparable quantity, previous to heavy application of lime, flax plants were no longer harmed. This emphasizes the marked similarity existing between the production of overliming injury on normal soils and the natural process of podzolization and leads one to conclude that this type of overliming injury is not due to a lack of available phosphates.

Almost any soil relatively high in organic matter may be converted by one or more of the above methods into a form highly injurious to seedlings when heavily limed. Just why soils behave thus is not known, yet there seems to be some fundamental process involved in the several procedures outlined here which is seemingly related to the natural leaching process by which podzol soils become acid. When one or more of these processes was applied to certain soils or soil-like materials devoid of organic matter, no overliming injury was observed. Thus, for example, a very heavy clay subsoil, practically devoid of organic matter, was leached but did no harm to flax after heavy applications of lime. Bentonite and kaolin were similarly treated with similar results. Seemingly, the organic matter content of the soil is in some way related to the toxic effects induced by excessive applications of lime (p. 18).

PREVENTING OVERLIMING INJURY ON SOILS

Injury to plant life occurring on overlimed podzol soils or on those so treated as to behave like an overlimed podzol soil is very difficult to relieve or prevent. The seemingly toxic substances activated by lime are not readily destroyed unless the treatment is extremely drastic. Their chemical effects also have been found to be exceedingly difficult to overcome.

Burning. The ashy grey layer of a podzol soil (A_2 horizon) in its normal condition produces severe injury when overlimed (p. 11). However, when repeatedly burned at white heat to a constant weight, the toxins were destroyed and were permanently harmless. The material then looks and acts like sand and can not be injured with lime. If lower temperatures are used and a constant weight not attained, the residue is not injurious to flax after heavy liming has been resorted to, but it may again become harmful after it has been leached with dilute acids. Apparently some of the toxic substance escapes destruction, although it is inactivated or inhibited in its toxic effect. Perhaps basic substances liberated in burning, which may be comparable to wood ashes, cause this beneficial effect. In this connection it should be said that it has never

been possible to produce overliming injury on susceptible soils with large applications of wood ashes.

Boiling with concentrated sulphuric acid. A sample representing the A₂ horizon of a podzol soil was boiled for an hour with an excess of concentrated sulphuric acid in order to destroy organic matter. Very heavy applications of lime on soils thus treated no longer injured flax seedlings. Similar results were secured with many soils and soil-like materials. Apparently, after its organic matter is destroyed by concentrated acids, a soil heretofore inducing injury ceases to be toxic when overlimed.

Potash fusion. Potash fusion breaks up certain types of organic matter into simple and more soluble compounds (1). Fifty grams of the A₂ horizon of a podzol soil were heated with 150 cc of a very concentrated potassium hydroxide solution until the mass became pasty. Its water content eventually evaporated and the material fused. It was then cooled, acidified with sulphuric acid, and filtered. The insoluble portion was then repeatedly washed with a large volume of water until the filtrate ceased to give a test for sulphates. The residue was then heavily limed and tested by growing flax plants on it. No typical injury was noted, a result which is in contrast to the original behavior of the soil. Evidently this A₂ horizon ceased to be injurious because its organic matter had been filtered out in a soluble form. Silicates are made soluble by alkali fusion and are reprecipitated by acid, but this does not seem so important a factor in the present situation as the destruction of the organic matter by such fusion. These trials indicate that the injuries wrought by this horizon were caused by some organic substance or substances.

Other ways of overcoming the injury are predicated on an attempt to inhibit the effects of the toxic substances rather than to destroy the substances themselves. Thus an injurious acid soil may be leached to approximate neutrality with a neutral salt, such as calcium acetate or chloride, prior to overliming. Its hydrogen ions are replaced by calcium ions and the former unite with the chlorine ions to form hydrochloric acid, which is filtered off. This method in some respects is the reverse of the acid leaching process, by which a soil becomes acid. When a soil which becomes injurious with heavy applications of lime is thus brought to neutrality, in most cases it may be overlimed with impunity. However, the A₂ horizon of a podzol soil seems to be only partially relieved in this manner. The writers have found this horizon very sensitive to overliming injury and less apt to respond to remedial treatments

than other soils. The use of calcium silicate on it has not been followed by normal crop growth, as has been the case with other soils. If large quantities are used overliming injury results, whereas on other soils normalcy obtains even when very large applications are made, although the roots tend to stay near the surface.

