3. Ozone

Ozone is a bluish gas, with a sharp, irritating odor. It occurs naturally in the upper atmosphere ("stratosphere"), where it forms continually from reactions promoted by the sun's radiation. Unlike the more common gas oxygen (O_2) , O_3 is highly unstable, reacting with other molecules in the atmosphere, so that its lifetime is only hours or days. The O₃ in the upper atmosphere serves a useful function by filtering out harmful UV radiation. However, pollutants entering the upper atmosphere deplete the O₃, thereby increasing the intensity of UV radiation at the earth's surface.

Ozone also occurs naturally near ground level, where it occurs at concentrations of 25-40 parts per billion by volume (ppbv). Along with other pollutants (e.g., nitrogen oxides, peroxides, peroxyacetyl nitrate, and particulate matter), groundlevel O₃ forms smog. The ill effects of smog on human health are reasonably well known, but its effect on plants has received little publicity. Yet, according to some estimates, O3 causes tens of millions of dollars worth of damage to crops in Canada annually, mainly in the Fraser Valley of British Columbia, the Quebec-Windsor corridor, and the southern Atlantic region.

Thus O_3 is unique among atmospheric gases: in the upper layer, it is highly beneficial; near ground level, it is a serious pollutant. Ironically, human activity has depleted O_3 in the upper atmosphere but increased its concentration at ground level. In this section, we describe the problem of ground-level O_3 ; the problems arising from depleting O_3 in the upper atmosphere we discuss later.

Source of groundlevel ozone

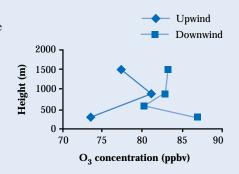
Low concentrations of O3 occur naturally at ground level, formed in the presence of sunlight by reactions between nitrogen oxides and volatile organic compounds (VOCs) (Fig. 25). Natural sources, such as vegetation and soils, release these compounds at low concentration. But human activities have increased the amounts released: VOCs from petroleum, chemical industries, and transportation and nitrogen oxides from combustion in power stations and automobiles. Consequently, O₃ is more concentrated and more smog occurs in densely populated and industrial regions. The health and environmental hazards of smog have prompted federal and provincial governments to impose limits on emissions of nitrogen oxides and VOCs into the atmosphere.



Ozone concentration measurements

Ozone concentrations are measured at only about 100 locations in Canada as part of the air-quality network operated by the Atmospheric Environment Service of Environment Canada. To see how representative these measurements are, scientists used low-level flights to measure ozone concentrations upwind and downwind of the city of Montreal.

The ozone concentrations were found to be greater downwind than upwind of the city



at all altitudes. Consequently, ozone concentrations reported by the network may have to be adjusted depending on the location of the measurement.

(J.I. MacPherson, NRC; R.L. Desjardins, AAFC)

Volatile organic compounds and agriculture

Volatile organic compounds (VOCs) include natural and artificial chemical compounds that contain carbon as a main constituent. Volatile organic compounds and nitrogen oxides combine in the presence of sunlight to form ozone at ground level. In rural areas, the VOCs are largely contributed by vegetation. Crops that emit VOCs include tomatoes, potatoes, soybeans, wheat, lettuce, and rice. Even if artificial VOCs were eliminated completely, ozone would still form from VOCs released from vegetation.

Air-quality objectives

Air-quality objectives are national goals for outdoor air quality that protect human health and the environment. These objectives are developed by a working group for various atmospheric pollutants under the Canadian Environmental Protection Act. The working group reviews the most recent scientific studies.

The current "maximum acceptable" air-quality objective for ozone is 82 ppbv averaged over a 1-hour period. The current ground-level ozone objective was established in 1976, based on the best scientific information. It was reaffirmed in 1989, but a new assessment of the science of ground-level ozone is now nearing completion.

