

Picloram Herbicide

A Technical Bibliography of Non-Target Effects



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Foreword

The following compilation into one sourcebook of an extensive collection of abstracts on the herbicide picloram is intended to provide users of this herbicide ready access to the breadth and evolution of scientific understanding of this herbicide. Deliberate effects – for example, efficacy were not included – as the sourcebook is intended more to assist in understanding the likelihood and type of non-target effects associated with using this herbicide. A literature search of 15 databases resulted in a total of literally hundreds of references. These were sorted into 13 generalized categories to ease access and allow users of the bibliography to target specific concerns quickly and easily. The bibliography reflects the breadth and depth of understanding picloram from the perspective of refereed journals and without input from the compiler.

The bibliography is designed as an information access tool, not as a stand-alone reference. Users are urged to identify literature of interest using the abstracts in the guide then to seek out the original publication(s) to more clearly understand the results and implications of the research. Abstracts from differing sources often varied slightly in extent and content. The compiler attempted to select the abstract, which provided the most information about both outcomes and methodologies. Where abstracts were not given none was prepared and the title alone was included in the bibliography. The literature search for compiling this bibliography was completed on February 2001. The thirteen categories of references were not used as exclusive sets – where an abstract suggested the article was cogent to several categories the attempt was made to include it in all appropriate categories.

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Table of Contents

Bibliography of References for Non-target Field and Laboratory Reports of Picloram Herbicide

<u>Subject</u>	<u>Page</u>
ANALYTICAL METHODOLOGY	1
AQUATIC INVERTEBRATES.....	23
ARTHROPOD TOXICITY	28
BIODIVERSITY	30
ENVIRONMENTAL FATE - PLANTS	37
ENVIRONMENTAL FATE - SOILS	45
ENVIRONMENTAL FATE - WATER	76
FISH & AMPHIBIANS.....	93
HUMAN TOXICOLOGY	99
MAMMALIAN TOXICOLOGY	106
AVIAN TOXICOLOGY	115
NON-TARGET PLANTS AND RECROPPING.....	118
SOIL MICROBIOTA	131

ANALYTICAL METHODOLOGY

Abramova, K.A., T.D. Panasyuk, and E.A. Kalinina. 1973. Determination of Tordon 22-K in soil and plants by a biological method. *Khimiya v Sel'skom Khozyaistve*. Vol. 11: 298-300. Russian Tordon 22-K picloram-potassium 24.9% was applied at 0.0036-0.0327 mg/kg to a 2:2:1 mixture of peat + soil + sand, in which French beans were sown as bioassay plants, in the glasshouse. The surface area of whole leaves was taken as a quantitative assessment of picloram residues in the soil. The sensitivity of the method was 0.003-0.004 mg/kg. Residues in the soil of 0.1 mg/kg reduced grain yields of wheat by 20% while 0.2 mg/kg almost entirely prevented grain formation. Residues in wheat straw from plants grown in soil containing 0.2-0.4 mg picloram/kg were determined by macerating plant tissues, mixing them in soil and leaving for 1-60 days before sowing French beans as bioassay plants; residues in the straw after 20 days in the soil averaged 5.47 mg/kg for the low application and 12.28 mg/kg for the high application.

Agriculture Canada, Research Station, Kentville. 1976. Research Branch Report 1975, pp. 17-30. P. 25. Picloram residues. The potassium salt of picloram (Tordon 22K) at 4.48 kg/ha (2 p.p.m.) was soil-incorporated to a depth of 15 cm. Analysis of the soil 18, 63, 145, 337, 504, 690 and 843 days later showed the presence of picloram at 1.86, 1.78, 1.32, 0.7, 0.28, 0.12 and 0.02 p.p.m., respectively. Soil containing 1.32 p.p.m. picloram inhibited the growth of carrots, parsnips, potatoes, table beets and rutabagas sown in the glasshouse. One year after the application of picloram, the growth of sweet corn and oats was reduced by about 20% while beans (*Phaseolus* sp.), parsnips and Swiss chard (*Beta vulgaris* var. *cicla*) failed to grow at all. Picloram residues 1055 days after application were 2.5 parts per billion (109) as determined by a bioassay using bean. P. 25. Test for picloram. A rapid, sensitive and specific fluorescence test for picloram was developed. Sulphuric acid 36 N solution was added to the dry residue in quartz tubes or on a white porcelain plate. Under short wavelength UV radiation, yellow fluorescence was observed. The test can also be carried out using glass test tubes and long wavelength UV radiation but this method is not so sensitive.

Agriculture Canada, Research Station, Regina. 1976. Research Branch Report 1975, pp. 265-272. P. 268. Herbicide behaviour in the environment. Results of investigations into the fate of herbicides in the environment are reported. The persistence of atrazine in Brown soils appeared to be related to Ca content and pH of the soil. The order of leachability of 3 uracil herbicides in a range of soil types was bromacil > terbacil > lenacil. Residue levels of 2,4-D of 0.002 and 0.017 $\mu\text{g}/\text{m}^3$ were detected in the air above Regina in June and July. The rate of volatilization of 2,4-D isooctyl ester from Asquith sandy loam soil was high for the first 24 h, after which time volatilization was negligible. The degradation of C-2242 (chlortoluron) in steam-sterilized soil was negligible,

indicating that microbiological processes are important for the breakdown of this herbicide. Residues from spring applications of benazolin, benzoylprop, alachlor, nitrofen, profluralin and picloram were detectable the following October while asulam had disappeared. Benzoylprop-ethyl, alachlor, nitrofen and profluralin were detected only in the top 5 cm of soil whereas residues of benazolin, picloram and the acid derivative of benzoylprop were observed at lower depths. In a study of the persistence of 4 herbicides in irrigation water, simazine was the most persistent, followed by atrazine, monuron and bromacil.

Albanis, T.A. and D.G. Hela. 1995. Multi-residue pesticide analysis in environmental water samples using solid-phase extraction discs and gas chromatography with flame thermionic and mass-selective detection. J. of Chromatography. 707: 283-292. A multi-residue analysis for 25 pesticides was developed as a rapid screening method for organic contaminants in river, lake and sea water samples. Gas chromatography with flame thermionic detection (GC-FTD) and mass selective detection (GC-MSD) using 2 different capillary columns, DB-1 and HP-5, were employed for the identification of 25 selected pesticides belonging to the triazines, organophosphorus compounds and substituted ureas, carbamates, anilides, anilines and amides. The extraction of various natural waters spiked with pesticide mixtures was effected with C18 Empore solid-phase extraction discs and filter-aid glass beads. The triazine compounds (atrazine, simazine, propazine, prometryne and cyanazine) were recovered from distilled and underground water samples at relative high levels (73.5-105%) compared with the river waters (39.9-80.5%), lake water (54.6-81.8%) and marine water (38.6-79.9%). The organophosphorus compounds studied (monocrotophos, terbufos, diazinon, methyl parathion, ethyl parathion, malathion and ethion) were also recovered from distilled and underground water samples at relatively high levels (62.4-118%) compared with river waters (27.3-98.9%), lake water (41.0-85.2%) and marine water (33.4-81.3%). The substituted ureas (monuron, diuron and linuron), substituted anilines and anilides (trifluralin, propanil, propachlor and alachlor), carbamates (EPTC and carbofuran) and other compounds (molinate, picloram, captan and MCPA isooctyl ester) were recovered at the same level as triazines. Confirmation of pesticide identity was performed by using GC-MS in the selected-ion monitoring mode.

Baur, J.R. 1980. Release characteristics of starch xanthide herbicide formulations. Journal of Environmental Quality. 9: 379-382. A laboratory procedure was developed using a cucumber root-length bioassay to measure the relative rate of release of herbicides entrapped in various starch xanthide (SX) matrices. SX herbicide formulations placed in vials containing deionized water were decanted periodically and evaluated by bioassay to examine herbicide released into the water. In leaching experiments, fractions of effluent were collected from glass columns containing SX herbicide formulations applied to a glass-wool pad resting on a sand bed. Collected aqueous fractions were bioassayed. The herbicides examined were salt and ester formulations of

picloram, ester formulations of 2,4-D and salt formulations of dicamba. Comparison of salt and ester starch xanthide formulations of picloram indicated that the ester formulation had a release rate three to five times slower than that of the salt formulation. Differences were noted between starch xanthide formulation of herbicide salts designated as fast and slow releases. From summary.

- Bush, P.B., D.G Neary, J.F. Dowd, D.G. Allison, and W.L. Nutter. 1986. Role of models in environmental impact assessment. Proceedings, Southern Weed Science Society, 39th annual meeting, pp. 502-516.** The agricultural field scale models CREAMS (Chemical Runoff and Erosion from Agricultural Management Systems) and PRZM (Pesticide Root Zone Model) were used to simulate pesticide movement from forested watersheds. Comparison with measured hexazinone loss showed that CREAMS accurately predicted hexazinone concn for storms occurring up to 75 days after application. For storms 75 and 270 days after application, CREAMS underpredicted herbicide concn. The model predicted the following potential residues in stormflow: bromacil>triclopyr>hexazinone>picloram>dicamba. PRZM accurately predicted sub-surface picloram movement using site modified runoff curve number, partition coefficient (K_d) and half-life (K_s). K_d , K_s and water infiltration terms affected pesticide leachability most strongly. Regarding K_d , PRZM predicts leaching from a forested mountain watershed as follows: high leaching for $K_d < 0.1$, potential leaching, given favourable hydrological conditions for $0.1 > K_d > 10$, and no leaching for $K_d > 10$. A half-life > 0.05 years is needed for a compound to leach.
- Butz, S. and H.J. Stan. 1995. Screening of 265 pesticides in water by thin-layer chromatography with automated multiple development. Analytical Chemistry Washington, 67: 620-630.** High-performance thin-layer chromatography with automated multiple development (AMD-HPTLC) was used to screen water samples for pesticides. A universal gradient based on dichloromethane was employed to check for the presence of pesticides from different classes such as phenylureas, carbamates, triazines and others. In total, 283 pesticides were analysed applying this gradient. The data for migration distances, the UV spectra and the instrumental detection limits were compiled. Eighteen pesticides show an instrumental detection limit of > 100 ng applied and can therefore not be analysed from 1 litre drinking water samples with AMD-HPTLC without further treatment. One litre drinking water samples were extracted by means of solid-phase extraction using RP-C18 material or liquid/liquid extraction with dichloromethane and screened with the universal gradient. The confirmation of suspect positive pesticide residues was performed with a second analysis applying special gradients optimized for the individual pesticide classes. Two examples of drinking water-spiked at the 100 ng/litre level are presented to demonstrate the merits of the method. In the first sample, the 2 triazine herbicides cyanazine and atrazine, forming a critical pair with identical reflectance spectra, were separated in a confirmatory run applying a

smoother gradient. In the second sample, acidic herbicides were unsatisfactorily resolved with the universal gradient but were separated with a confirmatory gradient of different composition, allowing easy identification of picloram, acifluorfen, haloxyfop-acid and MCPA.

- Cavalier, T.C., T.L. Lavy, and J.D. Mattice 1989. Assessing Arkansas ground water for pesticides: methodology and findings. Ground Water Monitoring Review. 9: 159-166.** During 1985-1987, 119 wells, springs and municipal drinking water supplies throughout Arkansas were monitored for the presence of acifluorfen, alachlor, aldicarb, atrazine, benomyl, cyanazine, cypermethrin, 2,4-D, dichlorprop, diuron, fenvalerate, fluometuron, hexazinone, linuron, metolachlor, permethrin, picloram and propanil. Not every sample was analyzed for every pesticide. Overall, results indicated that the pesticides were not present in the ground water samples studied. Detectable concentrations of alachlor, atrazine and metolachlor were found in one irrigation well at 5.5, 5.8, and 6.9 µg/litre, resp. However, since previous and subsequent sampling failed to detect these compounds, their presence is attributed to a localized spill or handling error rather than agricultural application.
- Cessna, A.J., R. Grover, L.A. Kerr, and M.L. Aldred. 1985. A multiresidue method for the analysis and verification of several herbicides in water. J. of Agric. and Food Chem. 33: 504-507.** An analytical method for determining and verifying residues of both neutral and acidic herbicides in water is presented. Acidic herbicides were derivatized by using diazomethane. Recoveries of MCPA, bromoxynil, 2,4-D, dicamba, picloram, tri-allate and trifluralin from distilled water at fortification levels of 0.1-1 ng/l ranged from 80 to 117%. Except for MCPA, all herbicide residues could be verified by using 2 different detector modes. The method was used successfully in a preliminary study to monitor herbicide residues in irrigation return flow waters.
- Cotterill, E.G. 1982. Determination of acid and hydroxybenzonitrile herbicide residues in soil by gas - liquid chromatography after ion-pair alkylation. Analyst. 107: 1270, 76-81.** The herbicides are extracted from soil with saturated calcium hydroxide solution. After clean-up the residues are ethylated using iodoethane and tetrabutylammonium hydrogen sulphate as counter ion. Liquid - liquid partition and the use of a macroreticular resin column were compared as clean-up steps and the reaction conditions for optimum yield of ethyl ester or ether were evaluated. Recoveries in excess of 80% were achieved for 2,4-D, dicamba, 3,6-dichloropicolinic acid, dichlorprop, picloram, 2,4,5-T, fenoprop, 2,3,6-TBA, bromoxynil and ioxynil.
- Crescenzi C., G. D'Ascenzo, A. di Corcia, M. Nazzari, S. Marchese, R. Samperi, and A. di Corcia. 1999. Multiresidue herbicide analysis in soil: subcritical water extraction with an on-line sorbent trap. Analytical Chemistry Washington 71: 2157-2163.** The feasibility was evaluated of selectively and rapidly extracting herbicide residues in soils by hot water and collecting analytes with a Carbograph 4 solid-phase extraction (SPE) cartridge

set on-line with the extraction cell. Phenoxy acid herbicides and those non-acidic and acidic herbicides which are often used in combination with phenoxy acids were selected for this study. Five different soil samples were fortified with target compounds at levels of 100 and 10 ng/g (30 ng/g of clopyralid and picloram) by following a procedure able to mimic weathered soils. Herbicides were extracted with water at 90°C and collected on-line by the SPE cartridge. After the cartridge was disconnected from the extraction apparatus, analytes were recovered by stepwise elution to separate non-acidic herbicides from acidic ones. The two final extracts were analysed by liquid chromatography/mass spectrometry with an electrospray ion source. At the lowest spike level considered, analyte recoveries ranged between 81 and 93%, except those for 2,4-DB and MCPB, which were 63%. For 16 herbicides out of 18, the ANOVA test showed recoveries were not dependent on the type of soil. The method detection limit was in the 1.7-10 ng/g range. For the analytes considered, method comparison showed this extraction method was overall more efficient than Soxhlet and sonication extraction techniques.

Deschamps, R. J. 1991. Development and evaluation of immunoassays for picloram detection in environmental samples. University of Guelph, 155 pp. The objective of the research project was to develop and evaluate immunochemical methods for the determination of picloram (4-amino-3,5,6-trichloro-2-pyridinecarboxylic acid) in environmental samples. A common immunogen was used to develop polyclonal and monoclonal anti-picloram antibodies. Polyclonal antiserum was obtained from New Zealand White rabbits while monoclonal antibodies were obtained from a mouse hybridoma cell line. The monoclonal antibody was superior in quality in terms of sensitivity. Neither the polyclonal antiserum nor the monoclonal antibody showed appreciable cross reactivity to any other pyridine herbicide. Several assay formats including radioimmunoassay (RIA), indirect enzyme immunoassay (iEIA), and direct enzyme immunoassay (dEIA) were investigated. A polyclonal antibody-based RIA employing a novel radiolabel consisting of ^3H glycine covalently linked to picloram was developed with a working range from 50 to 5000 ng/mL and an I_{50} value of 760 ng/mL. Both polyclonal antibody-based enzyme immunoassays had working ranges from 5 to 5000 ng/mL and an I_{50} values of 140 ng/mL and 180 ng/mL for the iEIA and the dEIA, respectively. Both monoclonal antibody-based enzyme immunoassays had working ranges from 1 to 200 ng/mL and I_{50} values of 10 and 18 ng/mL for the iEIA and the dEIA, respectively. In general, monoclonal antibody-based assays for picloram were more sensitive than polyclonal antibody based assays. The monoclonal antibody-based iEIA most accurately and precisely determined picloram concentrations in fortified samples. Picloram determinations by all assays were most accurate and precise when a reference matrix identical to the sample matrix was available. Authentic soil and vegetation samples were analyzed for picloram residues by the monoclonal antibody-based iEIA and results were compared to an independently conducted GC analysis. Coefficient of

determination r^2 values from regression analysis correlating immunoassay results to GC results ranged from 0.778 to 0.891. Picloram levels determined by immunoassay overestimated or underestimated levels determined by GC depending upon the efficiency of the soil extraction method. The immunoassay methods were also effective as a primary screen whereby samples were identified as either negative or positive for picloram residues with reference to a specific threshold concentration.