Various methods have been employed for overcoming injury from the use of excess lime, i.e., burning to constant weight, boiling with concentrated sulphuric acid, and potash fusion. These seem to bring about destruction of the toxic substances. Other methods, such as leaching with neutral salts, liming with calcium silicate or calcium peroxide, and extremely high rates of superphosphate usage (14), seem to mask or do away with the chemical effect of the injurious substances. Just why and how this blocking effect occurs is not yet understood. Of course, very few, if any, of these findings have practical value, but they are of service in the attempt to determine the underlying reasons why heavy applications of lime to certain acid soils cause toxicity.

OVERLIMING INJURY ON TANNIN MATERIALS

The results secured when burning, potash fusion, and boiling sulphuric acid were resorted to (pp. 17, 18) indicated that the toxic substances were of an organic nature. Furthermore, close examination showed that the flax roots seemed to be most severely injured when in contact with a reddish soil ingredient somewhat resembling hemlock bark in its appearance. This observation led the writers to question the possible causal relation of material of woody origin. Hence, several materials of plant origin, growing on podzolized soils, were secured, ground, and their lime requirements determined. When seedlings were grown in material representing a well-decayed log, too extensively decomposed for identification, the same type of overliming injury was noted as occurred when they were grown on a podzolized soil. When dead hemlock bark was used and overlimed, fewer plants were hurt than had been expected, although some manifested the characteristic symptoms. In view of this outcome, the bark was then leached for about a week with dilute hydrochloric acid, freed of soluble chlorides by prolonged washing, and overlimed as in the case of normal soil. Flax seedlings grown on this acidified and overlimed hemlock bark were as severely injured thereby as if they had been grown on a podzol soil. The tannin content of hemlock bark is high and it is sometimes used in industry as a source of tannin. Hence, several plant materials

were tested, especially those types of native vegetation which contained tannins.

Thorpe (17) and Allen (1) tell us that a surprising number of tree barks and plant materials which enter into soil structure contain tannins, including stems, leaves, roots, and even seeds. They are found in such materials as hemlock, spruce, larch, cinchona, chestnut, horse chestnut, elm, pine, birch, and willow barks, as well as in rhododendron, sumac, and tea leaves, hops, insect galls, and dozens of other plant tissues. Commercial tannic acid is only one of many substances of diverse chemical constitutions and properties which possess the common power of being able to convert hide into leather.

PRODUCING OVERLIMING INJURY ON TANNING MATERIALS

Boiling with dilute acids. Hemlock bark, boiled with a dilute acid and freed of soluble anions, was found to be as injurious as if leached. Many tanning materials were then ground, boiled with dilute hydro-

