# RECLAMATION OF SOIL STERILANT CONTAMINATED SOILS<sup>1</sup>

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Abstract. The Alberta Gas Transmission Division of NOVA Corporation of Alberta has more than 14,000 km of pipeline rights-of-way to operate and maintain. Above ground facilities associated with the pipeline system include approximately 850 meter stations, 36 compressor stations, numerous valve sites and several office and shop facilities. Total vegetation control at above ground facilities is an attempt to eliminate all vegetation under and within the fenced areas. In the past, total vegetation control was accomplished through the use of "soil sterilants" such as Hyvar-XL and Calmix. With the discovery of migration of soil sterilants outside fenced areas, vegetation control has recently been attempted using non-residual products such as Roundup. Mechanical methods involve using mowers, weed-eaters or hand-picking. Reclamation AGTD are directly related to the use of soil sterilants. Twenty-five above ground facilities have been monitored annually as a result of bromacil contamination. Two research projects were initiated a number of years ago to determine the best methods of bromacil dissipation in the field as well as the best methods of rehabilitating promacil contaminated topsoils in the laboratory and greenhouse. The two methods of bromacil dissipation occurring in the field were leaching and microbial degradation. Recommendations for the rehabilitation and reclamation of soils contaminated by bromacil include the use of activated carbon, manure, wetdry soil cycles, and plant seedlings to enhance adsorption, absorption, and degradation of bromacil.

Additional Key Words: bromacil, weed control, soil degradation, soil pollution.

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437

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# <u>Introduction</u>

In the Province of Alberta, the Electrical Protection Act has regulations governing electrical installation and equipment in the oil and gas industry. As well, the Weed Control Act requires industry to conduct a weed control program to prevent the introduction and spread of noxious and nuisance weeds. These Acts, along with an operating policy of safety and fire and explosion prevention, have resulted in the removal of all potentially combustible material within the fencelines of Alberta Gas Transmission Division (AGTD) facilities of NOVA Corporation of Alberta (NOVA).

Total vegetation control is the suppression or control of all vegetation in order to maintain a vegetation-free or barren area. Within the AGTD, total vegetation control has been used within the fencelines of 36 compressor stations, 850 meter stations, off-line sales stations, yards of maintenance and storage facilities, most valve sites and some rectifiers.

Prior to 1987, the AGTD used nonselective residual herbicides commonly referred to as soil sterilants for total vegetation control at above ground facilities. The two soil sterilants most commonly used were Calmix and Hyvar XL, both having bromacil as the major active ingredient. Soil sterilants were chosen for the total vegetation control program due to the long-term control provided (minimum of two to five years). This resulted in reduced labour requirements for weed control, as one major application was required every two to five years with touch-up applications applied as required. Both products were effective against most plants when correctly used. Due to problems with off-site migration, the AGTD suspended use of soil sterilants in 1987. Since then, total vegetation control has been conducted primarily using the nonselective, non residual herbicide known as Roundup.

#### <u>Bromacil</u>

Bromacil ( $C_9H_{13}BrN_2O_2$ ) is a residual herbicide which is selective, or nonselective, depending on the application rate. It is used at rates of up to 27 kg active ingredient/ha on non-cropland areas for non-selective control of a wide range of grasses and broadleaf weeds, and certain woody species. It is used for selective control at rates of 2 to 7 kg active ingredient/ha for weeds in orange, grapefruit and lemon orchards, and for seedling weeds in pineapple (Beste et al. 1983). Bromacil can be applied by spraying or spreading it dry on the soil surface, preferably just before or during a period of active growth of weeds. Bromacil has a high solubility and stability in water, whereas most other soil sterilants are less soluble and stable (Landsburg and Reinl-Dwyer 1989).

Bromacil may persist at phytotoxic levels for up to six months when applied at "normal" rates of 2 to 5 kg/ha (Gardiner 1975). According to Hassall (1982) bromacil applied at a rate of 1.7 kg/ha can be expected to persist at toxic levels for six months to a year. Phytotoxic levels in Israeli soils have been reported by Angemar et al. (1984) as being less than or equal to 0.1 mg bromacil/kg soil for mineral soils and 0.4 mg/kg for peat soils. Phytotoxicity values in ED50 (the dose that reduces test plants fresh weight by 50%) were found to be 0.4, 0.08, 0.06, and less than 0.01 mg/kg soil for an organic, clay loam, loess and a sandy loam soil, respectively (Angemar et al. 1984).