Deschamps, R.J.A and J.C. Hall. 1991. Validation of a monoclonal antibody-based indirect enzyme immunoassay method for picloram detection in soil and plants. Food and Agricultural Immunology 3: 3-4, 127-134. When picloram residues in authentic soil and plant samples were determined by indirect enzyme immunoassay (EIA) and by GC, the values obtained were shown to correlate well, with coeff. of determination ranging from 0.788 to 0.891. Picloram levels determined by EIA in soil extracts obtained by a potassium hydroxide extraction method (EIA-1) underestimated picloram levels determined by GC. Conversely, EIA determinations of soil extracts obtained by a more rigorous acetonitrile extraction method (EIA-2) yielded picloram levels that overestimated levels determined by GC. First order linear regression models using EIA determinations as the independent variables resulted in dependent variable coeff. of 0.325 and 1.42 for EIA-1 and EIA-2, resp. Picloram levels determined in plant extracts were approx. equivalent by EIA and GC methods. Using a point on the standard curve representing 5 ng/ml picloram as a threshold value, the EIA method effectively identified samples as either positive or negative for picloram residues based on the results obtained by GC analysis.

Deschamps, R.J.A. and J.C. Hall. 1990. Polyclonal and monoclonal immunoassays for picloram detection. ACS Symposium Series 442:66-78. A radioimmunoassay (RIA) and two indirect enzyme immunoassays for picloram were developed for the detection of the herbicide in river water, urine, as well as soil and plant extracts. The RIA method incorporated a rabbit anti-picloram serum as well as a novel radiolabel consisting of [^3H]glycine covalently linked to picloram. Using the RIA procedure, picloram concentrations in the range of 50 to 5000 ng/ml could be detected in fortified river water and urine when a standard curve was prepared in the respective matrix. The I_{50} value for picloram by the RIA method was 760 ng/ml. The two indirect enzyme assays were compared in terms of sensitivity, accuracy and precision for detection of picloram in various fortified matrices using standard curves prepared in buffer. The assay using the same rabbit anti-picloram serum employed in the RIA method had a linear working range from 5 to 5000 ng/ml with an I_{50} value of 88 ng/ml and a lower detection limit of 5 ng/ml. The assay using a monoclonal antibody obtained from a mouse hybridoma cell line yielded a linear working range of 1 to 200 ng/ml with an I_{50} value of 10 ng/ml and a lower detection limit of 1 ng/ml. From the analysis of fortified river water, soil extracts, plant extracts and urine, the monoclonal antibody-based enzyme immunoassay was

shown to be more sensitive, more accurate, and more precise than the polyclonal antiserum-based enzyme immunoassay.

Deschamps, R.J.A., J.C. Hall, and M.R. McDermott. 1990. Polyclonal and monoclonal enzyme immunoassays for picloram detection in water, soil, plants, and urine. J. of Agric. and Food Chem. 38: 1881-1886. Two indirect enzyme immunoassays for picloram detection were compared in terms of sensitivity, accuracy and precision. The assay using a rabbit anti-picloram serum had a linear working range of 5-5000 ng/ml with a mean I_{50} value of 140 ng/ml and a lower detection limit of 5 ng/ml. The assay using a monoclonal antibody obtained from a mouse hybridoma cell line yielded a linear working range of 1-200 ng/ml with a mean I_{50} value of 10 ng/ml and a lower detection limit of 1 ng/ml. Neither assay showed appreciable cross-reactivity with the structurally related pyridine herbicides clopyralid, fluroxypyr and triclopyr or with the phenoxy-acetic acid herbicide 2,4-D. From the analysis of fortified river water, soil extracts, plant extracts and urine, the monoclonal antibody based assay was shown to be sensitive, more accurate, and more precise than the polyclonal antiserum based assay. Only the monoclonal assay was suitable for quantitative determinations of picloram.

Draper, W.M. 1982 A multiresidue procedure for the determination and confirmation of acid herbicide residues in human urine. J. of Agric. and Food Chem. 30: 227-231. 2,4-D, 2,4,5-T, dichlorprop, 2,4-DB, fenoprop, dicamba, propyzamide, picloram, and PCP were determined simultaneously in human urine. Samples were hydrolyzed with mineral acid to liberate conjugated residues and to convert propyzamide metabolites to 3,5-dichlorobenzoic acid. Acids were isolated from the urine hydrolysate by acid/base partitioning and derivatized with ethereal diazomethane. The herbicides were determined quantitatively by electron capture gas chromatography (EC-GC), and structures were confirmed by computer-controlled gas chromatography-mass spectrometry (GC-MS). Recoveries were 80-104% for fortifications at 0.1 mg/litre and detection limits for the herbicides in urine were 0.05-0.1 mg/litre by EC-GC and 0.1-0.5 mg/litre by GC-MS. Derivatization with pentafluorobenzyl bromide was unacceptable for several reasons: it enhanced the electron capture response of urinary acids and the specific detection of the PFB analogues by mass spectrometry was limited by the similarity of their electron impact mass spectra. From summary.

Dumas, E., J.C. Vallee, C. Martin, G. Vansuyt, and R. Vernoy. 1977. Extraction, purification and characterization of picloram, dicamba or TBA residues from straws or earthy mixtures. (Extraction, purification et caracterisation de residus de piclorame, dicamba ou TBA a partir de pailles ou de melanges terreux). Weed Research 17: 173-179. LA: French LS: English, German The paper deals primarily with the establishment of a method for investigating picloram residues in straws by themselves or mixed with soil, combining bioassays with simple and conventional biochemical techniques. This method is reasonably reliable and precise with respect to picloram; it can,

moreover, establish whether soil mixtures or straws contain other herbicides of the phytohormonal type.

Ebbersten, S. 1972. Picloram (4-amino-3,5,6-trichloropicolinic acid). Studies concerning persistence in soil and plants and biological methods for determining picloram residues. [Pikloram (4-amino-3,5,6-trikloropikolinsyra). Studier av persistens i jord och växter samt metodstudier rörande biologisk bestämning av pikloramrester]. Uppsala, Institutionen för Vaxtödling, Lantbrukshögskolan 175 pp.

Swedish English This publication is divided into 2 main sections: 1. A literature survey including sections on (a) the effects of picloram on higher plants, soil micro-organisms and higher animals (mammals, birds and fish), (b) the persistence of picloram in plant tissue, soil and water and (c) methods for determining picloram residues. 2. Results of investigations carried out in Sweden during 1966-70 to study persistence and movement in the soil, determination of residues and the effects on following crops of wheat and potatoes.

Edgell, K.W., E.J. Elizabeth, R.J. Wesselman, and J.E. Longbottom. 1993. Gas chromatographic/electron capture detection method for determination of chlorinated acids in water: Collaborative study. J. of AOAC International 76: 1098-1112. A U.S. Environmental Protection Agency (USEPA) interlaboratory method validation study was conducted on USEPA Method 515.1, "Determination of Chlorinated Acids in Water by Gas Chromatography with an Electron Capture Detector." This method is one of the 6 pesticide methods developed for the USEPA National Pesticide Survey (NPS). Method recovery and precision for analyses of sub-ppb to low-ppb concentrations of chlorinated acids were determined in reagent water and -finished drinking waters. The analytes evaluated in the study included the 12 pesticides that were quantitatively measured in the National Pesticide Survey (bentazon, 2,4-D, 2,4-DB, 3,5-dichlorobenzoic acid, DCPA-diacid, dicamba, dichlorprop, 5-hydroxydicamba, pentachlorophenol, picloram, 2,4,5-T, and 2,4,5-TP) and 5 pesticides (acifluorfen, chloramben, dalapon, dinoseb, and 4-nitrophenol) that were only qualitatively assessed in the National Pesticide Survey because of recognized method imprecision. The study design was based on Youden's nonreplicate plan for collaborative tests of analytical methods. The waters were spiked with 17 chlorinated acids, each at 6 concentration levels, prepared as 3 Youden pairs. Eight laboratories extracted the spiked test waters at pH 1.2 with ethyl ether, performed a solvent exchange with methyl tert-butyl ether, prepared methyl esters of the extracted acids using diazomethane, and analyzed an aliquot of each derivatized extract by gas chromatography with electron capture detection. The submitted data were analyzed using a USEPA computer program, which measured recovery and precision for each of the 17 compounds and compared the performance of the method between water types. Method 515.1 was judged acceptable for the 12 NPS analytes recovered quantitatively; mean percent recoveries at 10-15 times the method detection limits ranged

from 79 to 105% in reagent water and from 75 to 123% in finished drinking water. In reagent water, overall precision (reproducibility relative standard deviation, RSD-R) ranged from 9.6 to 34.2% and in finished drinking water, the RSD-R ranged from 11.9 to 37.0%. Single-analyst precision (RSD for repeatability, RSD-r) ranged from 5.8 to 17.7% in reagent water and from 4.6 to 27.9% in drinking water. Results for the 5 other NPS analytes were too inaccurate or imprecise and, for these compounds, supported use of the method for qualitative measurements only; the 5 compounds are not included in the adopted method. The method has been adopted first action by AOAC INTERNATIONAL for determination of residues of 12 chlorinated acids in finished drinking water.

Garten, C.T. Jr. and J.R. Trabalka. 1983. Evaluation of models for predicting terrestrial food chain behavior of xenobiotics. *Environmental Science and Technology* 17: 10, 590-595. Results from an extensive literature review were used to evaluate the capabilities of existing simple empirical bioaccumulation models proposed for terrestrial vertebrates and fish. Generic application of such models appeared to be unsuitable; bioaccumulation in mammals and birds was very weakly correlated or uncorrelated with xenobiotic (exotic organic chemicals) bioaccumulation factors from fish tests (r^2 values were 0.09-0.43). The problem of wrongly classifying a compound, on the basis of physicochemical data, as not having a high bioaccumulation potential (e.g. methyl mercuric chloride) is discussed. Nontoxic substances were also given high bioaccumulation potentials by the screening model. Av. log-transformed bioaccumulation factors for xenobiotics such as buthidazole, dicamba, fenoprop, picloram, 2,4-D and other herbicides are tabulated for 6 mammal groups, fish, poultry and small birds. Other types of pesticide are also included in the data.

Haag, W.R. and C.C.D. Yao. 1992. Rate constants for reaction of hydroxyl radicals with several drinking water contaminants. *Environ. Sci. and Technol.* 26: 1005-1013. Rate constants for reactions of the hydroxyl (OH-) radical with 25 potential organic drinking water contaminants, including solvents, haloalkanes, esters, aromatics and pesticides (e.g. aldicarb, atrazine, 1,2-dibromo-3-chloropropane, endrin, glyphosate, haloforms, lindane and picloram), have been measured in water using relative rate methods. A variety of OH-radical generating techniques were used, including ozone decomposition, Fenton's reaction and a convenient new method employing photo-Fenton's chemistry. In addition, rate constants for 19 other compounds were estimated using structure-activity relationships. The present results were consistent with previous work that demonstrated that the OH-radical is relatively non-selective toward C-H bonds, but is least reactive with aliphatic polyhalogenated compounds. Olefins and aromatics all reacted at nearly diffusion-controlled rates in water, unlike in the gas phase where these compounds reacted more selectively. The rate constants were useful in estimating OH-radical induced oxidation rates of organic compounds in a

variety of aqueous systems including atmospheric water droplets, sunlit surface waters, supercritical and near-critical water reactors and room temp. radical oxidation processes.

Hall, J.C, R.J.A. Deschamps, K.K. Krieg. 1989. Immunoassays for the detection of 2,4-D and picloram in river water and urine. J. Agric. Food Chem. 37: 981-984.

Hall, R.C., C.S. Giam, and M.G. Merkle. 1970. A New Technique for the Determination of Picloram and Other Herbicides Containing Carboxylic Acid and Ester Groups. Analytical Chemistry 42: 423-425. The paper describes a technique for the determination of picloram and other herbicides containing carboxylic acid and ester groups. Previous methods relying on gas chromatography required that acids be esterified before chromatography. In the case of picloram, esterification in soil, water or forage samples has several disadvantages including a lack of usable sensitivity due to interference peaks. The new technique involves an on-column decarboxylation employing either ether saturated with water, anhydrous ether or benzene. Decarboxylation efficiency was found to depend on contact material, solvent, decarboxylation temperature and the presence of catalysts. The decarboxylated product is determined by electron-capture gas chromatography. Under ideal conditions, picloram can be decarboxylated to the extent of 95 +/- 2% and it can be detected in water and soil with efficiencies of 93 +/- 4% and 90 +/- 5% respectively. As a check on the procedure, samples should be compared with standards for it is quite easy to deviate from ideal decarboxylation conditions. Preliminary work indicates this technique could be used for the analysis of other herbicides (e.g., the benzoic acid herbicides). Because, as opposed to the boron trifluoride method, the lower limit of detection is not hindered by the presence of impurities, this technique is superior to the available methods for trace analysis of picloram residues.

Huston, P.L. and J.J. Pignatello. 1999. Degradation of selected pesticide active ingredients and commercial formulations in water by the photo-assisted Fenton reaction. Water Research 33: 1238-1246. The destruction of pesticide active ingredients (AI) and commercial formulations in acidic aqueous solution with the catalytic photo-Fenton, Fe(III)/H₂O₂/UV, advanced oxidation process has been studied. The AI are alachlor, aldicarb, atrazine, azinphos-methyl, captan, carbofuran, dicamba, disulfoton, glyphosate, malathion, methoxychlor, metolachlor, picloram and simazine. Complete loss of pure AI occurred in most cases in <30 min under the following conditions: 5.0 X 10⁻⁵ M Fe(III), 1.0 X 10⁻² M H₂O₂, T = 25.0°C, pH 2.8 and 1.2 X 10¹⁹ quanta l⁻¹ s⁻¹ with fluorescent blacklight UV irradiation (300-400 nm). Considerable mineralization over 120 min occurred in most cases as evidenced by the appearance of inorganic ions and the decline in total organic carbon (TOC) of the solution. Intermediate products such as formate, acetate and oxalate appeared in early stages of degradation in some cases. Observed rate constants calculated from initial rates varied by a factor of <3. The commercial

products. Furadan (AI, carbofuran), Lasso 4EC (AI, alachlor) and Lasso Microtech (AI, alachlor) were also tested. The "inert ingredients" (adjuvants) present in these products had no effect (Furadan), a slight effect (Lasso 4EC), or a strong effect (Lasso Microtech) on the rate of degradation of the AI. Lasso Microtech, in which the AI is micro-encapsulated in a polymeric shell wall microsphere, required slightly elevated temperatures to effect removal of alachlor in a timely manner. The results show that many pesticides and their commercial formulations in dilute aqueous solution are amenable to photo-Fenton treatment.

Jotcham, J.R., D.W. Smith, and G.R. Stephenson. 1989. Comparative persistence and mobility of pyridine and phenoxy herbicides in soil.

Weed.Technology 3: 155-161. Bioassays with soyabeans and lentils were used to compare the persistence of 2,4,5-T, triclopyr and picloram in soil after applying 0.038, 0.38 and 3.8 kg/ha under field conditions. Soil samples were collected 1-269 days after spraying and were kept frozen until growth room bioassays were conducted. Triclopyr was slightly less persistent than 2,4,5-T, but neither herbicide was biologically active during the next season. At least 90% of picloram disappeared within 7 months, but its biological activity was more persistent than that of either triclopyr or 2,4,5-T. Nine months after treatment, neither lentils nor soyabeans could be grown in soil treated with picloram at 3.8 kg/ha. Triclopyr and 2,4-D had similar soil TLC mobilities in 4 different soils. Picloram was significantly more mobile than either triclopyr or 2,4,5-T, primarily due to its lower adsorption in the soils examined.