TABLE 5.—OVERLIMING INJURY ON PLANT MATERIALS BOILED WITH DILUTE HYDROCHLORIC ACID AND WASHED FREE OF SOLUBLE CHLORIDES

Nature of material* used	Injury observed on flax plants†	
	Percent	Degree
Hemlock bark (<i>Tsuga canadensis</i>).....	100	Severe
Spruce bark (<i>Picea</i>).....	100	Severe
White pine bark (<i>Pinus strobus</i>).....	100	Severe
Willow bark (<i>Salix</i>).....	75	Severe
Chestnut bark (<i>Castanea dentata</i>).....	75	Severe
Horse chestnut bark (<i>Aesculus hippocastanum</i>)..	75	Moderate to severe
Alder bark (<i>Alnus incana</i>).....	75	Moderate to severe
Quebracho bark	59	Severe
Lombardy poplar bark (<i>Populus nigra italica</i>)..	75	Severe
Red oak bark (<i>Quercus rubra</i>).....	55	Severe
White oak leaves (<i>Quercus alba</i>).....	53	Moderate
Elm bark (<i>Ulmus americana</i>).....	50	Moderate to severe
White oak bark (<i>Quercus alba</i>).....	50	Moderate
Hemlock needles (not entirely clean).....	50	Moderate
Apple tree bark (<i>Pyrus Malus</i>).....	50	Moderate
Tamarack bark (<i>Larix laricina</i>).....	37	Moderate
Shagbark hickory bark (<i>Carya ovata</i>).....	33	Moderate
Sumac leaves (<i>Rhus</i>).....	20	Slight
Red oak leaves (<i>Quercus rubra</i>).....	12	Slight
Beech leaves (<i>Fagus grandifolia</i>).....	4	Doubtful
Black birch bark (<i>Betula lenta</i>).....	3	Doubtful
Rock maple leaves (<i>Acer saccharum</i>).....	None	
Elm leaves (<i>Ulmus americana</i>).....	None	
Swamp maple bark (<i>Acer rubrum</i>).....	None	
Oat straw	None	
Corn cobs	None	
Sumac bark (<i>Rhus</i>).....	None	

* The leaves used were mature and gathered in the fall. The following trees from which bark was secured grow on podzolized soils: hemlock, spruce, white pine, white oak, and black birch.

† Severe injury indicates that the epicotyl was unable to develop; moderate injury, that it was able to develop slightly before death; slight injury, that it was able to grow an inch or so.

chloric acid, washed absolutely free of all solutes, especially chlorides, and then overlimed. The quantity and strength of acid used and the technique were the same as those used on normal soils (p. 14). The results appear in table 5.

Many plant materials treated with dilute acids produced the typical type of injury after overliming, and all of them contained tannins.¹ This procedure has been most consistently successful in converting ground plant materials into a form injurious with heavy applications of lime.

TABLE 6.—TANNIN-YIELDING MATERIALS
Reproduced from Allen (1)

Tannin	Source	Products on heating with dilute acid	Products of fusion with caustic potash
Digallic acid	Gall nuts	Gallic acid	Pyrogallol and carbonic acid
Sumac tannin	Sumac leaves	Gallic acid	Pyrogallol, carbonic, and glucic acids
Pomegranate tannin	Pomegranate rind	Ellagic acid and glucose	Pyrogallol, carbonic, and glucic acids
Cinchotannic acid	Cinchona bark	China red and glucose	Protocatechuic and acetic acids
Quercitannic acid	Oak bark	Oak red	Protocatechuic acid and phloroglucinol
Ulmotannic acid	Elm bark	Elm red	Protocatechuic acid and phloroglucinol
Salitannic acid	Willow bark	Phlobaphene	Protocatechuic acid and phloroglucinol
Lingué tannin	<i>Larus caustica</i>	Phlobaphene	Protocatechuic acid and phloroglucinol
Hemlock tannin	Hemlock	Hemlock red	Protocatechuic acid and phloroglucinol
Catechu tannic acid	Catechu	Catechin	Protocatechuic acid and phloroglucinol
Chestnut tannin	Horse chestnut	Chestnut red	Protocatechuic acid and phloroglucinol
Quebrachitannic acid	Quebracho	Quebracho red	Protocatechuic acid and phloroglucinol
Alder tannin	Alder bark	Alder red and glucose	Protocatechuic and acetic acids and phloroglucinol
Lupulo tannic acid	Hops	Hop red and glucose	Protocatechuic and acetic acids and phloroglucinol

The plant materials listed were not injurious when only small applications of lime were made, in this respect behaving like potentially toxic soils. Certain leaves, after acid treatment, caused overliming injury. Little information is in hand concerning their tannin content, yet sumac leaves are used as a source of tannin. The leaf extracts which injured the flax seedlings reacted with ferric chloride, thus showing the presence

¹ Compare table 5 with table 6, the latter giving a partial list of tanning materials [Allen (1)].

of tannins and related compounds. Similar reactions were secured with certain soils, indicating that tannins of some sort occur therein. Tannins are likely to be present in many soils, being highly resistant to decay [Eames and MacDaniels (5)]. The writers have been informed of the existence of a pile of hemlock bark from an old saw mill which apparently had remained undecomposed for 90 years. It well may be that tannins remain undecomposed in the soil for many years.