One aspect of the Harmonization Accord, recently signed by the Canadian Council of Ministers of the Environment, identified ground-level ozone as a priority. Work currently under way will develop a Canada-wide standard for ambient ozone levels.

(M. Shepard, Atmospheric Environment Service, Environment Canada)

Major Canadian cities now experience, on several days each year, O_3 levels above the maximum acceptable air-quality level of 82 ppbv for 1 hour. Values of 170 ppbv have been recorded at several locations in Ontario. Stable air conditions during summer and fall especially favor the formation of smog. In light winds, smog can spread over large areas, often affecting regions on both sides of the Canada–US border. Because it requires sunlight to form, O_3 tends to diminish in concentration at night, whereas other smog constituents are unaffected.

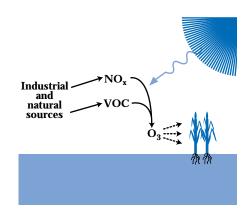


Figure 25

Conceptual diagram showing ground-level O_3 formation. Volatile organic compounds (VOCs), emitted into the atmosphere from vegetation and artificial sources, react with NO_x in the presence of sunlight to form O_3 .

Effect of ozone on plants

Ozone enters plant leaves via stomata, tiny valved pores on the leaf surface that regulate the exchange of gas between plant and air. During the day, the stomata are normally open to permit entry of CO_2 for photosynthesis. Unfortunately, at this time O_3 levels are highest.

Once inside the leaf, O_3 oxidizes molecules in cell membranes, causing the membranes to break down. Because O_3 occurs naturally in the atmosphere, plants have evolved some protective mechanisms, including "antioxidants" like vitamins C and E, and specialized proteins (enzymes) that repair injury from O_3 . But at higher O_3 levels, these protective mechanisms are inadequate to prevent injury to tissues.

Ozone can cause direct damage to leaf tissue, often visible as flecking, bronzing, water-soaked spotting, and premature aging of leaves. Furthermore, high O_3 concentrations may cause the stomata to close, which cuts the flow of

 CO_2 and shuts down photosynthesis. As a result of the direct damage and the reduced photosynthesis, yields of some plants can be dramatically reduced by long-term exposure to elevated O_3 levels.

Although scientists have studied the effects of O_3 on various crops in Canada and elsewhere for more than 40 years, fluctuations in O_3 concentrations in polluted air pose major difficulties in providing reliable estimates of the damage caused to crops.

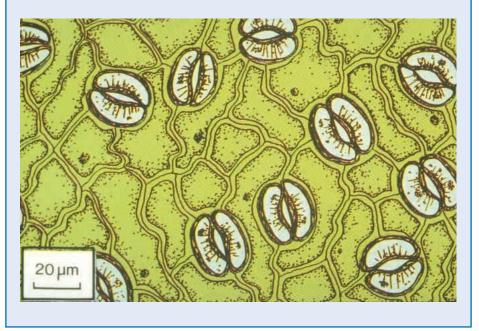
Ozone exposure and absorption by crops

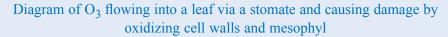
Air pollution monitoring sites across Canada routinely measure ground-level O_3 concentrations. But concentrations alone are insufficient to evaluate potential damage to plants. Plants are less sensitive at night and during periods of slower growth. Temperature and moisture conditions also affect sensitivity. Consequently, we must measure actual O_3 absorption to assess effects on plants.