Bromacil can be applied at either the pre- or post-emergent stage of plant growth. It is most readily absorbed through the plant root system with lesser amounts entering through the foliage and stems. Once in the roots, bromacil is transferred from root to shoot into the chloroplasts of the leaves (Shriver and Bingham 1973).

Bromacil is a powerful and selective inhibitor of photosynthesis (Hilton et al. 1964; Hoffman et al. 1964; Hoffman 1971). It inhibits photosynthesis in vascular plants, algae and blue-green bacteria by blocking a step in the electron transport chain of photosystem II (Scott 1987).

The movement of bromacil in soil seems to be closely related to soil water (Landsburg and Reinl-Dwyer 1989). Increased amounts of water may increase the degree of downward movement (Reed and Holt 1982). Weber (1972) showed that bromacil moved laterally over the soil surface in surface waters and that it leached vertically into the soil profile. Bromacil is also much less subject to adsorption on soil colloids than many other herbicides. The lower adsorption may reflect the high solubility (815 ppm in water at 25 degrees celsius) and leaching characteristics discussed earlier. Increased clay and organic matter concentrations have been found to increase bromacil adsorption in soil (Scott 1987; Hague and Coshow 1971; Angemar et al. 1984).

There are several possible methods of bromacil dissipation including plant uptake, adsorption, microbial degradation and leaching. Volatilization and photodecomposition are thought to be of minor importance (Bingeman et al. 1962; Gardiner 1975).

### Field Reclamation Program

#### Bromacil Monitoring Program

Bromacil has become a problem in reclamation within AGTD due to its use for total vegetation control in Hyvar (spray) and Calmix (pellets) on above ground facilities. The first AGTD bromacil contaminated site was identified in 1983 and more have since been identified as having phytotoxic concentrations of bromacil (0.1 ppm) both on and off-site. Concentrations have ranged from 0.1 to 16 ppm. Bromacil contaminated sites have been identified through various departments within AGTD, by landowners and Alberta Environment.

The AGTD Bromacil Monitoring Program involves the annual monitoring of those sites identified as having phytotoxic concentrations of bromacil as described above. Each year soil samples are taken from the facility pad as well as the affected off-site area. Samples are taken in 10 to 15 cm increments from the soil surface down to a minimum depth of 30 cm, or lower depending upon the concentration of bromacil. The soil sampling design is site specific and depends upon the: mode of contamination: size and shape of the affected area: topography of the area; vegetative growth; and the possibility of additional contamination from a neighbouring facility. Samples are collected and then sent to a laboratory for analyses for total bromacil, pH and electrical conductivity (EC). When results of the analyses are received, the data is interpreted and recommendations are made for handling the site and these are sent to the appropriate land agent. Each site is sampled yearly until there is no longer a problem and/or reclamation attempts have been successful.

There are a number of reclamation options available. The first is to do nothing to the site but pay crop compensation until the problem is gone. The second is to remove the contaminated soil and replace it with uncontaminated soil from elsewhere. Problems with this technique include finding a landfill that will accept bromacil contaminated soil, finding a good quality source of uncontaminated soil, and county by-laws concerning the removal of topsoil.

The third reclamation option and one used most widely within AGTD is to treat the contaminated soil in place. Treatments include: ditching and berming around the facility station pad to prevent further off-site contamination; applying activated charcoal to the affected off-site area to adsorb the bromacil; applying manure and fertilizers to the affected area to promote the adsorption and microbial decomposition of the bromacil; and seeding the site to barley or wheat, letting the crop germinate and take up some bromacil and when the crop dies, removing it and reseeding the area to promote more plant uptake and deactivation of bromacil.

The summer of 1989 should see the completion of the Bromacil Monitoring Program within AGTD. Those sites requiring reclamation will be amended with the suitable materials and plant growth monitored as an indication of reclamation success.

## Facility\_Retirements

In 1988 three meter stations were assessed for retirement or decommissioning. Field investigations included a site description, soil classification and sampling both on and off the meter station. Samples were analyzed for both organic and inorganic components. Follow-up included interpretation of the field data and analytical results. For each of the three sites, a large portion of the retirement plan involved the reclamation of bromacil contaminated soil.