While materials containing tannin may cause some slight overliming injury, they are not extremely harmful until stripped of their basic salts. Methods other than boiling with acids have been successful.

Leaching with dilute acids. Several tanning materials were changed into a form injurious with excess lime by leaching with dilute acid until the filtrate was free of soluble calcium, all soluble acid being subsequently removed by washing. This procedure proved less effective than did boiling. Thus, spruce bark wrought no injury when leached but did serious damage when boiled.

Boiling with water. When hemlock bark was boiled with water for four or five hours, it was converted into a highly injurious form when heavily limed. All soluble materials had to be washed out with water; otherwise, flax seedlings would hardly grow. As yet this method is only known to apply to hemlock bark, probably because it itself is rather acid. Whether the chemical composition of the organic matter is essentially altered by these various processes is not definitely known.

These trials show that the type of overliming injury found on podzol soils can be duplicated on certain tannin-bearing plant materials if they are subjected to a procedure which in many respects is like the process of podzolization. Seemingly a definite relationship has been established between tanning materials and overliming injury.

THE CHEMISTRY OF TANNINS RELATIVE TO OVERLIMING INJURY

When suspicion was cast upon tannins and tannin-containing materials, their chemistry was studied as well as the power of commercial tannic acid and of several related pure compounds to cause overliming injury. Since many of these related tannin materials can not be bought as such and since the structures of some are not known, progress was slow and difficult. Allen (1) defines a tannin as a compound of carbon, hydrogen, and oxygen containing a benzene nucleus and having the power of converting hide into leather. This definition includes many compounds of both natural and synthetic origin. The tannins are usually amorphous or subcrystalline substances of astringent taste, not fusible.

non-volatile, more or less soluble in water, soluble in alcohol or in a mixture of ether and ethyl acetate. Aqueous solutions give blue, black, or green colors or precipitates with ferric chloride. All of them are precipitated by lead acetate, copper acetate, and stannous chloride. Potassium ferricyanide and ammonia produce a red coloration. Some are precipitated by mineral acids. Their most characteristic property is the formation of leather with gelatin or gelatin-forming tissues. Rased hide or skin removes the tannin from solution under proper conditions. The fact that all tannins are powerful reducing agents and tend to absorb oxygen, especially in alkaline solution, seems important as being possibly related to overliming injury on soils. Indeed such injury may be due to this reducing effect, as has been suggested by one of us (14), although that such is the fact has not been proved. They are also stained by methylene blue, one part in 500,000, and by ethylnitrite.

Tannins are usually classed according to their ability to yield either pyrogallol or catechol on dry distillation.

The pyrogallol tannins include those occurring in oak galls, oak and chestnut woods, and sumac. Sumac leaves are only tanning material of this class thus far used by the writers which has induced overliming injury. They are identified by the blue-black coloration with ferric chloride and by lack of precipitate with bromine water.

The catechol tannins include most of the tanning materials whose use has brought about overliming injury. The barks of pine, hemlock, oak, horse chestnut, larch, willow, alder, elm, birch, and quebracho are included in this class. They are differentiated from pyrogallol tannins by the greenish-black color produced with iron alum, although it is sometimes obscured by other coloring matters. A yellow-brown precipitate forms when treated with bromine water until the solution smells strongly. Their most important characteristic, from the standpoint of this study, is that "phlobaphenes"¹ or tannin anhydrides are produced when any tannin-bearing barks are boiled with dilute acid. Their complete precipitation from solution by formaldehyde and hydrochloric acid is another important reaction from the standpoint of this problem [Stiasny test (p. 26)].

TANNIN DERIVATIVES


Several tannin derivatives, including resorcinol, hydroquinone, phloroglucinol, ellagic acid (commercial alizarin yellow), and rufigallic

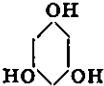
¹ Acid treatments were usually necessary to convert tanning materials into a form toxic with heavy applications of lime and in this respect the process is parallel to that by which phlobaphenes are formed.