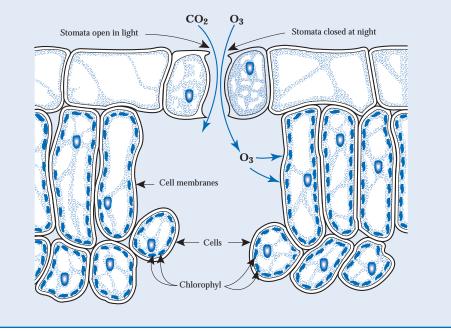
One way of estimating O_3 absorption is to measure the instantaneous O_3 concentration in downward- and upwardmoving air, using sensors mounted on towers. If the concentration is greater in air moving down than in air moving up, that indicates O₃ absorption: the greater the difference, the higher is the absorption rate. This approach allows almost continuous measurement of O₃ flux and provides daily and seasonal patterns of absorption. In one study, for example, the O₃ flux above a soybean field increased during the day but then dropped sharply when the stomata began closing (Fig. 26). Because the opening and closing of

Ozone and leaf stomata

When plants take in CO_2 for photosynthesis through their stomata, ozone can also enter. The ozone causes the cells surrounding the stomata to decrease in turgidity, which reduces the size of the opening. This closing helps to protect the plant from further ozone damage. Once inside the leaf, however, ozone is highly reactive and can destroy the leaf cells, which can substantially reduce crop yield.







stomata is controlled by water stress, there is a strong relationship between O_3 absorption and transpiration (the amount of water lost from the plants).

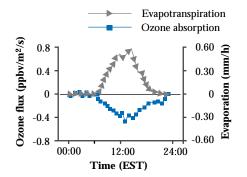
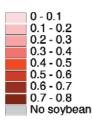


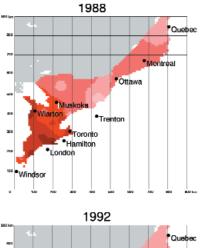
Figure 26

Ozone absorbed and water transpired by soybean on a sunny day in August in Ottawa. (E. Pattey, AAFC)

For larger-scale measurements, instruments can be mounted on aircraft, as described for CO_2 , N_2O , and CH_4 measurements. Aerial O_3 surveys have already been made for many crops, weather conditions, and O_3 concentrations. One observation from this approach is the strong relationship between O_3 absorption and the amount of green vegetation.

The scale can be increased still further by using satellites. Scientists can calculate transpiration from environmental conditions and can obtain a "greenness" index from satellite images. Because of its close relationship to transpiration, O_3 absorption can then be estimated for the entire growing season on large areas, using O_3 concentrations from measurement networks (e.g., Fig. 27).





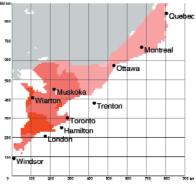


Figure 27

Estimated O₃ absorbed by soybeans in the Windsor–Quebec corridor, 1988 and 1992. (R.L. Desjardins and Y. Guo, AAFC)

This approach, however, only estimates average absorption over the long term and cannot describe the short-term fluctuations associated with daily changes in moisture stress or plant development. Furthermore, it tends to "dilute" relatively brief exposures to high concentrations that are likely to be most harmful to plants. Nevertheless, these estimates provide a useful indicator of potential plant damage.

Measuring plant response to ozone

The simplest way to measure plant response to O_3 is to grow them inside open-top enclosures into which O_3 is then continually released in concentrations that reflect the daily variations. This method allows researchers to evaluate the effect of several concentrations of O_3 (typically up to three times that in outside air) as well as those of other gases or pollutants that can be added simultaneously.

In a less disruptive approach, called the "zonal air pollution system" (ZAPS), a series of pipes over the crop continuously releases O_3 into the plant canopy at various rates in different plots. This method avoids some of the artificial conditions inside chambers but costs more. As well, the maximum enrichment achieved by this technique is not high, because of the continual mixing with untreated air.

Open-topped enclosures and ZAPS are useful for detailed research studies, but they do not provide information on O_3 damage over large areas. Networks of instruments that continuously record O₃ concentrations exist in many populated regions but are sparse in rural areas. To provide O₃ information in such areas, scientists use "biomonitors" or "passive" monitors. Biomonitors are plants, like the tobacco variety "Bel-W3," that are highly sensitive to O₃. They are set out throughout a region and then inspected regularly for flecks of dead-tissue, which are symptoms of injury from O₃. The biomonitors therefore provide an estimate of O₃ absorption by leaves and indicate potential damage to other lesssensitive crops, even though these may show no visual signs of stress. Passive monitors are simply filter papers treated



Open top enclosures, zonal air pollution system, and biomonitors.

with indigo dye. When exposed to O_3 , the dye changes color. The degree of color change provides an index of the total exposure to O_3 during the period.