Kiryukhina, N.I. 1982. Determination of Tordon residues. Zashchita Rastenii 10: 59. Russian Methods of extraction and determination of the residues of Tordon [picloram] in green and dry plants of maize are described.

Kiryukhina, N.N. 1982. Determination of Tordon residues in cereal grains.

Khimiya v Sel'skom Khozyaistve 20: 55-56. Russian The suggested method of determining Tordon [picloram] residues in cereal grains is based on the extraction of the herbicide with acetone, followed by incorporation of fatty acids from the extract into hard ammonium soaps and determination of the herbicide with thinlayer chromatography or luminescence.

Krzyszowska, A.J. and G.F. Vance. 1994. Solid-phase extraction of dicamba and picloram from water and soil samples for HPLC analysis. Journal of Agricultural and Food Chemistry 42: 1693-1696. Methods are presented for the analysis of dicamba and picloram in water and soil samples. The methods utilize solid-phase extraction (SPE) and HPLC. For separation and concentration of the herbicides, 2 types of SPE cartridges were used - aminopropyl (NH₂) weak anion exchange adsorbent for dicamba and octadecyl (C18) strong polar adsorbent for picloram. Detection limits for the HPLC analysis of dicamba were 1 ppb for water and 10 ppb for soil samples. Recovery experiments for dicamba indicated 90-99% recovery for the concn range 10-60 ppb in water samples and 836% recovery of dicamba added at 10

ppb to soil samples. Detection limits for picloram were 8 ppb for water and 10 ppb for soil samples. Recovery of picloram from water samples was between 85 and 96% for the 10-60 ppb concn range and 886% recovery of picloram added at 10 ppb to soil samples. The recovery of standard solutions by different brand name SPE cartridges was also tested. Differences in the efficiencies of various SPE cartridges were determined, not only among manufacturers but also between lots. It is suggested that one brand name of SPE cartridge, all of the same lot number, be used throughout a particular study and that no changes in manufacturers and lots be made without adequate evaluation of the SPE cartridge for their ability to separate and concentrate the pesticide of interest.

Krzyszowska-Waitkus, A.J., R.D. Allen, G.F. Vance, R.Zhang, and D.E. Legg.

1999. A field lysimeter study to evaluate herbicide transport in a Wyoming irrigated pasture. *Commun. soil sci. plant-anal.* 30: 245-263. A field study was conducted to assess the fate and mobility of two commonly used herbicides, dicamba (3,6-dichloro-2-methoxybenzoic acid), and picloram (4-amino-3,5,6, trichloro-2 pyridinecarboxylic acid), in an irrigated pasture. The herbicides were applied at two application rates to four plots (two replicates) that contained soil-water collectors. Herbicide concentrations as a function of depth and application rate were evaluated statistically to determine if replicate data could be combined. Results indicated dicamba concentration variations were low, suggesting the mean value of the replicate plots could be compared; however, picloram concentration variations were high, and the replicate plot data could not be combined. Half-time values for herbicide disappearance (time required for herbicide concentration to diminish from its maximum to half maximum levels), calculated from the arithmetic mean of the logistic equations, were found to be useful in describing herbicide transport. Half-time values were dependent upon application rate, collector depth, pesticide type, and plot location. Dicamba applied at the low application rate was detected at 15 and 30 cm depths only, and was not detected throughout the entire study period (467 days) at deeper depths. Significant differences occurred between plots receiving the high dicamba application rate, which was attributed to permeability differences that affected herbicide migration in the soil profile. Picloram half-time values were also affected by soil organic carbon, which increased picloram adsorption. In general, differences in herbicide concentrations were observed within plots receiving the high picloram application rates, which was primarily attributed to spatial differences in hydraulic conductivity. Herbicide disappearance was most rapid at the shallow depth (e.g., 15 cm) within plots receiving lower herbicide application rates.

Lee, H.B., Y.D. Stokker, A.S.Y. Chau. 1986. Chemical derivatization analysis of pesticide residues. X. Analysis of ten acid herbicides in natural waters. *Journal of the Association of Official Analytical Chemists* 69: 557-560. An improved and augmented GC method using a capillary column and electron capture detector was developed for determination of the following phenoxy acetic acid herbicides in natural water: dicamba, MCPA, dichlorprop,

2,3,6-TBA, 2,4-D, fenoprop, 2,4,5-T, MCPB, 2,4-DB and picloram. The herbicides were extracted with methylene chloride after the water sample was acidified to pH <1. Concentrated extracts in acetone were derivatized with pentafluorobenzyl bromide to form the corresponding pentafluorobenzyl esters. Derivatives were cleaned up on a deactivated silica gel column. A SE-54 fused silica capillary column was used to separate and identify the products. Recoveries from water samples fortified with 1-0.05 µg of the herbicides/l were 73-108% with the exception of picloram which was only 59% recovered at 0.1 µg/l.

- Mattice, J.D. and T.L. Lavy. 1986. Gas chromatographic determination of picloram in human urine. *Bulletin of Environmental Contamination and Toxicology* 37: 938-941.** Residues of picloram in urine samples were acidified with HCl, extracted with ether, evaporated to dryness combined with boron trifluoride-methanol and cleaned up with a Baker 10 Extraction System using a C18 cartridge (thus avoiding the use of potentially hazardous diazomethane). The picloram methyl ester was eluted with toluene and analysed by GC with ⁶³Ni electron capture detection. Operating parameters are given. Limit of detection was 10 p.p.b.
- Michaud, H.H., and P.E. Hoggard. 1988. Metal complexes of picloram. *J. of Agric. and Food Chem.* 36: 208-209.** Insoluble complexes of picloram with Ni²⁺ and Fe²⁺ were formed at near-neutral pH. This presents a mechanism for the possible removal of picloram from contaminated groundwater.
- Monnig, E. 1992. Pesticides and human health: the complexities of risk. *Western Wildlands*. 18: 27-32.** A brief account is given on how people perceive risks, with reference to the health risk posed by pesticides. Herbicides used frequently in the USA, such as 2,4-D, picloram, dicamba, clopyralid and glyphosate, are used as examples to highlight short-comings in the U.S. Environment Protection Agency's toxicity data requirements for pesticides.
- Norris, L.A. 1986. Accuracy and precision of analyses for 2,4-D and picloram in streamwater by ten contract laboratories. *Weed Science* 34: 485-489.** In a test of laboratory precision and accuracy, streamwater samples fortified with 0, 10, or 50 µg/L 2,4-D ((2,4-dichlorophenoxy)acetic acid) and picloram (4-amino-3,5,6-trichloro-2-pyridinecarboxylic acid) were submitted in quadruplicate for residue analysis to 10 laboratories that analyze samples for a fee. Varying amounts of the herbicides were detected by eight laboratories, and two reported no residues. Analyses from most laboratories had a negative bias (ranging from -2 to -92%), although a positive bias appeared in a few instances. Precision was highly variable, the coefficient of variation ranging from 3.4 to 200%. The accuracy range in 19 to 20 cases was plus or minus 100 to plus or minus 78% for 10 and 50 µg/L 2,4-D and plus or minus 100 to plus or minus 114% for 10 and 50 µg/L picloram, respectively. Results show that careful selection of contract laboratories and a quality assurance program should be part of monitoring for water contamination with herbicides.

- Nutter, W.L., T. Tkacs, P.B. Bush, and D.G. Neary. 1984. Simulation of herbicide concentrations in stormflow from forested watersheds. *Water Resources Bulletin* 20: 851-857.** The breakpoint rainfall hydrology and pesticide options of the field scale model CREAMS (Chemicals, Runoff, and Erosion from Agricultural Management Systems) were used to predict average concentrations of hexazinone in stormflow from four forested watersheds in the upper Piedmont region of Georgia. Predicted concentrations were compared with measured concentrations recorded over a 13-month period. CREAMS accurately predicted hexazinone concentrations in the initial stormflow events which also contained the highest concentrations. The model underestimated the hexazinone concentrations in stormflow two months and greater following pesticide applications. In a companion study, the daily rainfall option of the CREAMS model was used to evaluate the relative risk associated with the maximum expected concentration of hexazinone, bromacil, dicamba, and triclopyr in stormflow from small forested watersheds. The model predicted the following order of potential residue appearance in stormflow: bromacil > triclopyr > hexazinone > picloram > dicamba. Subsurface movement of residues via interflow and deep leaching losses are not simulated by the version of CREAMS used in these studies.
- Oakes D.J. and J.K. Pollak. 1999. Effects of a herbicide formulation, Tordon 75D(R), and its individual components on the oxidative functions of mitochondria. *Toxicology* 136: 41-52.** This investigation evaluates the toxicity of a herbicide formulation, as well as testing its active and other components (other components comprise all components of Tordon 75D(R) excluding the active components: i.e. the solvents, triisopropanolamine and diethyleneglycol monoethyl ether, a silicone defoamer and a proprietary surfactant, polyglycol 26-2). The results showed that Tordon 75D(R) (a mixture of the triisopropanolamine salts of 2,4-dichlorophenoxy acetic acid (2,4-D) and 4-amino-3,5,6-trichloropicolinic acid (picloram) and its other components) impaired the oxidative functions of submitochondrial particles (SMPs). The effective concentrations that caused 50% inhibition of SMP activity (EC50S) for Tordon 75(R) were in the low micromolar range for 2,4-D and picloram in the presence of the other components, while in the absence of the other components exposure to 136 times higher concentrations of the triisopropanolamine forms of 2,4-D and picloram administered as a mixture were required to inhibit the oxidative functions of SMPs. Tordon 75(R) also significantly decreased the respiratory control ratio of intact rat liver mitochondria. The results show that the toxic effects of Tordon 75(R) on SMPs (at the EC50) and intact rat liver mitochondria were not due to any additive or synergistic actions of a mixture of its active and other components, but rather were caused solely by the proprietary surfactant. Since mitochondria are responsible for over 90% of the energy production in all eukaryotic organisms, the use of the SMP assay provides a convenient in vitro assay for evaluating

cellular toxicity and can be regarded as an informative screening assay when designing chemical products which contain mixtures of chemicals.

- Pang, L., M.E Close, J.P.C. Watt, and K.W. Vincent. 2000. Simulation of picloram, atrazine, and simazine leaching through two New Zealand soils and into groundwater using HYDRUS-2D. J. contam. hydrol. Amsterdam : Elsevier Science B.V. 44: 19-46.**
- Peijnenburg, W.J.G.M., K.G.M. De Beer, H.A. Den Hollander, M.H.L. Stegeman, and H. Verboom. 1993. Kinetics, products, mechanisms and QSARs for the hydrolytic transformation of aromatic nitriles in anaerobic sediment slurries. Environ. Toxic. and Chem. 12: 1149-1161.** The degradation of several substituted benzonitriles was examined in anaerobic sediment-water systems under laboratory conditions. Formation of the corresponding benzoic acids was the main transformation process taking place. The pseudo-first-order rate constants of this process were shown to depend on both the chemical structure of the starting compound and the sediment characteristics. The starting compounds were selected with the aim of obtaining a maximum variation in chemical reactivity and physical properties, and the sediments were selected with the aim of assessing several environmental factors influencing the kinetics of transformation. Quantitative structure-activity relationships were developed for both ortho- and meta/para-substituted nitriles by relating pseudo-first-order disappearance rate constants for reductive hydrolysis of 27 aromatic nitriles in anoxic sediment slurries to some readily available molecular descriptors. The best correlations were obtained with the octanol/water partition coefficient of the nitriles and the summation of the inductive constants of the substituents as parameters. The correlations were strongly enhanced by taking into account the fraction of the compounds sorbed to the solid phase. Also it was found that upon correction for sorption, rate constants for reductive hydrolysis of three substituted benzonitriles obtained in six sediment samples did not differ significantly. Thus the obtained relationships may be used to calculate rates of transformation of given aromatic nitriles in given sediment systems.
- Peterson, H.G., C Boutin, P.A. Martin, K.E. Freemark, N.J. Ruecker, and M.J. Moody. 1994. Aquatic phyto-toxicity of 23 pesticides applied at expected environmental concentrations. Aquatic Toxicol. 28: 275-292.** Environment Canada uses an Expected Environmental Concentration (EEC) in evaluating the hazard of pesticides to nontarget aquatic organisms. This concentration is calculated by assuming an overspray of a 15 cm deep waterbody at the label application rate. The EEC of pesticides is then related to the EC50 (concentration causing a 50% reduction in a chosen toxicity endpoint) for a given aquatic test organism. At present, the use of an uncertainty factor is suggested in the literature if only a few species are tested because of important interspecific differences in pesticide sensitivity. The phytotoxicity of the EEC of 23 different pesticides to ten algae (24 h inhibition of super(14)C uptake) and one vascular plant (7-day growth inhibition) was determined in an effort to examine the question of interspecific sensitivity and its relation to the

development of pesticide registration guidelines. Chemicals included five triazine herbicides (atrazine, cyanazine, hexazinone, metribuzin, and simazine), four sulfonylurea herbicides (chlorsulfuron, metsulfuron-methyl, ethametsulfuron-methyl, triasulfuron), two phenoxy-alkane herbicides (2,4-D and MCPA), two pyridine herbicides (picloram and triclopyr), a substituted urea, an amine derivative, and an imidazolinone herbicide (tebuthiuron, glyphosate and imazethapyr, respectively), a bipyridylium (diquat), a hydroxybenzonitrile (bromoxynil), an aldehyde (acrolein) and an acetanilide (metolachlor) herbicide, as well as two carbamate insecticides (carbofuran and carbaryl) and a triazole derivative fungicide (propiconazole). Test organisms were selected based on ecological relevance and present use in test protocols.

Popov, V.G. 1979. Determining picloram and 2,4-D in water and soil by gas-liquid chromatography. In, Vsesoyuznyi Nauchno-Issledovatel'skii Institut Khimicheskikh Sredstv Zashchity Rastenii: Third All-Union Conference on the Analysis of Pesticide Residues to clarify the Conditions for their Safe Use in Agriculture in the light of the decision of the July 1978 Plenary Session of the Central Committee of the Communist Party, Moscow. Summaries of papers, pp. 37-38.

Russian 2,4-D and picloram are extracted from soil in a 0.01-N solution of potassium hydroxide, acidified in a solution of ortho-phosphoric acid, partitioned in ether, cleaned on a column of aluminium oxide or Florisil and determined by GLC after methylation with diazomethane; an electron-capture detector was used for 2,4-D and a TID [thermionic detector] and electron-capture detector for picloram. The lower limit of detection is 0.005 mg/kg and the recovery 80-95%. The herbicides are extracted from water in ether after acidification with orthophosphoric acid; the lower limit of detection is 0.001 mg/litre and recovery 90-95%.

Rieger, A.W., D.C.C. Muir, and M.R. Hendzel. 1985 Gas chromatographic determination of picloram in fish. Journal of the Association of Official Analytical Chemists 68: 59-61. A simple method for determining picloram in fish is described. The sample is homogenized with ethyl acetate, acidified with 1N HCl, and extracted twice more with ethyl acetate. Ethyl acetate fractions are pooled, derivatized with diazomethane, cleaned up by column chromatography and analysed by electron capture gas chromatography. Rainbow trout exposed to ^{14}C -picloram were used to evaluate the efficiency of 2 methods of extraction and to provide data on the rate of uptake and the bioconcentration factor. The detection limit for this method was 5 ng/g using a 4 g sample.

Robens, J.F. 1978. Tests For Possible Carcinogenicity Of 20 Pesticides In Osborne Mendel Rats And B-6c-3f-1 Mice Toxicol. And Appl. Pharmacol. 45 (1), pp. 236

Sahai, R., M. Chauhan, and S.S.S. Kushwaha. 1984. Verification of a theoretical model for pesticidal pollution. Sci. Total Environ. 35: 13-21. Lin, Sahi and Eyring's model for the accumulation of pesticide residues in soil, which may relate to pollution by pesticides, has been further developed to estimate

maximum pesticide residues in soil and vegetation as a function of time for different orders of pesticide decomposition reactions. The developed model has also been verified from some experimental data available in the literature on solbar, carbofuron, phorate, picloram, linuron and 2,4,5-T pesticides for first or second order reactions using correlation methods. From this model, the eventual persistence of pesticide residues in soil and vegetation may be predicted.