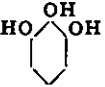
acid, as well as commercial tannic acid, were studied in their relation to overliming. These were obtained in pure form, diluted with sand, and limed in excess to see whether they were able to damage flax plants in a manner similar to that observed when podzol soils were overlimed.

In no instance was the characteristic injury noted, apparently because these substances were so very toxic that flaxseed could not germinate at all, unless the medium was used in a very weak concentration. In some cases it seemed as though they were too soluble and, thus, spent themselves too rapidly in the presence of lime.¹ Perhaps the injury might have been induced had extremely small quantities been continually supplied to the growing plants. This procedure has not as yet been attempted, but is in contemplation. More insoluble tannin-like derivatives from natural and synthetic substances have been sought but with little success as yet.


If one is to understand these materials, one must know certain of the phenols. They resemble each other in that they contain a benzene ring² with (OH) groups substituted in different positions.

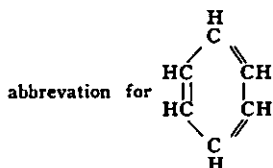
Catechol  is the most important decomposition product of the natural tannin materials which have been found to cause overliming injury. It is somewhat soluble in water and crystallizes from benzene.

Phloroglucinol  is likewise important because it is produced from catechol tannins of such barks as pine, hemlock, and oak by potash fusion. Apple tree bark, not a catechol tannin, is also a source of this phenol. All of these barks have been made to cause overliming injury.


Pyrogallol  is produced from dry distillation and, indirectly, by potash fusion of certain tannins, such as those derived from sumac and oak galls. It is less important in this study because some of the materials from which it is derived have not induced typical overliming


¹These derivatives or phenols are very strong reducing agents in alkaline solution and readily absorb oxygen from the air. When oxidized, their action is spent.

²The organic chemist designates the structural formula of benzene as  which is an

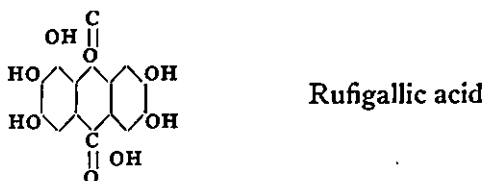
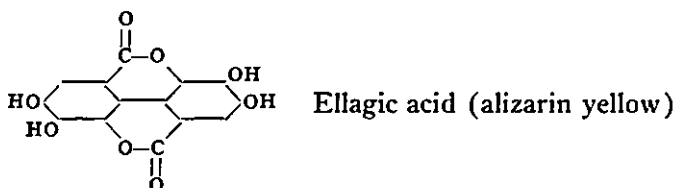
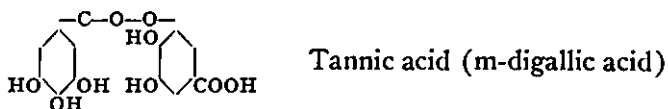


injury. This phenol is very soluble in water and is used in gas analysis to absorb oxygen in alkaline solutions.

Resorcinol  is not a true constituent of tannins but is found in very similar substances (glucosides). This phenol may be derived from a plant source known as gum asafoetida, is soluble in water, and crystallizes from benzene.

Hydroquinone  is another phenol of this type which may be obtained from such indigenous plants as the bear berry and mountain cranberry. It is soluble in hot water but less so in cold water.

These compounds as a class not only respond to some of the usual tests for tannins, e.g., coloring with ferric chloride, but also are structural units in the molecules of tannins, themselves. Some of the structures of compounds already mentioned will serve to illustrate how the phenols are linked into larger molecules.



These formulas merely illustrate one step in the formation of more complex and insoluble tannin-like compounds from phenol units.