Final recommendations for retirement included: removing the surface 20 cm of the meter station pad due to bromacil contamination followed by the addition of organic matter to the remaining soil to promote residual bromacil degradation; mixing 30 kg of activated charcoal into the surface 30 cm of a 0.2 ha site to promote the adsorption of bromacil; and incorporating 20 kg of activated charcoal into the surface 30cm of a 0.2 ha site to adsorb bromacil before replacing previously removed topsoil.

#### <u>Research Programs</u>

# <u>Dissipation Of Bromacil In Humic Luvic</u> <u>Gleysols In Northwestern Alberta</u>

On August 24, 1983 bromacil in the form of Hyvar XL was sprayed on the Mulligan Creek Meter Station in northwestern Alberta. The following year crops failed to grow on portions of the adjacent farm field. The affected area was in a discontinuous strip parallel to Highway 681 extending approximately 500 m east from the meter station. A preliminary investigation in July 1984 indicated that soil from the affected area was contaminated with bromacil.

In April 1985, two sites were selected within the bromacil contaminated area east of the meter station. Each site was selected to ensure location within the contaminated area. Site 1 was 12 m long and 12 m wide, and Site 2 was 4 m wide and 36 m long. Each was divided up into nine, four by four metre sampling plots or replicates.

In May 1985, approximately 20 cm of well-decomposed cow manure was applied and disced into Site 1 and Site 2. Anhydrous ammonia at a rate of 56 kg/ha and 112 kg/ha of the fertilizer 11-51-0 was also added to both sites. Each subsequent year the sites were fertilized with anhydrous ammonia at a rate of 70 kg/ha and 11-51-0 at 30 kg/ha. The cropping pattern consisted of a wheatalfalfa rotation.

In November 1984, eighteen locations were sampled for background soils information: nine from an area surrounding and including Site 1, and nine from an area surrounding Site 2. Soil samples were collected in August 1985, 1986 and 1987 from each of the eighteen sampling plots, nine from Site 1 and nine from Site 2. At each sampling location a pit was excavated. Soil samples were taken in 4 cm increments from the vertical face of a soil pit from the soil surface down to 40 cm. Each sample was placed in a plastic bag and stored frozen until analyzed.

Inorganic analyses were performed using techniques listed in McKeague (1978) as follows: pH (3.14); electrical conductivity (3.21); particle size analysis (2.12); and total carbon (3.611). Total bromacil determinations were done using a shake/sonicate method developed for this project. For the statistical analyses, Sites 1 and 2 were treated as two separate experiments as preliminary statistical evaluations showed the background soil samples from each site to be significantly different in terms of pH, electrical conductivity (EC), and organic carbon (OC) (Landsburg and Reinel-Dwyer 1989). Significant differences between means at each site were determined using confidence intervals according to the procedure outlined in Snedecor and Cochran (1980) at the 95% confidence level. This procedure was used to determine significant differences between each study year, at each depth, for each parameter monitored.

Through both the addition of cow manure and root turnover, OC contents increased significantly ( $p \le 0.05$ ) at both sites over the three year study (Landsburg and Reinel-Dwyer 1989). The increase from 1984 to 1985 ranged from 0.8 to 3.4 percent in the surface 0 to 12 cm. The percent OC decreased in 1986 from the 1985 level by anywhere from 0 to 2.0 percent in the same depth interval. In 1987, OC levels increased by 0.2 to 3.3 percent in the 0 to 16 cm depth intervals, probably due to the sporadic alfalfa, wheat and weed growth on the sites. Interestingly, the largest increases in 1987 occurred at the 8 to 16 cm depth.

The addition of manure in 1985 resulted in a significant  $(p \le 0.05)$ increase in pH levels from 1984 to 1985 (1.2 to 2.2 units change in the 0 to 12 cm depth and 0.3 to 0.4 units at 12 to 16 cm) (Landsburg and Reinel-Dwyer 1989). In 1986, pH values decreased in the surface 0 to 16 cm by 0.2 to 1.2 pH This was likely due to the impact units. of microbial decomposition of the added organic material. In 1987, pH values increased by 0.2 to 1.3 pH units in the surface 0 to 16 cm. This change was probably due to the re-establishment of the soil equilibrium following large hydronium ion additions from the microbial decomposition activity in 1986. These trends are similar to those reported for organic carbon.