Samosvat, L.S. and N.A. Todua. 1975 Determining residues of Tordon in water and fruits by the method of thin-layer chromatography. Khimiya v Sel'skom Khozyaistve 13: 816. Russia Tordon (picloram [25%]) has a solubility in water of only 0.043% and tends to accumulate in the environment. A chromatographic method was developed for determining picloram residues in water, apples, pears and mandarins. Orthophosphoric acid is added to water samples before extracting the picloram in a 1:3 mixture of acetone + chloroform. The dried extract is developed on silica-gel with a 17:7.5 mixture of chloroform + glacial acetic acid as solvent and visualized with silver ammoniate (0.5 g silver-nitrate is dissolved in 5ml water and 15 ml 25% ammonium hydroxide and 80 ml acetone added) and u.v. irradiation; the sensitivity is 1-2 μ g. Picloram is extracted from apple and pear samples as from water after the addition of a saturated aqueous solution of sodium sulphate and a 20% aqueous alkaline solution, filtering and acidifying with 10% sulphuric acid. An 8:3 mixture of acetone + hexane is used as the solvent for the first phase and chloroform + acetic acid (17:7.5) for the second phase of 2-dimensional chromatography. The sensitivity is 0.01-0.02 mg/kg and the recovery 70-80%. Picloram is extracted from mandarin fruits in acetone + chloroform (1:3) and the extract concentrated and mixed with 0.5% aqueous sodium hydroxide. The filtrate is mixed with 0.5% alkali, 0.5 g activated carbon and chloroform and the supernatant acidified; picloram is further determined as in the analysis of water. The sensitivity is 0.02 mg/kg and the recovery 70-80%. Picloram residues in fruits from applications of 5 kg [product?]/ha under trees did not exceed 0.02 mg/kg in apples and 0.04 mg/kg in mandarins.

Samosvat, L.S. and N.A. Todua. 1975. Chromatographic determination of Tordon residues in plants. Khimiya v Sel'skom Khozyaistve 12: 11. Russian The method described was used to analyse leaves from tea bushes during the year of treatment and one and 2 years later. No Tordon [picloram] residues were found in samples taken several months after treatment, but 0.2-0.8 mg/kg of leaves was found one year after treatment. No herbicide was found 2 years after treatment.

Scifres C.F., R.W. Bovey, and M.G. Merkle. 1972. Variation in bioassay attributes as quantitative indices of picloram in soils. Weed Research. 12: 58-64. Symptom ratings were more effective than fresh wt. or oven-dry wt. of field beans or sunflowers to quantify ng amounts of picloram in river sand. Fresh wt., dry wt. or symptom ratings of soybeans effectively quantified ng quantities of picloram in river sand or sandy clay loam. From 92 to 97% of the variation

in bioassay reaction was attributed to variation in picloram concn. with the species studied, except cucumber, for which the functional relationship log concn. versus symptom rating was developed. Results from gas-liquid chromatography (GLC) analyses and the sensitive bioassay methods were closely correlated but GLC demonstrated less inherent variability than the bioassay methods. By utilizing the proper functional relationship and indicator variable, regression analyses of bioassay reaction were used to determine picloram residues of 0-250 ng/g soil on a statistical basis. From summary.

Sharma, M.P. and W.H.V. Born 1972. Picloram effects on ribonucleic acid and protein biosynthesis in excised plant tissues. Can. J. of Botany. 50: 2489-2501. Excised hypocotyls of soyabeans cv. Harosoy 63 and excised coleoptiles and leaf sections of barley cv. Parkland were incubated at 24 deg C for 8 h with 0, 10 or 500 mu g picloram/ml. In all untreated controls, contents of RNA and protein were decreased by 20-30 and 7-16%, respectively, during the incubation period. In soyabeans, incubation with 10 and 500 mu g picloram/ml caused 51 and 19% increases in RNA and 44 and 12% increases in protein compared with untreated controls. In barley coleoptiles and leaf sections, only 500 mu g picloram/ml decreased the net loss of RNA and protein and caused increases relative to the controls. 100 mg picloram/ml enhanced whereas 500 mg picloram inhibited RNA and protein biosynthesis. Incorporation of radioactivity into RNA and protein of particulate and supernatant fractions appeared to be equally sensitive to picloram. Addition of 10 mu g actinomycin-D and 2 mu g cycloheximide/ml to the incubation medium markedly inhibited both normal (control) and picloram-induced growth and RNA and protein biosynthesis; 40 mu g puromycin/ml was less effective in inhibiting growth and protein biosynthesis. 10 mu g picloram, 50 mu g GA and 50 mu g IAA/ml all promoted growth and RNA synthesis.

Shmelev, S.I., G.P. Zykova, and V.T. Dubonosov. 1988. Role of extraction equilibrium in quantitative analysis of pesticide residues in soils. Agrokhimiya 9: 97-105. Russian. On the basis of an analysis of sorption-desorption equilibria in soil-pesticide-extractant systems a number of principles were found that defined the level of recovery of a pesticide during extraction as a function of the extraction conditions and the pesticide content in the soil sample. The validity of such an approach was confirmed experimentally using picloram and bromacil as model pesticides. It enables a quantitative relationship to be established between the parameters of the extraction isotherm, the pesticide content in the soil sample and the level of its recovery under the conditions of a standardised extraction procedure. It is suggested that a preliminary stage should be included in the procedure for quantitative determination of pesticides in soils in which an extraction isotherm is constructed for each soil-pesticide-extractant combination.

Shukla, S., S. Mostaghimi, V.O. Shanholtz, and M.C. Collins. 1998. A GIS-based modeling approach for evaluating groundwater vulnerability to pesticides. J. Am. Water Resour. Assoc. 34: 1275-1293. The Attenuation Factor (AF), a

screening model, was used to evaluate the relative degree of vulnerability of groundwater to pesticide contamination in Louisa County, Virginia. For evaluating the contamination potential of pesticides, three scenarios of pesticide leaching represented by high, moderate, and low cases of degradation and sorption in the soil were considered. Data layers were overlaid within a Geographic Information System (GIS) for spatial computation of AF for the actual and 2m groundwater depths. This spatial database was divided into five contamination potential categories namely high, medium, low, very low, and unlikely, based on the numerical values of the AF for each cell (1/9 ha). The results for the three most mobile pesticides are presented in this paper. The performance of the AF model was evaluated by comparing its predicted results with the field data from an experimental watershed. The AF model was able to identify most of the frequently detected pesticides in the watershed. A sensitivity analysis was also performed. The results of this study provide information about the potential groundwater threat by pesticides to the citizens and decision-makers in the County and can be used for formulating an appropriate land use management plan to protect the groundwater quality.

Smith, A.E. and L.J. Milward. 1983. Comparison of solvent systems for the extraction of diclofop acid picloram simazine and triallate from weathered field soils. J. Agric. Food Chem. 31: 633-637. The extraction of diclofop acid, picloram, simazine and triallate from 3 field soils that had received treatments of the individual herbicides 12 mo. previously was compared using different solvent systems. The highest recoveries for diclofop acid and triallate were achieved with 30% aqueous acetonitrile containing 2.5% glacial acetic acid. The same extraction solvent was also the most effective for recovering weathered residues of picloram and simazine from a clay soil. For the extraction of picloram and simazine from treated clay loam and sandy loam soils, acetonitrile containing 18% water and 12% ammonium hydroxide was the most effective solvent system. In all cases for maximum recoveries, the soils were initially extracted for 0.5 h on a wrist-action shaker and then allowed to stand for 18 h before being shaken for a further 0.5 h.

Stalling, D.L., L.M. Smith, and J.D. Petty. 1979 Approaches to comprehensive analysis of persistent halogenated environmental contaminants. Special Technical Publications, American Society for Testing and Materials 686: 302-323. A series of chromatographic processes has been integrated into an automated sequential procedure specifically developed for uninterrupted purification and fractionation of multi-class organic chemical residues from environmental samples. The effectiveness and general applicability of this sequential clean-up and fractionation procedure were demonstrated by the recovery of 39 chemicals representing a broad range of residue classes from a fortified fish sample. A chromatographic controller under construction is designed to carry out the numerous sample and solvent manipulation in an automated and continuous procedure. Alkali metal hydroxide treated silica gel

effectively separated phenols and acids, including 2,4-D, 2,4,5-T and picloram, from neutral compounds. From summary.

- Thomas, M.W. B.M. Judy, W.R. Lower, G.F. Krause, and W.W. Sutton. 1990.** Time-dependent toxicity assessment of herbicide contaminated soil using the green alga *Selenastrum capricornutum*. In Plants for toxicity assessment, Wang, W., Gorsuch, J.W., Lower, W. R.(eds.). A symposium on use of plants for toxicity assessment held in Atlanta, USA, 19-20 April 1989. Philadelphia, USA; American Society for Testing and Materials (ASTM), pp. 235-254. Bioassays with *S. capricornutum* were performed on filtered eluates from a clay loam soil treated 1 h-10 d beforehand with 6 herbicides (glyphosate, imazapyr, triclopyr, picloram, 2,4-D and hexazinone) at recommended rates. The 96-h EC50 (effective concn) values indicated growth inhibition (relative to control sample) for all treatments when assayed 1 h after herbicide application. Algal EC50 values of +100 (control), +27.3 (glyphosate), -20.4 (imazapyr), -22.4 (triclopyr), -49.4 (picloram + 2,4-D) and -100 (hexazinone) were obtained. Assays conducted 10 d after herbicide application to soil revealed substantially reduced toxicity. A slight reduction in toxicity was noted for triclopyr and picloram + 2,4-D, and no change was observed with hexazinone. When the herbicides were applied to water, the following 96-h EC50 (in µg/ml) were obtained: 5300-5500 (imazapyr), 5000 (picloram + 2,4-D), 5000 (triclopyr), 2600 (glyphosate) and 1.2-2.5 (hexazinone).
- Tondeur Y. and R.C. Dougherty. 1981. New Screening Methods For Acidic Toxic Substances Using Negative Chemical Ionization Mass Spectrometry Tetra Chloro Terephthalate In Human Urines. Environ. Sci. Technol. 15: 216-219.** A screening technique was developed to detect 2,4-dichlorophenoxyacetic acid (94757) (2,4-D), picloram (1918021) and other water soluble, acidic toxic substances in urine. Acidic toxic substances were isolated from human urine samples from individuals occupationally exposed to herbicides were subjected to derivatization and chromatography. Toxic substances screening for contamination with polychlorinated organics was accomplished by using negative chemical ionization mass spectrometry. The recoveries for pentachlorophenol (87865) ranged from 76 to 80 percent at 10 parts per billion (ppb), the recoveries of 2,4-D ranged from 86 to 107 percent at 40ppb, and the recoveries of picloram ranged from 60 to 63 percent at 40ppb. The use of negative chemical ionization also revealed the presence of Dacthal (1861321). The presence of the recovered compounds was confirmed by gas chromatography and mass spectrometry.
- United States Department of the Interior Fish and Wildlife Service, Columbia, Missouri. 1979. Development of analytical methods for select herbicides and toxic substances. Columbia National Fisheries Research Laboratory: Annual report of research highlights, 1978, pp. 15-17.** Progress in the development of methods for the analysis of herbicides including trifluralin, picloram and 2,4,5-T in water and fish tissue is reported briefly.

Wells, M.J.M. , J.L. Michael, and D.G. Neary. 1984 Determination of picloram in soil and water by reversed-phase liquid chromatography. Archives of Environ Contamin and Toxicol. 13: 231-235. Clean-up procedures are described for soil, water and soil sol. samples before determination of picloram; combinations of liquid/liquid extraction and adsorption trapping on basic alumina and reversed-phase sorbents were used. Picloram was determined by HPLC and detection at 254 nm; derivitization was not necessary. Recovery was $92 \pm 7.1\%$ from water and $61.8 \pm 11.1\%$ from soil.

Woodruff, R.C., J.P. Phillips, and D. Irwin. 1983. Pesticide Induced Complete And Partial Chromosome Loss In Screens With Repair Defective Females Of *Drosophila melanogaster*. Environmental Mutagenesis. 5: 835-846. Induction of chromosome breakage and loss by pesticides was investigated using a mutant strain of *Drosophila-melanogaster* defective for DNA repair. Male *Drosophila* that were used contained a ring X-chromosome and a doubly marked Y-chromosome. These males were placed for 3 days in vials containing chemical treated feeding solutions and thus were exposed by both ingestion and inhalation. Treated and control males were mated for 3 days to repair defective females, and F1 male progeny were examined for ring chromosome loss (total loss) and loss of Y-chromosome markers (partial loss). Chlorpyrifos (2921882) at 50 parts per billion (ppb) induced complete losses in 1.32 percent of male progeny, compared to 0.99 percent in concomitant controls and 1.02 percent in overall controls, but did not induce a significant increase in partial losses. In positive controls, 1 part per million (ppm) N-nitrosodimethylamine (62759) and 1ppm methylmethanesulfonate (66273) induced complete losses of 2.02 and 5.07 percent, respectively, and partial losses of 0.80 and 3.52 percent (untreated control was 0.05 percent). No significant increases in complete or partial losses were found for 1200ppm captan (133062), 10000ppm maneb (12427382), 10000 bromacil (314409), 200ppm paraquat (4685147), 650ppm picloram (1918021), 1000 2,4-D (94757), 200ppm carbaryl (63252), 1ppm dimethoate (60515), 25ppm DDT (50293), 100ppb diazinon (333415), 2ppm carbofuran (1563662), or 5ppm permethrin (52645531). The authors conclude that mating schemes with repair defective females are useful screens for genetic damage induced in *D-melanogaster* males by toxic chemicals; similar screens might be possible in other higher eukaryotes.

Yufu, S and J.J. Pignatello. 1993. Activation of hydrogen peroxide by iron(II) chelates for abiotic degradation of herbicides and insecticides in water. J. Agric. and Food Chem. 41: 308-312 Degradation of selected pesticides was carried out in water at pH 6 using hydrogen peroxide and soluble Fe(III) chelates of picolinic acid, gallic acid, or rhodizonic acid as catalysts and with or without near-UV irradiation. The catalysts were selected on the basis of an earlier screening. Without UV light, transformation of baygon, carbaryl, picloram, 2,4-D, 2,4,5-T, and atrazine was complete within a few minutes to about 2 h. Trifluralin reacted slowly. Ring- and carboxy-labeled (^{14}C)-2,4-D and ringlabeled (^{14}C)-2,4,5-T were 70-80% mineralized to $^{14}\text{CO}_2$ in 2-4 h.

Rign-labeled (^{14}C)atrazien yielded no $^{14}\text{CO}^{-2}$. UV light accelerated degradation by the above chelates, as well as by thermally inactive oxalate and citrate chelates. UV acceleration is most likely due to charge-transfer photoreduction of the chelate to give Fe(II) , which then reacts with H_2O_2 to generate hydroxyl radical in the Fenton reaction. These reactions are potentially useful for detoxifying pesticide wastes.

AQUATIC INVERTEBRATES

Baarschers, W.H., J.G. Donnelly, and H.S. Heitland. 1988. Microbial toxicity of triclopyr and related herbicides. Toxicity Assessment. 3: 127-136. Microbial toxicity of triclopyr was measured with several microorganisms in comparison with 2,4-D and picloram. Growth inhibition of three fungi (*Trichoderma viride*, *Mortierella isabellina*, and *Saprolegnia parasitica*) was measured in terms of colony size on agar plates and in terms of cell counts for two algae (*Chlorella vulgaris* and *C. pyrenoidosa*). Dehydrogenase measurement by a direct 2-(4-iodophenyl)-3-(4-nitrophenyl)-5-phenyl tetrazolium chloride method was used for the bacteria *Pseudomonas pictorum* and *Arthrobacter globiformis*. Dose-response curves were determined to obtain EC50 values for triclopyr, 2,4-D, picloram, their commonly used amine salts, and the degradation products, 3,5,6-trichloro-2-pyridinol, 2,4-dichlorophenol and decarboxy picloram. Toxicities of triclopyr and 2,4-D were similar in most cases, and both compounds were more toxic than picloram. The 3 degradation products were substantially more toxic than the respective parent compounds. The algae were most sensitive and gave much lower EC50 values than the fungi and bacteria.