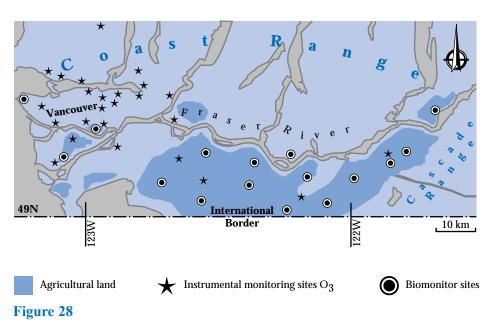
Observations from biomonitors and passive monitors can be related to potential crop effects by placing these monitors inside a ZAPS along with other crop plants. "Flecking" of biomonitor leaves or color change in passive monitors can then be directly related to crop damage. Using these relationships, scientists can use biomonitors and passive monitors placed throughout a region to estimate yield effects of O₃ absorption throughout that area. Researchers have used an extensive network of this type to monitor O_3 effects on yields in the Fraser Valley, a highly populated area with intensive agriculture (Fig. 28).

Examples of crop response to ozone

The effect of O_3 has already been widely studied and some extensive reviews are now available. Here we present only a few examples to illustrate the nature and objectives of some recent research.

Effect of ozone on broccoli

Broccoli is a high-value crop that is harvested about 6–8 weeks after transplanting. Rapid leaf growth after transplanting feeds the developing flower head. Any stress on leaves during this time usually results in smaller heads and lower yield. Studies using a ZAPS showed that ozone injures leaves in two ways: it kills some of the tissue directly (Fig. 29a) and makes other tissue prone to attack by downy mildew, a fungal disease (Fig. 29b). Severity of damage was directly related to O₃ enrichment.



Map of the ozone monitoring network in the Fraser Valley, B.C. (P. Bowen, AAFC)

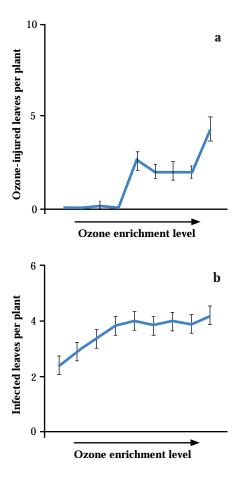


Figure 29

Response of broccoli to O₃: a) O₃ injury to broccoli leaves; b) Leaves infected with downy mildew on broccoli exposed to O₃. (V.C. Runeckles, University of British Columbia, Vancouver, B.C.)



Broccoli is sensitive to O₃

Effect of ozone on orchardgrass

Orchardgrass is the main feed of dairy cows in the Fraser Valley. The grass can be harvested for hay up to five times a year. Loss in yield at any harvest depends on O₃ exposures received during the preceding growing period. One study examined the relationship between level of O₃ and orchardgrass yield in a ZAPS (Fig. 30). The data show how yield decreased as the exposure increased (reported as the number of days during which hourly concentrations exceeded 50 ppbv). Because orchardgrass is a perennial, its early spring growth partly depends upon the reserves stored in the roots and stems during the previous growing season. Studies over successive years have shown that exposing plants to O_3 in the fall suppresses yield the next spring.

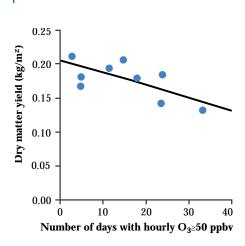


Figure 30

Dry matter yield of orchardgrass as affected by exposure to O₃. (V.C. Runeckles, University of British Columbia)

Effect of ozone on strawberry

Increased exposure of strawberry plants to O_3 reduces the number and weight of good fruit. A network of calibrated passive monitors in the Fraser Valley indicated that fruit losses can be as high as 15%.