Electrical conductivity values were significantly increased ( $p \le 0.05$ ) from 1984 to 1985 in the 0 to 12 cm layer at Site 1 (range of 0.5 to 2.9 mS/cm increase) and in the 0 to 16 cm depth at site 2 where the increases varied from 1.3 to 6.0 mS/cm (Landsburg and Reinel-Dwyer 1989). The EC values below 20 cm significantly decreased at both sites over this time by anywhere from 0.2 to 2.1 mS/cm. By the time of the 1987 sampling, EC values had significantly decreased in the surface 0 to 12 cm at Site 1 (by 0.1 to 2.1 mS/cm) and in the 0 to 20 cm depth at Site 2 (by 0.2 to 5.5 mS/cm). The 24 cm and lower depth at Site 1 showed significant increases in the range of 0.3 to 0.4 mS/cm while at Site 2 significant increases occurred at all sampling intervals below 20 cm. The range of the increases was between 0.6 to 1.2 mS/cm. These trends in EC levels suggest that leaching of salts is predominant over upward migration through capillary movement of the soil solution. This also suggests that water soluble bromacil was also moving primarily downward.

Since the laboratory technique used in this project analyzed for total bromacil, that amount adsorbed by organic matter was not determined. Only those dissipation methods resulting in complete removal of bromacil from the soil system will be discussed. Plant uptake, photodecomposition and volatilization are assumed to be negligible in terms of the dissipation of bromacil at Sites 1 and 2.

Between 1985 and 1987, bromacil concentrations decreased within the surface 12 cm at Site 1. Below 12 cm, concentrations decreased in 1986 and increased in 1987. These trends for bromacil coincided with those exhibited by the other parameters monitored. The addition of manure to the surface 12 cm of the soil at Site 1 correlated well with the decrease in bromacil within the same depth over time. The decrease and subsequent increase in bromacil below 12 cm can be attributed to leaching. At Site 2 between 1985 and 1987, bromacil concentrations decreased at all depths monitored. Microbial degradation and leaching were probably responsible: microbial degradation within the surface 24 cm where OC percentages were increased by the manure, and leaching below 24 cm.

Conclusions reached as to the dissipation of bromacil in Humic Luvic Gleysols in northwestern Alberta were as follows:

- OC promoted the microbial degradation of bromacil at Sites 1 and 2. Degradation occurred within the same depths as the increased OC percentages.

 Bromacil concentrations decreased within the surface 12 cm at Site 1 and throughout the entire soil profile at Site 2. Site 1 had restricted dissipation to 12 cm due to the presence of a high water table which reduced leaching.

- The two apparent methods of bromacil dissipation in Humic Luvic Gleysols in northwestern Alberta were microbial degradation and leaching.

# Laboratory Degradation Of Bromacil

The rehabilitation of bromacil contaminated topsoil from Chernozemic and Luvisolic soils is being studied in greenhouse and laboratory experiments as part of a Ph.D. research project being conducted at the University of Texas (Scott 1989). The purpose of the study is to determine methods for the rehabilitation of soil contaminated by bromacil.

Topsoil from a Calcareous Eluviated Black Chernozem and an Orthic Gray Luvisol was used for the study. Uncontaminated soils were collected in 1985, packed in separate copolymer plastic containers and shipped to the Controlled Ecosystem Lab at the Brackenridge Field Laboratory of the University of Texas in Austin.

Orthic Gray Luvisols have a well developed eluviated A horizon of 0 to 25 cm; may or may not have an Ah; they have a Bt horizon; and usually have a mean annual soil temperature of <8°C. The Orthic Gray Luvisol study soil was silt loam in texture with a pH (1:1 soil/water) of 5.4 and a cation exchange capacity (CEC) of 24.5 mg/100 gm. Eluviated Black Chernozems have well developed Ah horizons of 15 to 40 cm in thickness with an organic carbon content of 1 to 17 percent. They also have a Bt horizon and a mean annual soil temperature of 0 to 5.5°C. This Eluviated Black Chernozem was clay loam in texture with a pH of 7.5 and a CEC of 44.3 mg/100 gm.

Amendments used for the rehabilitation of the contaminated topsoil included commercially available cow manure, organic fiber, chemically modified peat and activated carbon powder. All experiments were conducted using 98% purity bromacil.