Donald D.B. and J. Syrgiannis. 1995. Occurrence of pesticides in prairie lakes in Saskatchewan in relation to drought and salinity. Journal of Environmental Quality 24: 266-270. Following the severe drought of 1988 in Saskatchewan, Canada, the concn of 11 pesticides were determined in water, sediment, and zooplankton in 10 permanent and 9 semipermanent lakes (those lakes that did not have standing water in 1988). The detection frequency for lindane, alpha-HCH, and 2,4-D in water was 57, 70, and 78%, resp., with the maximum concn 0.011, 0.004, and 0.43 mug/litre, resp. Tri-allate was detected in 39% of sediment samples and 54% of zooplankton samples at a maximum concn of 31 and 10.2 mug/kg, resp. When the lakes were grouped by salinity, detection frequencies of these pesticides were significantly higher in brackish lakes, which tended to be semipermanent (N = 6, mean specific conductance 3100 muS/cm) than in saline lakes, which tended to be permanent (N = 6, mean specific conductance 60 900 muS/cm). Other pesticides were detected in <205 of samples (diclofop-methyl, atrazine, MPCA, dicamba, and bromoxynil) or not at all (trifluralin and picloram). With one exception, pesticide concentrations in these lakes were below those levels that might be deleterious to aquatic life, suggesting that these pesticides have not affected the food of avifauna at these lakes.

Dunkel, F.V. and D.C. Richards. 1998. Effect of an azadirachtin formulation on six nontarget aquatic macroinvertebrates. Environmental Entomology 27: 667-674. Effects of a botanical pesticide, azadirachtin, were evaluated on nontarget aquatic macroinvertebrates found in SW Montana. A neem product formulated for commercial use and its petroleum-based, inert carrier alone were used to test the hypothesis that a commercial, U.S. Environmental Protection

Agency-approved formulation of the pesticide, azadirachtin-A, derived from extracts of neem tree seeds, *Azadirachta indica* A. Juss. (Family: Meliaceae), is toxic to nontarget aquatic macroinvertebrates in Montana river systems. LC sub(50)s (24 h) for 5 insect species, *Drunella grandis* (McDunnough), *Drunella doddsi* (Needham), *Skwala parallela* (Frison), *Brachycentrus occidentalis* Banks, and *Brachycentrus americanus* (Banks), and 1 isopod species, *Caecidotea intermedia* (Forbes) varied from 1.8 to 9.2 ppm of the full formulation. The full formulation consisted of: azadirachtin (3% wt:wt) other neem-extracted material (32% wt:wt) petroleum solvents (65% wt:wt). LT sub(50)s for 4 ppm of this formulation were 9.4 to 748 hours for these field-collected macroinvertebrates. Without azadirachtin, but with the petroleum-based carrier, LT sub(50)s were 13.6-46.7 h. These bioassays conducted late in winter and early spring of 1994 and 1995 and late summer and early fall of 1994 indicated mortality from the neem formulation was similar to herbicides 2,4-D and picloram, but mortality could be accounted for by action of petroleum solvents in the inert materials. This suggests the registration process of new pesticides should also include documented potential toxicity of inert components in the formulation to non-target aquatic insects.

Ebbersten S. 1972. Picloram (4-amino-3,5,6-trichloropicolinic acid). Studies concerning persistence in soil and plants and biological methods for determining picloram residues. [Pikloram (4-amino-3,5,6-trikloropikolinsyra). Studier av persistens i jord och växter samt metodstudier rörande biologisk bestämning av pikloramrester.]. Uppsala, Institutionen for Vaxtodling, Lantbrukshogskolan, Sweden, 175 pp. Swedish. This publication is divided into 2 main sections: 1. A literature survey including sections on (a) the effects of picloram on higher plants, soil micro-organisms and higher animals (mammals, birds and fish), (b) the persistence of picloram in plant tissue, soil and water and (c) methods for determining picloram residues. 2. Results of investigations carried out in Sweden during 1966-70 to study persistence and movement in the soil, determination of residues and the effects on following crops of wheat and potatoes.

Forsyth, D.J., P.A. Martin, and G.G. Shaw. 1997. Effects of herbicides on two submersed aquatic macrophytes, *Potamogeton pectinatus* L. and *Myriophyllum sibiricum* Komarov, in a prairie wetland. *Environmental Pollution* 95: 259-268. Clopyralid, picloram, 2,4-D and a mixture of 2,4-D plus picloram, (Tordon R 202C) were added to the water of 1 m square enclosures in a prairie wetland in Saskatchewan, Canada to produce concentrations of 0.01 and 0.1 mg active ingredient litre⁻¹. Effects on the submersed macrophytes, *Potamogeton pectinatus* and *Myriophyllum sibiricum*, were monitored by taking repeated measurements of plant weight, flower and tuber production and inspecting for injuries at 30 and 60 days after application. Clopyralid did not inhibit weight gain (growth) in either species, but stimulated growth and flowering by *M. sibiricum* at 0.01 mg litre⁻¹ and tuber production by *P.*

pectinatus at both rates. The low rate of 2,4-D stimulated flowering by *M. sibiricum* and tuber production by *P. pectinatus*, whereas the high rate inhibited growth of *M. sibiricum* and injured both species. Picloram did not affect growth of either species, but injured *M. sibiricum* at both concentrations and inhibited flowering at 0.1 mg litre⁻¹. Tordon R 202C at 0.1 mg litre⁻¹ caused reduced growth and flowering in *M. sibiricum* and injured both species; 0.01 mg litre⁻¹ also injured *M. sibiricum*. Mortality resulted only from Tordon R 202C and 2,4-D.

- Gardner, G.R., P.P. Yevich, J. Hurst, P. Thayer, S. Benyi, J.C. Harshbarger, and R.J. Pruell. 1991. Germinomas and teratoid siphon anomalies in softshell clams, *Mya arenaria*, environmentally exposed to herbicides. *Environmental Health Perspectives* 90: 43-51.** After histopathological studies revealed abnormalities in the reproductive organs of *M. arenaria*, a survey of the Maine coastline along 3 estuaries was carried out. It was concluded that Tordon 101 [2,4-D + picloram], 2,4-D and 2,4,5-T used in blueberry [Vaccinium] agriculture and forestry had caused these abnormalities, and not petroleum products spilled in 1971, as was originally thought.
- Gersich, F.M., D.L. Hopkins, and D.P. Milazzo. 1985. Acute and chronic toxicity of technical picloram (4-amino-3,5,6-trichloropicolinic acid) to *Daphnia magna* Straus. *Bull. Environ. Contam. Toxicol.* 35: 121-126.** The max. acceptable toxicant concn. of picloram for *D. magna*, as estimated from chronic toxicity data, was 11.8-18.1 mg/l. The 48-h LC50 value was 68.3 mg/l, while no kill and 100% mortality concn. were 34.5 and 94.5 mg/l, resp.
- Mayes, M.A. and D.C. Dill. 1984. The Acute Toxicity Of Picloram Picloram Potassium Salt And Picloram Tri Iso Propanolamine Salt To Aquatic Organisms. *Environ. Toxicol. Chem.* 3: 263-270.**
- Mayes, M.A. and G.R. Oliver. 1985. An aquatic hazard assessment: Picloram. In *Aquatic Toxicology And Hazard Assessment. Eighth Symposium. Bahner, R.C. and D.J. Hansen (eds). Spec. Tech. Publ. Am. Soc. Test. Mater., No. 891, pp. 253-269.*** Picloram (4-amino-3,5,6-trichloropicolinic acid) exhibits herbicidal activities on broadleaf weeds and woody plants. The runoff potential of picloram is normally limited to less than 5% of the applied chemical removed from the site in runoff waters. Picloram is relatively nontoxic to freshwater fishes, with acute LC sub(50) values for technical acid ranging from 4.3 mg/L for lake trout (*Salvelinus namaycush*) to 55.3 mg/L for fathead minnows (*Pimephales promelas* Rafinesque). Freshwater invertebrates show similar susceptibility to technical picloram with acute LC sub(50) values ranging from 27 mg/L for *Gammarus lacustris* to 68.3 mg/L for *Daphnia magna*. The most sensitive marine invertebrate tested is the eastern oyster (*Crassostrea virginica*) with 18 > EC sub(50) < 32 mg/L when exposed to a potassium salt formulation of picloram. Because of its relatively low toxicity to aquatic organisms and low potential for substantial quantities to enter the aquatic

environment, picloram is not expected to present a hazard to the aquatic environment.

Morre, and D. James. 1974. Brush control along agricultural drainage ditches. Environmental safety and efficacy of herbicide formulations. Tech. Rep. - Purdue Univ. Water Resour. Res. Cent., Vol. 49, 108 pp.

Peterson H.G., C. Boutin, P.A. Martin, K.E. Freemark, N.J. Ruecker, and M.J. Moody. 1994. Aquatic phyto-toxicity of 23 pesticides applied at Expected Environmental Concentrations. Aquatic Toxicology 28: 275-292. The phytotoxicity of the Expected Environmental Concentration (EEC, used to evaluate the hazard of pesticides to nontarget organisms) of 23 pesticides to 9 species of algae and cyanobacteria (24-h inhibition of ^{14}C -labelled pesticide uptake), and 1 aquatic plant (7-d growth inhibition) was determined in order to examine the question of interspecific sensitivity and its relation to the development of Canadian pesticide registration guidelines. Chemicals included 5 triazine herbicides (atrazine, cyanazine, hexazinone, metribuzin and simazine), 4 sulfonyleurea herbicides (chlorsulfuron, metsulfuron-methyl, ethametsulfuron-methyl and triasulfuron), 2 phenoxyalkane herbicides (2,4-D and MCPA), 2 pyridine herbicides (picloram and triclopyr), a substituted urea (tebuthiuron), an amine derivative (glyphosate), an imidazolinone herbicide (imazethapyr), a bipyridylium (diquat), a hydroxybenzonitrile (bromoxynil), an aldehyde (acrolein), an acetanilide herbicide (metolachlor), 2 carbamate insecticides (carbofuran and carbaryl) and a triazole derivative fungicide (propiconazole). The following test organisms were selected: green algae (*Scenedesmus quadricauda* and *Selenastrum capricornutum*); diatoms (*Nitzschia* sp. and *Cyclotella meneghiniana* [*C. meneghiniana*]); cyanobacteria (2 strains of *Microcystis aeruginosa*, *Oscillatoria* sp., *Pseudoanabaena* sp., *Anabaena inaequalis* and *Aphanizomenon flos-aquae*); and duckweed (*Lemna minor*). The 5 triazine herbicides, acrolein and diquat inhibited the C uptake of all algae and cyanobacteria by >50%. Carbaryl and tebuthiuron caused >50% inhibition in 90% of the algae tested. The triazine herbicides, sulfonyleurea herbicides, acrolein, diquat, metolachlor and tebuthiuron inhibited the growth of duckweed by >50%. Duckweed was the most sensitive organism tested, being equally affected by all pesticides (with the exception of carbaryl), as well as being acutely affected by sulfonyleurea herbicides. Green algae were least sensitive to diquat; diatoms and 1 cyanobacterium were the only organisms that showed sensitivity to glyphosate. It is concluded that there are considerable differences in sensitivity among species and that an uncertainty factor is necessary to provide an acceptable margin of safety in evaluating the hazard presented by these chemicals to the aquatic environment.

Schulz, C.O., P.K. LaGoy, and M.B. Paxton. 1986. Reviewing the literature on the health effects of phenoxy herbicides and associated dioxins. In, Chlorinated Dioxins And Related Compounds [5th International Symposium on Chlorinated Dioxins and Related Compounds, Bayreuth (FRG) , 1985 Sep 16-19.] O. Hutzinger. W. Crummett, F.W. Karasek, E. Merian, G.

Reggiani, M. Reissinger, and S. Safe (eds.). Chemosphere vol. 15, no. 9-12, pp. 2099-2102. This review covers all the available scientific information on the health effects of phenoxy herbicide formulation, phenoxy herbicide active ingredients, polychlorinated dibenzo-p-dioxin impurities, cacodylic acid, and picloram. Also included are scientific studies on the absorption, distribution, metabolism, and excretion of these substances in mammals. Unpublished reports that are in the public domain are covered in the review. The review does not include information on analytical methodology, analytical results, or information on environmental distribution and fate.

Task Force on Water Quality Guidelines (Canada). 1990. Canadian water quality guidelines : updates, March, 1990 : appendix VI. Inland Waters Directorate, Water Quality Branch, 67 pp. Update to the Canadian Water Quality Guidelines, giving guidelines for amounts of picloram, metribuzin and cyanazine in raw water for drinking, recreational water, freshwater for aquatic life, agricultural uses, and industrial water supplies. Background information on uses and production, sources and pathways, environmental concentrations, and forms and fates in the aquatic environment are also included.

Trotter, D.M., R.A. Kent, and M.P. Wong. 1990. Canadian water quality guidelines for picloram. Environment Canada, Inland Waters Directorate, Water Quality Branch, v, 62 p. This report summarizes a literature review on the uses, fate, and effects of picloram (herbicide) on raw water for drinking water supply, freshwater aquatic life, agricultural water uses, recreational water quality and aesthetics, and industrial water supplies. Water quality guidelines for the protection of specific water uses are recommended in this report.

United States Department of the Interior Fish and Wildlife Service, Columbia, Missouri. 1979. Acute toxicity of benomyl, trifluralin and picloram to freshwater organisms. Columbia National Fisheries Research Laboratory: Annual report of research highlights, 1978, pp.1. The fungicide benomyl was more toxic to fish and freshwater invertebrates than either trifluralin or picloram. Trifluralin was more toxic to rainbow trout than channel catfish and picloram was slightly more toxic to young channel catfish than to rainbow trout. The results suggest that contamination of aquatic habitats by these chemicals during spawning could reduce the survival of young fish.

ARTHROPOD TOXICITY

- Elliott R.H., D. Cmiralova, W.G. Wellington. 1979. Olfactory repellency of herbicides to foraging honey bees (Hymenoptera: Apidae). Canadian Entomologist 111: 1131-1135.** Foraging honey bees were offered various sucrose-herbicide solutions. Despite the visual attractiveness of the feeding dishes to foragers, 6 of 7 herbicides significantly reduced the incidence of feeding and were judged to be olfactory and gustatory repellents. The most repellent herbicide was 2,4,5-T, which totally inhibited feeding at concns. as low as 1000 p.p.m. The next most repellent was 2,4-DB, followed by linuron, picloram, 2,4-D and monuron. Paraquat was the only herbicide that did not exhibit marked repellency at concns. up to 4000 p.p.m. The implications of these findings are discussed in terms of impact of herbicide applications on honey bee foraging behaviour, brood development, pollination and honey production.
- Lym, R.G. and R.B. Carlson. 1994. Effect of herbicide treatment on leafy spurge gall midge (*Spurgia esulae*) population. Weed Technology 8: 285-288.** An experiment was conducted within a leafy spurge (*Euphorbia esula*) biocontrol insectary near Valley City, North Dakota, in 1991 to investigate the effects of herbicide application on the *S. esulae* population by monitoring both gall density and the number of larvae/gall. The following herbicides were applied 2,4-D (1.1 kg/ha), picloram + 2,4-D (0.28 + 1.1 kg) and imazethapyr (0.28 kg). Herbicide applications reduced the number of *S. esulae* galls (from 26-29 to 8-16 galls/m²) but not the number of larvae/gall. Long-term *S. esulae* population density was not affected by herbicide application. It was concluded that the integration of herbicides with the use of *S. esulae* would prevent leafy spurge spread from a wooded area and would reduce seed production within an area where herbicides generally cannot be used.
- Morton H.L., J.O. Moffett, and Mac Donald R.H. 1972. Toxicity Of Herbicides To Newly Emerged Honey Bees. Environmental Entomology 1: 102-104.**
- Pratissoli, D. and J.B. Torres. 1998. Susceptibility of dung beetle *Onthophagus gazella* (F.) (Coleoptera: Scarabaeidae) to pesticides and herbicide in the nest phase. [Suscetibilidade de *Onthophagus gazella* (F.) (Coleoptera: Scarabaeidae) a carrapaticidas e herbicida na fase de nidificacao.]. Revista Ceres. 45: 245-253. Portuguese.** *Onthophagus gazella* showed high tolerance to the pesticide trichlorfon at 0.3% a.i., deltamethrin at 0.4% a.i., and amitraz. However, trichlorfon at 10.0% a.i., caused lower survival (77.5%), among the pesticides, at 3, 6 and 9 days after spraying. This figure is considered high according to previous selectivity studies. The herbicide picloram caused high mortality at 2, 4, 6, 8 and 10.0% a.i., at 6 and 9 days after spraying. It presented an LD₉₉ to males and females of 17.06 mg/ml and 21.60 mg/ml, respectively. The pesticides had a lower impact on *O. gazella* adults, being selective when utilized as sprays. The herbicide picloram is not selective, causing an average of

22.2 and 17.9% survival of males and females, respectively, at 9 days after spraying.