Effect of ozone on lettuce

Visual appearance of leaves affects the market value of crops like lettuce. In ozone exposure studies, lettuce leaves showed no visible symptoms. Even at the highest exposure levels, the crop appeared healthy. Surprisingly, however, O_3 reduced head size and weight, indicating that O_3 damage can be subtle and detectable only with careful scrutiny.

Combined effect of ozone and carbon dioxide on alfalfa

Under high O_3 concentrations, alfalfa grows more slowly and competes less against weeds. Like orchardgrass, exposing alfalfa to O_3 in the fall of one year may reduce its yield the year after. Its ability to survive cold winters, however, does not seem to be affected. One study measured the effects of increasing both O_3 and CO_2 concentration on alfalfa growth. Increasing the CO_2 concentration actually increased the tolerance of alfalfa to high concentrations of O_3 (Fig. 31), probably because the stomata are partially closed at high CO_2 levels. This finding may have important implications if, as expected, atmospheric CO_2 concentration doubles some time in the next century.

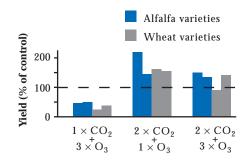


Figure 31

Relative effects of O_3 and CO_2 on yield of alfalfa and wheat. The values in the legend indicate concentration relative to background. (G. Allard, Université Laval)

Differences in ozone tolerance among varieties

Plants show a wide range of tolerance to O_3 in the air, even among varieties of the same crop. Comparing two alfalfa varieties ("Apica" and "Team") in opentopped enclosures for 2 years showed that "Apica" was unaffected by low O_3 levels but was strongly affected by higher concentrations in both years. "Team" was almost unaffected in a cool and rainy summer, but was affected almost as severely as "Apica" in a warm and sunny summer. In a similar study, spring wheat varieties "Bluesky" and "Opal" were exposed to air with no O_3 , and 1.0, 1.5, and 3.0 times the ambient O_3

concentration (Fig. 32). "Opal" appears more tolerant to O_3 . The pattern of tolerance was different for the 2 years tested. This finding suggests not only that varieties have different tolerances to O_3 but also that weather conditions affect those tolerances.

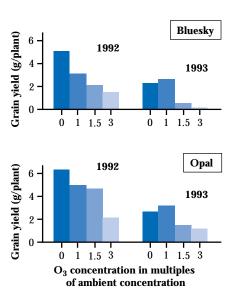


Figure 32

Yield response of two wheat cultivars to increasing concentration of O₃. (G. Allard, Université Laval)

New crop varieties tolerate disease better, are better adapted to local conditions, and generally produce higher yields. Do they also do better under higher O₃ concentrations? One study compared the O₃ tolerance of wheat varieties released at various times, from the 1950s (when O₃ concentrations were generally lower) to the early 1990s. Under current O₃ concentrations, the newer varieties yielded better, but, at higher O₃, they fared worse. One explanation is that newer varieties need more CO₂ to support higher rate of photosynthesis; hence, the stomata stay open longer and absorb more O₃.

Another explanation is that the improved yield of newer varieties results from a higher ratio of grain to leaf tissue. With relatively less leaf area to absorb CO_2 for grain production, leaf injury by O_3 may be more pronounced.

Environmental interactions

Unfortunately, crops are rarely exposed to only one pollutant. Plants growing in high O₃ concentrations may also suffer injury from sulfur dioxide, nitrogen oxides, acid rain, and UV radiation. The net effect of exposing plants to more than one pollutant may be equal to, greater than, or less than the sum of their individual exposures. The effects are further complicated by crop type, time of exposure, weather conditions, previous exposure, and other environmental stresses. Consequently, recent studies have only provided some knowledge about the potential effects of O_3 on a few major crops and regions.