In connection with the search for insoluble tannin derivatives which might induce overliming injury, certain reactions of catechol tannins (e.g., hemlock) seem important. The products which command attention in this respect are known as "phlobaphenes" or anhydrides produced by boiling tannins with dilute acids or by any other method which tends to remove water, such as heating to a high temperature, prolonged boiling, or heating under pressure. Not only are these sub-

stances derived from tannins, but they often occur in nature along with the tannins. In fact, Allen (1) says that a whole series of such bodies occurs in hemlock bark along with soluble tannin. They are red substances, insoluble in water, but somewhat soluble in alkalis, alcohol, and alkaline carbonates. When in solution they give all of the tests for catechol tannins and yield the same decomposition products with heat or fusion with alkali as does the parent tannin. Tanners seek to avoid such bodies because they are difficultly soluble, but they do have tanning properties when dissolved.

In order to determine the relation of such bodies to overliming injury, hemlock bark was extracted with alcohol, the extract precipitated with hydrochloric acid and washed free of chlorides. A portion of this was mixed with sand, overlimed, and flax grown upon it. When the precipitate constituted 10 percent by weight of the medium, flax plants were severely injured in the typical manner. Since such large quantities of the material were needed to produce injury, it is quite evident that it was not in a pure form. Further work is needed before one can with certainty state a causal relationship. However, the toxic substances, whatever their nature may be, have been transferred. Their relative insolubility and other characteristics indicate that they represent the type of compound sought. The results secured in further work along this line, as well as with phenolic resins¹ synthetically produced and made to cause typical overliming injury, will be presented in a subsequent bulletin.

SUMMARY

Injury to plant life following heavy applications of lime occurs naturally only on very acid soils. Crops grown on neutral or basic soils similarly treated are not thus injured. Much damage ensues when podzolized soils are heavily limed, especially the severely leached A horizons.

Such crops as flax, rape, cabbage, clovers, alfalfa, lettuce, and tomatoes are injured when certain soils are brought to a neutral or basic reaction. Some soils are much more sensitive to overliming than others and may induce severe toxicity even before they are completely neutralized. This is particularly true of the A₂ horizon of a podzol soil.

Normal soils relatively high in organic matter may be made to produce similar injury if, before liming, they are treated with acid to remove their bases, in a way comparable to the processes of podzoliza-

¹ Phenolic resins form the basis of Stiasny's test (6) for catechol tannins, as they are completely precipitated with formaldehyde and hydrochloric acid forming insoluble red resins.

tion. Leaching or boiling with dilute acids, boiling with acid salts, and electro dialysis may be used for this purpose.

The type of injury thus brought about differs sharply from that wrought by nutritional disorders. The latter are usually evidenced by decreased yields, whereas the former is apt to kill plant growth before it has a chance to exhaust even the small amount of the food reserves in the seed. This is also evidenced by the fact that flax seedlings grow normally beyond the point where overliming injury occurs on many inert and plant-nutrient-free materials, such as distilled water and pure lime, as well as by the fact that they fail to benefit by several methods of providing available nutrients.

Flax is more severely injured than other crops. The plants germinate and grow normally at the start but often are unable to develop an epicotyl and die in the seedling stage.

The toxin is hard to destroy but it is possible to get rid of it by completely removing the organic matter. Burning to constant weight, boiling with concentrated sulphuric acid, and fusion with potash were effective.

Many plant tissues and tree barks, made acid in a manner equivalent to the process of podzolization, caused typical overliming injury when used as media on which to grow flax seedlings. Only tannin-bearing materials produced this trouble, the barks of hemlock, spruce, pine, and other plants normally growing on podzolized soils being especially harmful.

Tannins are divided chemically into two main classes—catechol and pyrogallol—according to the phenol product yielded on destructive distillation. Most of the toxic plant tissues may be relegated to the former class.

Commercial tannic acid and as many pure tannin derivatives as could be secured, all of them relatively soluble, having been overlimed, were used as media. They failed to produce the characteristic symptoms of injury. While they were strongly activated by an alkaline solution, they were too soluble and, paradoxically, too toxic.

Partial success was attained in producing the symptoms of overliming injury when anhydrides of catechol tannins ("phlobaphenes") were produced by boiling a tannin, like hemlock, with acid. The chemical structure of the natural bodies causing overliming injury is not known. They seem to be phenolic resinous substances related to tannins. Further work with them is in progress.

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