Rees N.E. and P.K. Fay. 1989. Survival of leafy spurge hawk moths (*Hyles euphorbiae*) when larvae are exposed to 2,4-D or picloram. *Weed Technology* 3: 429-431. Larvae of the leafy spurge hawk moth were sprayed with and/or were fed leafy spurge (*Euphorbia esula*) plants sprayed with 2,4-D or picloram. Larval survival was not affected from contact with the chemicals, from feeding on contaminated foliage, or from a combination of both. Viable second-generation adult moths were produced in all treatments. Thus, leafy spurge infested with the biological control agent leafy spurge hawk moth can be sprayed with 2,4-D or picloram without injury to larvae that have reached the fourth and fifth instar stages.

Woodruff, R.C., J.P. Phillips, and D. Irwin. 1983. Pesticide Induced Complete And Partial Chromosome Loss In Screens With Repair Defective Females Of *Drosophila melanogaster*. *Environmental Mutagenesis*. 5: 835-846. Induction of chromosome breakage and loss by pesticides was investigated using a mutant strain of *Drosophila-melanogaster* defective for DNA repair. Male *Drosophila* that were used contained a ring X-chromosome and a doubly marked Y-chromosome. These males were placed for 3 days in vials containing chemical treated feeding solutions and thus were exposed by both ingestion and inhalation. Treated and control males were mated for 3 days to repair defective females, and F1 male progeny were examined for ring chromosome loss (total loss) and loss of Y-chromosome markers (partial loss). Chlorpyrifos (2921882) at 50 parts per billion (ppb) induced complete losses in 1.32 percent of male progeny, compared to 0.99 percent in concomitant controls and 1.02 percent in overall controls, but did not induce a significant increase in partial losses. In positive controls, 1 part per million (ppm) N-nitrosodimethylamine (62759) and 1ppm methylmethanesulfonate (66273) induced complete losses of 2.02 and 5.07 percent, respectively, and partial losses of 0.80 and 3.52 percent (untreated control was 0.05 percent). No significant increases in complete or partial losses were found for 1200ppm captan (133062), 10000ppm maneb (12427382), 10000 bromacil (314409), 200ppm paraquat (4685147), 650ppm picloram (1918021), 1000 2,4-D (94757), 200ppm carbaryl (63252), 1ppm dimethoate (60515), 25ppm DDT (50293), 100ppb diazinon (333415), 2ppm carbofuran (1563662), or 5ppm permethrin (52645531). The authors conclude that mating schemes with repair defective females are useful screens for genetic damage induced in *D-melanogaster* males by toxic chemicals; similar screens might be possible in other higher eukaryotes.

BIODIVERSITY

- Barrons, K.C. 1969. Some Ecological Benefits of Woody Plant Control with Herbicides. Science. 165: 465-468.** The ecological benefits of woody plant control with selective herbicides are discussed. Literature concerning use of such substances as 2,4-D, 2,4,5-T, silvex, and picloram is reviewed. Examples of increased productivity of range and pastureland through use of agricultural chemicals are given. Use of 2,4-D and 2,4,5-T to control hardwood brush is discussed in light of the effect of such use on water conservation. Use of these chemicals for controlling woody plants which endanger powerlines and road utility is discussed. In areas treated with the herbicides, rabbits, grouse, and wild turkeys appear to benefit from the stable low cover induced by the treatments. Planting of new forest trees is simplified by site preparation using herbicides to kill weed trees and shrubs. The toxicity of the chemicals apparently is of a low order in birds, fish, and algae. Possible future uses of selective herbicides are discussed.
- Beasom, S.L., J.M. Inglis, and C.J. Scifres. 1982. Vegetation and white-tailed deer responses to herbicide treatment of a mesquite drainage habitat type. Journal of Range Management 35: 790-794.** Texas rangeland dominated by honey mesquite [*Prosopis glandulosa*] was aerially sprayed in May 1977 with 1.1 kg/ha of a 1:1 mixture of 2,4,5-T plus picloram. Relative density indices of forbs, canopy cover reduction of woody plants (treated area only), relative deer (*Odocoileus hemionus*) use (by faecal pellet accumulation) and standing crops of grasses and forbs were determined up to 27 months after treatment for the treated area and for adjacent untreated range with honey mesquite, blackbrush acacia (*Acacia rigidula*), mixed *A. rigidula*/brush, creeping mesquite (*P. glandulosa* var. *reptans*) and mixed creeping mesquite/brush. Cover of honey mesquite, twisted acacia (*A. tortuosa*), *A. rigidula*, lotebush (*Ziziphus obtusifolia*), spiny hackberry (*Celtis pallida*), Texas paloverde (*Cercidium texanum*), and Texas prickly pear (*Opuntia lindheimeri*) was significantly reduced on treated range and grass standing crop was significantly increased. Deer use of treated range was not consistently affected by herbicide application. It is suggested that lack of change in deer use was due to the minor effect of spraying on forb populations, retention of ample cover for deer and the increased abundance of grasses, which probably reduced the use of preferred deer food items by cattle.
- Bramble, W.C., W.R. Byrnes, and R.J. Hutnik. 1985. Effects of a special technique for right-of-way maintenance on deer habitat. Journal of Arboriculture 11: 278-284.** Sections of a power line right-of-way in an oak/hickory forest in central Pennsylvania were treated in 1982. The right-of-way was divided into a central 23 m-wide wire zone and 2 border zones 18 m wide. Only tall-growing trees were treated in the border zones, while all trees and tall shrubs were treated in the wire zone, by handcutting (control), summer basal spray of

Garlon 4 (triclopyr), stem foliage spray of dichlorprop with picloram and 2,4-D, or selective frill and squirt application of Tordon RTU (picloram and 2,4-D). The wire zone was also treated by broadcast application of Tordon 10 K pellets (picloram). A transect across the right-of-way, including forest edge, was evaluated for suitability as habitat for white-tailed deer (*Odocoileus virginianus*). Direct factors - food plant abundance and diversity, and low plant and tall shrub cover, and indirect factors - external shrub borders, interspersions of cover types and stages of plant succession were noted. Deer use was evaluated in July 1982, 1983 and 1984 by faecal counts, and browsing was evaluated in 1984. Although there were changes in individual habitat factors, total habitat values remained high. Deer spent more time on the right-of-way after it was treated.

Brooks J.J., J.L. Rodrigue, M.A. Cone, K.V. Miller, B.R. Chapman, A.S. Johnson, and M.B. Edwards. 1995. Small mammal and avian communities on chemically-prepared sites in the Georgia sandhills. Proceedings of the Eighth Biennial Southern Silvicultural Research Conference, Auburn, Alabama, 1-3 November, 1994 Southern Research Station, USDA Forest Service. No. SRS-1, 21-23. The effects of 3 forestry herbicide site preparation treatments (hexazinone, picloram + triclopyr, and imazapyr) on small mammal and avian communities were compared at pre-treatment, and 1, 2, and 3 years post-treatment in the Sandhills physiographic region of Marion County, Georgia. Few differences in small mammal capture rates occurred among treatments. Capture rates declined immediately following site preparation, but returned to pre-treatment levels by 18 months post-treatment. The greatest winter avian abundance occurred at 3 years post-treatment; however, no differences in winter avian abundance were observed among treatments. In year 3 post-treatment, summer birds favouring forest edge + scrub habitats were higher on hexazinone-treated sites. Summer avian abundance was strongly associated with residual woody vegetation.

Brooks, J.J., A.S. Johnson, and K.V. Miller. 1993. Effects of chemical site preparation on wildlife habitat and plant species diversity in the Georgia sandhills. Gen-tech-rep-SO. [New Orleans, La.] : Southern Forest Experiment Station. 93: 605-612.

Luken, J.O., S.W. Beiting, S.K. Kareth, R.L. Kumler, J.H. Liu, and C.A. Seither. 1994. Target and nontarget discrimination of herbicides applied to vegetation in a power-line corridor. Environmental Management. 18: 251-255. In field trials conducted in Clermont County, Ohio, during 1990-91, 2 cutting regimens (cut/spray and cut/delay spray) and 4 radiarc-applied herbicides (11.7 litres/ha Garlon (triclopyr) + 18.71 litres Tordon (picloram), 18.71 litres Accord (glyphosate), 18.71 litres Accord + 0.141 litres Escort (metsulfuron), and 28.11 litres Krenite (fosamine)) were tested in a power-line corridor to determine which management combination best eliminated target species (trees) and preserved non-target species (low shrubs, vines, perennial herbs and grasses). When spraying was delayed after cutting, the herbicide with

the least impact on non-target species (Krenite) was also least efficient at killing target trees. Spraying soon after cutting improved the tree-killing efficiency of several herbicides, but it also increased the negative impact on non-target species. The herbicide with the most consistent tree-killing ability (Accord + Escort) had the most impact on non-target species. It was concluded that, because none of the herbicide/cutting treatments performed ideally, resource managers must decide the acceptable impact on non-target species when considering herbicide use.

McComb, W.C., and R.L. Rumsey. 1983. Characteristics and cavity-nesting bird use of picloram-created snags in the central Appalachians. *Southern Journal of Applied Forestry* 7: 34-37. Four herbicide treatments, 10% picloram (TORDON 10K) at (a) 20, (b) 40 or (c) 60 lb/acre and (d) 5% picloram (M-3864) at 80 lb/acre, were applied as pellets in May 1976 to plots in uneven-aged mixed mesophytic forest in Kentucky. The condition of sample trees and the presence of cavities and other habitat features were recorded in May 1980. Birds were counted from Jan. to June 1980. Snags were most numerous on (b) and (d), and characteristics of these snags and those on other plots are described. The numbers of cavity-using birds (10 species) were significantly greater for treatment (b) than (d) or control plots (untreated); numbers for (a) and (c) were intermediate.

Miller, J.H., R.S. Boyd, M.B. Edwards, D.G. Thompson (ed.), and R.G. Wagner. 1999. Floristic diversity, stand structure, and composition 11 years after herbicide site preparation. *Proceedings of the third International Conference on Forest Vegetation Management, Sault Ste. Marie, Ontario, Canada, August 24-28, 1998. Canadian Journal of Forest Research* 29: 1073-1083. A study was conducted to investigate the effects of site preparation herbicides applied 11 years earlier on plant species richness, diversity and stand structure and composition. Four study sites in 3 physiographic provinces were established in central Georgia, USA, in 1984. Six herbicide treatments were included on each site (hexazinone liquid, hexazinone pellets, glyphosate, triclopyr, picloram or a mixture of dicamba and 2,4-dichlorophenoxyacetic acid (2,4-D)). Herbicide and untreated plots were prescribed-burned and *Pinus taeda* planted. Eleven years after treatment, 177 total species were identified in these dense pine plantations, 99 species being forbs and grasses. Treated and check plots did not differ in species richness or diversity. Structurally, the total basal area of the tree canopy was not significantly altered, but the proportion of pine to hardwoods and shrub stem density were influenced by treatment. Latent effects were detected in the abundance and frequency of *Pinus taeda*, *Prunus serotina*, *Quercus stellata*, *Diospyros virginiana*, *Vaccinium stamineum*, *Vitis rotundifolia* and *Lespedeza bicolor*. Most were potential mast producers for wildlife. It is concluded that herbicide site preparation had little influence on total species numbers or their diversity 11 years after treatment but affected composition by altering perennial species abundance.

- Miller, K.V. and Chapman B.R. 1995. Responses of vegetation, birds and small mammals to chemical and mechanical site preparation, In, FRI Bulletin, No 192; Popular Summaries from Second International Conference on Forest Vegetation Management. R.E. Gaskin and J.A. Zabkiewicz (eds). New Zealand Forest Research Institute, Rotorua, New Zealand. p 146-148 1995**
- Nolte, K.R. and T.E. Fulbright. 1997. Plant, small mammal, and avian diversity following control of honey mesquite. *Journal of Range Management* 50: 205-212.** A field trial was conducted in the Welder Wildlife Foundation Refuge, Texas, on a mesquite-mixed grass community dominated by *Prosopis glandulosa* (honey mesquite), interspersed with chaparral (e.g. *Acacia smallii*, *Celtis pallida* and *Zanthoxylum fagara*) and grasses (*Stipa leucotricha*, *Panicum obtusum* and *Setaria leucopila*), to investigate the effects of herbicide application to *P. glandulosa* on community plant and vertebrate species richness and diversity. A 1:1 mixture of triclopyr + picloram was applied to three 13 ha plots during 1992 and to 3 additional plots in 1993. Mesquite and forb canopy cover in the zone \leq 1 m from the soil surface were lower within treated plots than in control plots in both years. Grass canopy cover did not differ between herbicide-treated plots and control plots. Vegetation species richness and evenness, Shannon's index, beta diversity and the proportion of rare plant species did not differ between controls and sites treated during 1992 and 1993. Rodent and avian relative frequency, richness and diversity were not significantly different in 1992 on herbicide treatment plots and untreated controls. It is suggested that the application of triclopyr + picloram in mesquite-mixed grass communities in the Texas Coastal Bend does not significantly reduce plant and vertebrate species richness and diversity within the first 2 years after treatment.
- Pettit, R.D. 1979. Effects of picloram and tebuthiuron pellets on sand shinnery oak communities. 1979. *Journal of Range Management.*, 32: 196-200.** [See FA 40, 2318]. In May 1971, picloram was applied at the recommended dosage of 7 kg/ha a.i. to sandy rangeland in W. Texas dominated by sand shinnery oak (*Quercus havardii*). In 1973, 1975 and 1976 herbage yields on the treated plots were n.s.d. from untreated plots, but the species composition was dramatically changed with better forage plants increasing and most oak being killed. In further tests picloram or tebuthiuron were applied at 1,3,5 and 7 kg/ha in June 1974, and tebuthiuron at 1 kg/ha in Jan. 1975. Tebuthiuron applied in winter or late spring killed most of the oak at 1 kg/ha, but at higher dosages some of the better forage plants were killed. Picloram killed all the oak at 3,5 or 7 kg/ha, but only partially controlled it at 1 kg/ha. Picloram did not disturb the rest of the plant community as much as tebuthiuron. The herbicides are not recommended for use on poor rangeland, or where there is a shortage of perennial grasses in the ground cover.
- Rice, P.M., D.J. Bedunah, and C.E. Carlson. 1992. Plant community diversity after herbicide control of spotted knapweed. Research Paper-**

Intermountain Research Station USDA Forest Service. INT-460, 6 pp.

Herbicides were applied in 1985 to replicated treatment plots at 4 rangeland sites in W.-central Montana with light to moderate spotted knapweed (*Centaurea maculosa*) infestations. Plant community diversity was determined for 2 seasons before the herbicide treatments and for 2 years after spraying. Although knapweed suppression was high, the communities were not converted to grass monocultures. Herbicide-caused depressions in community diversity measurements were small and transitory. Plots treated with Tordon (picloram at 0.25 lb/acre) and Curtail (clopyralid + 2,4-D at 0.19 + 1.0 lb) showed a small 1-year post-spray decline. Diversity in those plots began to increase relative to the untreated plots during the 2nd post-spray growing season. Stinger (clopyralid at 0.25 lb) had the least effect on diversity. No large declines in diversity were caused by these herbicide treatments, and the small depressions observed were probably transitory. Community response data collected from a limited set of pilot study plots suggested that the herbicide treatments increased diversity by 3 years post-spray. Only small amounts of herbicide were leached below 25 cm. Herbicide residues in the soil at 25- to 50-cm depth were generally undetectable and did not exceed 26 ppb at 30 d and trace levels after 1 year. No herbicide residues were detected after 2 years.