Adsorption experiments showed the Chernozem to have adsorbed more bromacil than the Luvisol. The clay and organic matter content of a soil are generally regarded to be the components which adsorb most of the herbicide (Appleby 1985). The results from the adsorption experiments show this to be the case when comparing the Chernozem and Luvisol. The Chernozem, which had a high clay and high organic matter content compared to the Luvisol, adsorbed more bromacil (Scott 1989).

It is well known that the major method of bromacil degradation in the soil is by microbial organisms (Nemec and Tucker 1983; Pancholy and Lynd 1969). Preliminary Controlled Ecological Life Support System (CELSS) experiments showed that bromacil did not affect respiration, therefore most soil fungi and bacteria were not directly inhibited (Scott 1989) As a result, enhancing the soil microbial community should assist in the adsorption and degradation of bromacil. Enhancing a microbial community could be done by adding amendments required for microbial growth, and providing a suitable environment for growth (i.e. appropriate temperature and moisture). The addition of manure to bromacil contaminated soils in these experiments showed a slight decrease of biologically available bromacil compared to the no amendment contaminated control after a one year incubation period (Scott 1989).

Extensive adsorption experiments showed that powdered activated carbon amended to soils at rates as low as 0.1 g/kg soil doubled the adsorptive capacity for bromacil of the Chernozem and increased the adsorptive capacity of the Luvisol by eight times (Scott 1989). Therefore, the phytotoxicity of bromacil in soils can be reduced by the addition of activated carbon powder. Rates of activated carbon to be added to soil depend on the soil type, specific soil parameters, and the amount of bromacil in the soil.

Scott's (1989) results showed that activated carbon assists in the rehabilitation of bromacil contaminated soils by first adsorbing the bromacil and second, providing conditions conducive to the microbial growth which is responsible for degrading bromacil. Therefore after adding activated carbon as a slurry, the soil should be cultivated and dried to provide proper conditions for bromacil molecules to be adsorbed to the activated carbon. The contaminated area should then be supplemented with manure after the soil dries and then re-cultivated and watered (and possibly fertilized) to provide the proper environment for soil microbial growth.

Adding activated carbon to the soil not only increases the soil's adsorptive capacity, but alters other soil properties as well. The moisture holding capacity and pH are properties affected by carbon (Scott 1989). The soil pH was found to decrease with the addition of activated carbon while the moisture holding capacity increased. Therefore. the levels of activated carbon used for rehabilitation of bromacil contaminated soils should take into account a given soil's field capacity and its soilmoisture dynamics. Information concerning the soil type and texture, as well as site location and habitat, and climatic conditions must be taken into account when determining levels of activated carbon to be used as a rehabilitation amendment.

Results of this research project included recommendations for the rehabilitation and reclamation of soils contaminated by bromacil. These included the use of activated carbon, manure, wetdry soil cycles, and plant seedlings to enhance adsorption, absorption and degradation of bromacil.

#### <u>Summary</u>

The AGTD of NOVA Corporation of Alberta has more than 14,000 km of pipeline rights-of-way to operate and maintain. Above ground facilities associated with the pipeline system include approximately 850 meter stations, 36 compressor stations, numerous valve sites and several office and shop facilities.

Total vegetation control at above ground facilities is an attempt to eliminate all vegetation under and within the fenced areas. In the past, total vegetation control was accomplished through the use of "soil sterilants" such as Hyvar-XL and Calmix. With the discovery of migration of soil sterilants outside fenced areas, vegetation control has recently been attempted using nonresidual products such as Roundup. Mechanical methods involve using mowers, weed-eaters or hand-picking.

Reclamation problems associated with vegetation management in AGTD are directly related to the use of soil sterilants. Twenty-five above ground facilities have been monitored annually as a result of bromacil contamination. These sites will be reclaimed in 1989.

Two research projects were initiated a number of years ago to determine the best methods of bromacil dissipation in the field as well as the best methods of rehabilitating bromacil contaminated topsoils in the laboratory and greenhouse. The two methods of bromacil dissipation found occurring in the field were leaching and microbial degradation. Recommendations for the rehabilitation and reclamation of soils contaminated by bromacil included the use of activated carbon, manure, wet-dry soil cycles, and plant seedlings to enhance adsorption, absorption, and degradation of bromacil. In our experience, plants will grow to maturity on the site when bromacil reaches a concentration of <0.1 ppm, but it is species dependent.

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