Rice, P.M., J.C. Toney, D.J. Bedunah, and C.E. Carlson. 1997. Plant community diversity and growth form responses to herbicide applications for control of *Centaurea maculosa*. Journal of Applied Ecology. 34: 1397-1412. A field experiment conducted from 1988-95 in western Montana, USA, compared the effects of herbicide treatments (picloram, clopyralid and clopyralid + 2,4-D, each at two timings and the recommended rates for control of the exotic forb *Centaurea maculosa*), on the structure and species diversity of native plant communities. The floristic composition of replicated treatment plots was sampled before spraying and for 3 years after the initial herbicide applications at two grassland and two early seral forest sites. Following the third year post-spray measurements, half the treatment plots were randomly selected to be resprayed and community sampling was continued for two more years. Diversity was quantified as species richness and Shannon diversity index. Standing crops by growth form were estimated by double sampling at the conclusion of the experiment. Herbicide treatments had a high efficacy on the target weed, shifting the plant communities back to a grass-dominated structure. Depressions in plant community diversity were small and transitory. In the third year after the initial applications, there were no significant differences among treatments, and some herbicide-treated plots had begun to surpass the untreated plots in community diversity measures. With most treatments, respraying 3-4 years after the initial applications did not reduce plant diversity compared to untreated levels. Late season applications, made after most herbicide-susceptible forbs had entered summer drought-induced dormancy, minimized impacts on plant community diversity. The behaviour of herbicide residues in the soil is described in relation to community-level effects.

Implications of the results for exotic weed management in conservation settings are discussed.

Tanner, G.W., J.M. Inglis, L.H. Blankenship. 1978. Acute impact of herbicide strip treatment on mixed-brush white-tailed deer habitat on the northern Rio Grande Plain. Journal of Range Management 31: 386-391. Aerial sprays of 2,4,5-T + picloram (1:1) were applied to 1800 ha of mixed brush pasture (6 vegetation types made up of *Aloysia lycioides*/*Prosopis glandulosa*/*Acacia rigidula*/*A. tortuosa*/*Opuntia lindheimeri*) in Texas, at 0.56 and 1.12 kg/ha in 1000 m and 500 m wide strips respectively, in May, 1973. Numbers of white-tailed deer (*Odocoileus virginianus*) were analysed by pellet group counts and aerial censuses, and decreased from 312 to 51 by Aug. 1973, but increased to above normal in the next winter (following succulent woody plant regrowth), returning to normal by April 1974. Deer did not rearrange their use of the area to favour untreated or less treated strips. Woody plant cover was significantly reduced on treated strips, but brush ht. was reduced only at higher treatment rates; screening at deer ht. was unaffected, and density of live brush stems was reduced by less than 20%.

Thompson, M.J. 1996. Winter foraging response of elk to spotted knapweed removal. Northwest Science 70: 10-19. Picloram was used to convert 110 ha of an historically cultivated grassland (hereafter referred to as old-field) from being dominated by spotted knapweed (*Centaurea maculosa*) on an elk (*Cervus elaphus*) winter range in western Montana. About 30 ha were left untreated. It was hypothesized that knapweed removal would not: affect winter foraging activity of elk; affect winter diets; vary in its effects on foraging activity and diets across the first four winters after knapweed removal; and affect elk population distribution. Elk walked in adjacent knapweed and grass stands indiscriminately, but foraged almost exclusively in the grass stand. Diets sampled before and after knapweed removal were not rank-correlated, and forage species characteristic of the old-field (i.e., *Poa*, *Bromus* and *Phleum*) ranked higher in diets after knapweed removal. Elk foraging activity was significantly higher in the first winter than in subsequent winters. A higher proportion of the estimated elk population used the old-field after knapweed removal. It was concluded that abundant green grass attracted elk to the old-field in the first winter after knapweed removal. Cured grass apparently attracted elk foraging activity and affected winter diets to a lesser extent in subsequent winters.

Thompson, M.W., M.G. Shaw, R.W. Umber, J.E. Skeen, and R.E. Thackston. 1991. Effects of herbicides and burning on overstory defoliation and deer forage production. Wildlife Society Bulletin 19: 163-170. The effectiveness of Tordon (picloram + 2,4-D), Velpar (hexazinone) and Graslan (tebuthiuron), and controlled burning in providing openings and increasing deer (*Odocoileus virginianus*) forage was studied in an oak/hickory (*Quercus*/*Carya*) forest in northeastern Oklahoma. Overstorey defoliation and understorey standing biomass were measured for 4-5.5 yr. Deer forage availability was improved by

canopy reduction, and the forb component was enhanced most when Tordon injection was combined with burning.

Wardle, D.A., K.S. Nicholson, and A. Rahman. 1994. Influence of herbicide applications on the decomposition, microbial biomass, and microbial activity of pasture shoot and root litter. *New Zealand Journal of Agricultural Research*. 37: 29-39. Pure swards of each of 4 pasture species (*Lolium perenne*, *Trifolium repens*, *Senecio jacobaea* and *Carduus nutans*) were grown under greenhouse conditions and were sprayed with either 2,4-D + picloram at 1.5 + 0.38 kg/ha or glyphosate at 1.44 kg, or left unsprayed. After the sprayed swards died, all above-ground and below-ground tissue was harvested, air-dried, and placed in nylon mesh litter-bags which were placed in a field with a Horotiu silt loam soil near Hamilton during 1991-92. Decomposition, microbial basal respiration, and substrate-induced respiration (proportionally related to the glucose-responsive microbial biomass) of this litter was then monitored over 338 d. Both herbicide treatments inhibited decomposition of *T. repens* and *L. perenne* shoot tissue and *C. nutans* root tissue, but stimulated that of *C. nutans* shoot tissue, indicating that herbicides may influence decomposition of different species in different ways; the possible reasons for this are discussed. However, it was suggested that the rapid decomposition of most of the tissues considered in this study shows that the herbicides are unlikely to exert substantial long-term effects on plant litter persistence. Microbial basal respiration and substrate-induced respiration of most of the litter types considered were initially very strongly enhanced by both herbicide treatments; however, this effect was highly transitory for all tissue types except one, and for some of the tissue types a strong inhibition of these microbial variables in the herbicide treatments followed. The retardation of leaf litter decomposition after herbicide treatment was often associated with reduced microbial activity and biomass, indicating strong linkages between soil-associated microflora and decomposition processes.

ENVIRONMENTAL FATE - PLANTS

- Abramova, K.A., T.D. Panasyuk, and E.A. Kalinina. 1973. Determination of Tordon 22-K in soil and plants by a biological method. Khimiya v Sel'skom Khozyaistve. Vol. 11: 298-300. Russian** Tordon 22-K picloram-potassium 24.9% was applied at 0.0036-0.0327 mg/kg to a 2:2:1 mixture of peat + soil + sand, in which French beans were sown as bioassay plants, in the glasshouse. The surface area of whole leaves was taken as a quantitative assessment of picloram residues in the soil. The sensitivity of the method was 0.003-0.004 mg/kg. Residues in the soil of 0.1 mg/kg reduced grain yields of wheat by 20% while 0.2 mg/kg almost entirely prevented grain formation. Residues in wheat straw from plants grown in soil containing 0.2-0.4 mg picloram/kg were determined by macerating plant tissues, mixing them in soil and leaving for 1-60 days before sowing French beans as bioassay plants; residues in the straw after 20 days in the soil averaged 5.47 mg/kg for the low application and 12.28 mg/kg for the high application.e.
- Abramova, K.A., T.D. Panasyuk, E.A. Nikanorova, and V.F. Vasil'chenko. 1975. Picloram behaviour in water, soil and plants. Materialy 10go Mezhdunarodnogo Simpoziuma Stran-Chlenov SEV, Pushchino, SSSR. Vol. 2: 98-100. Russian.** Field trials in 1968-73 on a dark-chestnut soil in a region of inadequate rainfall showed that 1 kg picloram/ha persisted in the top 40 cm of soil for 46 months and 2% of the amount originally applied was recovered from the top 80 cm of soil. Picloram residues in plants growing on treated soil amounted to 6 mg/kg found in proso millet straw and 0.2 mg/kg found in the grain. Maize plants growing in pot soil containing 1.5 mg picloram/kg accumulated 83 mg picloram/kg during 6 months. Cereal plants assimilated 1-3% of the applied amount and maize up to 10% with adequate moisture and dense sowing. In trials in 400-g capacity pots, 2 ml picloram/pot completely killed French beans and tomatoes and 4 ml/pot inhibited sunflower growth by 50%.
- Berezovskii, M. Ya. 1974. Residues of herbicides in plants and soil. Doklady Vsesoyuznoi Akademii Sel'skokhozyaistvennykh Nauk imeni V.I Lenina. 6: 16-18. Russian.** Picloram at 2-2.5 kg/ha completely kills Russian knapweed [*Centaurea repens*] but residues persist in soil for >3 years. Although proso millet and maize are not sensitive to picloram at 1.5-2 kg/ha, picloram residues were found in these plants 3 years after the soil had been treated. These residues in tolerant crop plants are a potential health hazard to people and animals. Dicamba at 15-20 kg/ha was completely degraded in soil within 1 year but its metabolite 3,6-dichlorosalicylic acid persisted longer in soil and was detected in crop plants 2-3 years after application to soil. Although dicamba and its metabolite have a low toxicity to animals, the application of high rates of dicamba might lead to the accumulation of metabolites in crop products above the official tolerance level.

- Berezovskii, M. Ya. and A.M. Krumzdorov 1974. Picloram residues in soils and plants. Doklady TSKhA. No. 180, II, 151-156. Russian.** Trials were carried out in 1969-70 on permanent plots on a pale-chestnut, calcareous-solonchic, heavy loam soil in the low-rainfall area of the Stavropol' District. Picloram-potassium (as Tordon-22K) at 1.5-3 kg/ha was compared with dicamba-dimethylamine (as Banvel D) 10-15 kg/ha for the control of Russian knapweed [*Centaurea repens*] with application at the shooting stage. A little regrowth was noted at 2 years after the application of dicamba at 10-15 kg/ha whereas picloram 1.5-3 kg/ha still showed complete control after 3 years. Dicamba residues were determined by t.l.c. and picloram residues by a bioassay technique; [the herbicide is extracted from plant material by incubating the plant samples in soil and French beans are grown on this soil]. Picloram applications of 1.5-2 kg/ha left residues in the top 40 cm of soil for >4 years whereas dicamba was inactivated within 1 year. Although maize is relatively tolerant to picloram, residues 2 years after soil application accumulated in plants (especially leaves) and were not inactivated before harvest; residues in plants increased with the rate of the initial application. Picloram residues from applications of 1 kg/ha were detected in proso millet leaves 4 years after the application to the soil. The use of picloram is recommended on uncropped land only or on patches of heavy infestation of *C. repens*.
- Bovey, R.W., F.S. Davis, and M.G. Merkle. 1967. Distribution of picloram in huisache after foliar and soil applications. Weeds 15: 245-9**
- Brady, H.A. 1978. Picloram and dicamba persistence in forest environments [Pesticide residues in litter under *Quercus stellata*, toxicity to cucumbers]. Proc. South. Weed Sci. Soc. 28: 230-235.**
- Cessna, A.J., J. Waddington, and S. Bittman. 1989. Residues of 2,4-D and picloram in aspen poplar and soil after application with a roller. Canadian Journal of Plant Science. 69: 205-212.** The use of wipers for herbicide application to brush regrowth in pastures was suggested for reducing damage to the forage understory. Estimates of picloram in the soil around the base of aspen poplar (*Populus tremuloides*) regrowth and of picloram and 2,4-D in poplar tissues were made 84 and 39 d, resp., after a roller application of the herbicides in a 7.3:1 w/w 2,4-D: picloram mixture. Bioassay revealed that 11-16% of the picloram applied reached the soil and that, when the herbicide mixture was applied at a high enough concn to kill the trees, sufficient picloram reached the soil around them to affect legume establishment. Chemical assay revealed that only about 2% or less of the picloram and 2,4-D remained in the poplar tissue and that >80% of this was in the leaves. These residues were unlikely to cause environmental problems because of the small quantities and the slow release from poplar tissue by leaching and decay. The remainder of the applied picloram and 2,4-D was unaccounted for and was assumed lost through metabolism and photochemical degradation.

- Chkanikov, D.I., A.M. Makeev, N.N. Pavlova, and T.A. Nazarova. 1983.**
Formation of picloram N-glucoside in plants. Fiziologiya Rastenii. 30: 95-101. Russian. From sunflower plants treated with ^{14}C -picloram, an acid-labile water-soluble metabolite was isolated and identified as N-(2-carboxy-3,5,6-trichloropyridine-4-yl) glucosamine. The picloram N-glucoside accumulated mainly in the shoot apex throughout the 7-day experimental period. It was not toxic to green *Phaseolus vulgaris* plants and were not translocated out of the treated leaves, and can hence be regarded as an immobilized detoxication product of the herbicide.
- Couture, M. and J.A. Fortin. 1985. Suppression of the vegetation by herbicides, its impact on the dynamics of woody material degradation in the soil. [La suppression de la vegetation par les phytocides, son impact sur la dynamique de la degradation de la matiere ligneuse du sol.]. Revue d'Ecologie et de Biologie du Sol. 22: 271-279. French.** Decomposition of wooden probes over 2 seasons was followed in mor or mull humus with or without application of 28 kg Eramox 80W (atrazine + simazine)/ha or of 67.2 kg Tordon 10K (picloram)/ha. In mull humus Eramox inhibited decomposition during the first season and strongly stimulated it during the second, while Tordon had little effect during the first season but gave a stimulation during the second season. In the mor humus the pattern of effects was similar but the stimulation due to Tordon reached the same level as that due to Eramox during the second season. The high rate of decomposition was similar to that given by application of 336 kg urea/ha. The differences were due to the destruction of the vegetation by the herbicides.
- Ebbersten, S. 1972. Picloram (4-amino-3,5,6-trichloropicolinic acid). Studies concerning persistence in soil and plants and biological methods for determining picloram residues. [Pikloram (4-amino-3,5,6-trikloropikolinsyra). Studier av persistens i jord och växter samt metodstudier rörande biologisk bestämning av pikloramrester]. Uppsala, Institutionen för Vaxtodling, Lantbrukshögskolan 175 pp. Swedish English** This publication is divided into 2 main sections: 1. A literature survey including sections on (a) the effects of picloram on higher plants, soil micro-organisms and higher animals (mammals, birds and fish), (b) the persistence of picloram in plant tissue, soil and water and (c) methods for determining picloram residues. 2. Results of investigations carried out in Sweden during 1966-70 to study persistence and movement in the soil, determination of residues and the effects on following crops of wheat and potatoes.
- Hickman, M.V., C.G. Messersmith, and R.G. Lym. 1989. Picloram Release From Leafy Spurge (*Euphorbia esula*) Roots In The Field. Weed Sci. 37: 167-174.** Picloram release by leafy spurge roots, as affected by picloram rate, plant growth stage, and time intervals after treatment, was quantified under field conditions. Picloram was pipe-wick applied to leafy spurge in the vegetative, flowering, and seed-filling growth stages. Percent leafy spurge control was

evaluated and picloram residues were determined in soil samples from 0- to 13-, 13- to 26-, to 39-cm depths taken 1, 2, and 3 weeks after treatment. Leafy spurge was controlled (frequently >85%) by all picloram concentrations applied, although control tended to increase as solution concentration increased. Picloram release from roots was greater from plants treated in the flowering and seed- filling stages than from plants in the vegetative stage. Picloram release from roots generally was correlated with application rate, averaging 490, 820, and 1420 ppbw in soil for the 30, 60, and 120 g ae/L application rates, respectively. Picloram release from roots occurred rapidly with 86% of the picloram detected in the 0- to 13-cm soil depth present by 1 week after treatment. Picloram was detected at all soil depths sampled, but over 84% was in the upper 13 cm and 8% was in both the 13- to 26- to 39-cm depths. Leafy spurge shoots emerged through a 7.5- and 15-cm depth of picloram- treated soil at concentrations up to 1000 ppbw within 14 to 21 days after the untreated control. Picloram soil residue had little effect on leafy spurge root growth.

Hilton, H.W., S.S. Kameda, and N.S. Nomura. 1973. Distribution of picloram residues in sugarcane. J. Agric. and Food Chem. 21: 124-126. ¹⁴C picloram (1.2 mg, 4.8 μ Ci) was supplied to sugar-cane plants (*Saccharum* spp. hybrid H50-7209) growing in nutrient solution when these were about 1 ft in height (6-8 expanded leaves) and the plants harvested after 1, 2, 4, 8 and 13 weeks. ¹⁴C residues were measured in the various component parts of the plant, using combustion analysis with a Parr oxygen bomb. ¹⁴C picloram absorbed through the roots, accumulated in the leaves. Residues retranslocated from older to younger leaves without there being any ¹⁴C detectable in the apical meristem of the primary stalk or in basal suckers prior to leaf expansion. As the ¹⁴C picloram available to the roots declined over a period of 13 weeks, leaf residues reached a maximum and began to decline. A portion of the radioactivity was lost from the plant in senescent abscised leaves. The transfer of picloram from older to younger leaves is attributed to phloem mobility which is supported by the data. Picloram had a constant linear inhibiting effect on the elongation of leaf tissue from the primary spindle.

Lym, R.G. and C.G. Messersmith. 1987. Leafy spurge control and herbicide residue from annual picloram and 2,4-D application. J. Range Manage. 40: 194-198. Annual applications of picloram and picloram + 2,4-D and 2 applications of 2,4-D/year for 5 consecutive years was evaluated for *Euphorbia esula* control. The picloram treatments were evaluated for soil residue. The experiment was located at 2 sites in eastern North Dakota and 1 site in western North Dakota on various soil types. Picloram at 0.28, 0.42 and 0.56 kg/ha provided 48, 75 and 90% control of *E.esula* after 4 annual treatments, resp. Control increased to 85 and 91% when 2,4-D at 1.1 kg/ha was added to the annual treatment of picloram at 0.28 and 0.42 kg/ha, resp. 2,4-D with picloram at 0.56 kg/ha did not increase control compared with picloram alone. Picloram did not accumulate in the upper 15 cm of the soil profile and was generally not detected above the 2 p.p.b.w. level 12 months following each annual

application. Greater picloram residue was found deeper in sandy than clay soil with high rather than low OM. Picloram at 500 and 250 p.p.b.w. was required to reduce *E.esula* seedling emergence and subsequent survival by 50%, resp. Picloram at 125 p.p.b.w. reduced regrowth from root segments of 4 lengths to near zero. Picloram at 8 to 32 p.p.b.w. stimulated seedling emergence compared with the control. Annual application of picloram at low rates gradually controlled *E.esula* but picloram soil residues were not high enough to control subsequent seed germination and shoot regrowth from roots.

- McKinley, R.S. and G.P. Arron. 1987. Distribution of 2,4-D and picloram residues in environmental components adjacent to a treated right-of-way. Report / Ontario Hydro, Research Division ; no. 87-49-K v, 27.** Selective herbicide application to non-compatible tree species is an integral part of vegetation management of Ontario Hydro rights-of-way. Tordon 101 is presently being used to control the growth of non-compatible woody plant species (those which have the potential for interfering with power transmission) on rights-of-way in Northern and Eastern Ontario, whereas 2,4-D and picloram is generally used in Southern Ontario. The study was conducted at two sites along the Des Joachims power corridor located along the eastern boundary of Algonquin Park, including a chain of 4 lakes whose watershed included part of the right-of-way. Sampling for residues in soil, vegetation lake water, sediment and representative fish and mammal species was conducted in areas adjacent to the right-of-way before herbicide treatment and at pre-selected times within a 22-month period after application.
- Michael, J.L. and D.G. Neary. 1993. Herbicide dissipation studies in southern forest ecosystems. Environ. Toxicol. Chem. 12: 405-410.** Results of research on the movement of hexazinone, imazapyr, picloram, and sulfometuron in first-order watersheds in the southern United States are presented. Herbicides contaminate surface waters to varying degrees, depending on application rate, method of application, product formulation, and site-specific characteristics. Highest concentrations are observed in streams in ephemeral pulses during the first three storm events after application. Streamside management zones greatly reduce the amount of herbicide entering streams from forestry applications. Soil persistence of herbicides is highly variable and a function of many site characteristics. Plant residues have been monitored and found to dissipate rapidly, with half-lives < 40 d.
- Miller, K.V. and Chapman B.R. 1995. Responses of vegetation, birds and small mammals to chemical and mechanical site preparation, In, FRI Bulletin, No 192; Popular Summaries from Second International Conference on Forest Vegetation Management. R.E. Gaskin and J.A. Zabkiewicz (eds). New Zealand Forest Research Institute, Rotorua, New Zealand. p 146-148 1995**
- Newton, M., A. Allen, D.E. White, B.E. Kelsas, and F. Roberts. 1982. Deposits and degradation of herbicides in sclerophyll brushfield foliage.**

Proceedings of the Western Society of Weed Science. Vol. 35, 45-47.

2,4-D-ester at 2.2 and 3.3 kg/ha, triclopyr-amine at 2.2 and 4.4 kg/ha, triclopyr-ester at 1.65 and 3.3 kg/ha and picloram-K at 0.55 kg/ha were applied from the air on to brush (mainly *Lithocarpus densiflorus*) 1-3 m high representing 6-8 years development after clearcutting conifer stands. Residues of the herbicides in the foliage of the canopy and browse layers of the brush and in the litter underneath were examined 0, 18, 37, 79, 153 and 325 days later. The canopies contained higher levels of all the herbicides than the browse layers. The lower foliage intercepted between one-half and one-sixth the amount intercepted by the canopy. Residues in litter were highly variable, ranging from the levels found in the canopy to less than one-tenth that amount. All the herbicides showed substantial degradation with time. Picloram degraded most rapidly with a half-life of <1 month. 2,4-D was the most persistent with a half-life of 6 months. Initially, triclopyr-amine declined more rapidly than the ester, but rates were similar after 2 months.

Newton, M., F. Roberts, A. Allen, B. Kelsas, D. White, and P. Boyd. 1990.

Deposition and dissipation of three herbicides in foliage, litter, and soil of brushfields of southwest Oregon. J. Agric. Food Chem.: American Chemical Society. 38: 574-583. The herbicides 2,4-D ((2,4-dichlorophenoxy)acetic acid), triclopyr ([3,5,6-trichloro-2-pyridinyl)-oxy]acetic acid), and picloram (4-amino-3,5,6-trichloro-2-pyridinecarboxylic acid) were applied by helicopter to test grids in mountainous southwestern Oregon brushfields on shallow, rocky, clay loam soils. Herbicide concentrations were observed in crown twigs and foliage, browse twigs and foliage, litter, and soil. Initial deposits in the target area ranged from 61 to 115% (average 82%) of the nominal dosage, with coefficients of variation of 29-104%. Initial concentrations in crown foliage were 44-mg/kg for each kilogram per hectare applied; deposits on browse foliage and litter were 38% and 74%, respectively, of crown concentrations. Early after application, decreases were more rapid for salt formulations than for esters. After 79 days, decrease of all herbicides was slight in foliage, but continued in soil. Picloram disappeared most rapidly and was least mobile, followed by triclopyr and 2,4-D. Triclopyr and 2,4-D remained nearly constant in foliage through winter. Disappearance was rapid in litter.

Ralps, M.H., G.D. Manners, and D.R. Gardner. 1998. Toxic alkaloid response to herbicides used to control tall larkspur. Weed Science 46: 116-119.

Herbicides have been used to control tall larkspur to prevent cattle deaths. There is some evidence that tall larkspur may become more toxic and more palatable during the desiccation process following herbicide treatment. A series of studies were conducted to measure toxic alkaloid concentration in tall larkspur following treatment with metsulfuron, picloram, and glyphosate. Herbicides were applied to larkspur plants grown in a greenhouse (1990), to field plots infested with larkspur (1993), and to individual larkspur plants in the field (1995). Leaves were harvested up to 14 or 28 d following treatment, and

toxic alkaloids were measured. Metsulfuron increased toxic alkaloid concentration in the 1990 greenhouse study and in 1993 field plot studies, and increased both concentration and absolute amount of toxic alkaloids in 1995 individual plant treatments. Alkaloids in plants treated with picloram either remained unchanged or declined slightly in all three studies and were similar to control plants. In the 1995 study, glyphosate caused the relative concentration of alkaloids to increase as the plants desiccated, but the absolute amount of alkaloids was similar to control plants. Picloram and glyphosate did not reduce alkaloid concentration; thus, the risk of poisoning remains until plants desiccate. Metsulfuron increased alkaloid concentration, thus increasing the risk of poisoning. Cattle should not be allowed to graze sprayed areas until larkspur desiccates and withers.

Sterling, T.M. and H.S. Jochem. 1995. Uptake, translocation, and metabolism of picloram and metsulfuron methyl by two locoweed species. Weed Science 43: 13-17. The locoweeds, woolly loco and silky crazyweed, contribute to livestock poisoning in the western United States. Differences in response of these two locoweeds to foliar-applied picloram and metsulfuron was investigated by evaluating differences in herbicide uptake, translocation, and metabolism. Silky crazyweed compared to woolly loco was more than 10 times as sensitive to increasing rates of either herbicide. The two species absorbed 8 to 15%, and 11 to 17% of applied picloram and metsulfuron, respectively. Translocation of picloram and metsulfuron out of treated leaflets of either species was less than 3% of that absorbed after 96 h. Approximately 70 and 100% of the absorbed herbicides remained as picloram and metsulfuron, respectively, in both species. Therefore, differences in picloram or metsulfuron uptake, translocation, and metabolism appear inadequate to account for the differential response to each herbicide by the two locoweed species. Selectivity differences between these locoweed genera to picloram and metsulfuron most likely are due to sensitivity differences at sites of action.

Watson, V.J., P.M. Rice, and E.C. Monnig. 1989. Environmental fate of picloram used for roadside weed control. J-Environ-Qual: American Society of Agronomy. v. 18: 198-205. The herbicide picloram (4-amino-3,5,6- trichloro-2-pyridine carboxylic acid) was applied to control spotted knapweed (*Centaurea maculosa* Lam.) in the northern Rockies to determine persistence in soils and vegetation, losses by photodegradation, rainfall induced migration, and potential contamination of surface and groundwater. Two sites were selected to represent best case and worst case conditions (within label restrictions) for on-site retention of picloram. A valley bottom terrace was treated with 0.28 kg/ha of picloram in the spring of 1985, and sampled over the following 445 d. In the spring of 1986, 1.12 kg/ha of picloram was applied to both sides of a minimal construction logging road extending 4 km along a stream (102 to 815 m³) that drains a granitic upper mountain watershed. Of the 17.1 km² watershed, 0.15% (2.5 ha) was sprayed. Vegetation, soils, surface water, and groundwater near the road were sampled during the 90 d following

application. At the valley bottom site, 36, 13, and 10.5% of the picloram applied persisted after 90, 365, and 445 d, respectively. At the mountain watershed site, 78% persisted after 90 d, and picloram was not detected in the surface or groundwaters during the 90 d following application. Depending on the timing of delivery, as little as 1% or less of the application could have been detected after delivery to the stream. Loss by photodegradation during the first 7 d after treatment was important at both sites.

ENVIRONMENTAL FATE - SOILS

Aamissepp, A. and H. Nilsson. 1982. Control of herbs and woody plants in meadows and wooded pastures. Weeds and Weed control. 23rd Swedish Weed Conference, Uppsala, 1982. Sveriges Lantbruksuniversitet. Uppsala; Sweden. Vol. 2, 290-307. Picloram was tested alone or in mixtures with bentazone and bromofenoxim as alternatives to phenoxy acids, the use of which is prohibited in Sweden in meadows and wooded pastures to which the public have access. Picloram at 1 kg/ha or at 0.5 kg + Basagran 480 (bentazone) at 2.5 litres/ha or + Faneron 50 WP (bromofenoxim) at 2.5 kg/ha controlled broad-leaved weeds, including *Taraxacum officinale*, *Ranunculus* spp. and *Cirsium* spp. with the mixtures, to the benefit of grasses. These treatments were more persistent than mixtures of Basagran + Faneron with dicamba. Among herbicides tested for brush control, picloram gave the most rapid effect, combined with good residual control; glyphosate and fosamine proved equally good for long term control. Two trials were conducted to investigate the persistence and mobility of picloram in the soil: results showed considerable residues at 35-40 cm depth 4 months after applying the herbicide: residues were still present 1 yr after treatment both inside and outside the sprayed plots. Horizontal movement of at least 2 m was also recorded.

Abramova, K.A. T.D. Panasyuk, and E.A. Nikanorova. 1977. The persistence of Tordon 22K [picloram-potassium] in soil and its residual effects on crop plants. Khimiya v Sel'skom Khozyaistve. 15: 55-58. Russian. In trials in Stavropol' and Zaporozh'e provinces, picloram at 1 kg/ha, applied in autumn, gave almost complete control of Russian knapweed [*Centaurea repens*]. Herbicide inactivation was investigated over a period of 46 months after application. Proso millet [*Panicum miliaceum*] and maize were the most resistant cereal crops to picloram residues and crops could be sown in the year following treatments; yields were reduced but were higher than in knapweed-infested fields. Winter wheat could not be sown for 3 years after application of 1 kg/ha. It was found that picloram residues were present in plant tissues at concns. many times greater than those in the soil and both residues in soil and in crop debris could put sensitive crops at risk.

Abramova, K.A., T.D. Panasyuk, and E.A. Kalinina. 1973. Determination of Tordon 22-K in soil and plants by a biological method. Khimiya v Sel'skom Khozyaistve 11: 298-300. Russian. Tordon 22-K picloram-potassium 24.9% was applied at 0.0036-0.0327 mg/kg to a 2:2:1 mixture of peat + soil + sand, in which French beans were sown as bioassay plants, in the glasshouse. The surface area of whole leaves was taken as a quantitative assessment of picloram residues in the soil. The sensitivity of the method was 0.003-0.004 mg/kg. Residues in the soil of 0.1 mg/kg reduced grain yields of wheat by 20% while 0.2 mg/kg almost entirely prevented grain formation. Residues in wheat straw from plants grown in soil containing 0.2-0.4 mg picloram/kg were determined

by macerating plant tissues, mixing them in soil and leaving for 1-60 days before sowing French beans as bioassay plants; residues in the straw after 20 days in the soil averaged 5.47 mg/kg for the low application and 12.28 mg/kg for the high application.e.

Abramova, K.A., T.D. Panasyuk, E.A. Nikanorova, and V.F. Vasil'chenko. 1975. Picloram behaviour in water, soil and plants. Materialy 10go Mezhdunarodnogo Simpoziuma Stran-Chlenov SEV, Pushchino, SSSR. Vol. 2: 98-100. Russian. Field trials in 1968-73 on a dark-chestnut soil in a region of inadequate rainfall showed that 1 kg picloram/ha persisted in the top 40 cm of soil for 46 months and 2% of the amount originally applied was recovered from the top 80 cm of soil. Picloram residues in plants growing on treated soil amounted to 6 mg/kg found in proso millet straw and 0.2 mg/kg found in the grain. Maize plants growing in pot soil containing 1.5 mg picloram/kg accumulated 83 mg picloram/kg during 6 months. Cereal plants assimilated 1-3% of the applied amount and maize up to 10% with adequate moisture and dense sowing. In trials in 400-g capacity pots, 2 ml picloram/pot completely killed French beans and tomatoes and 4 ml/pot inhibited sunflower growth by 50%.

Agriculture Canada, Research Station, Kentville. 1976. Research Branch Report 1975, pp. 17-30. Picloram residues. The potassium salt of picloram (Tordon 22K) at 4.48 kg/ha (2 p.p.m.) was soil-incorporated to a depth of 15 cm. Analysis of the soil 18, 63, 145, 337, 504, 690 and 843 days later showed the presence of picloram at 1.86, 1.78, 1.32, 0.7, 0.28, 0.12 and 0.02 p.p.m., respectively. Soil containing 1.32 p.p.m. picloram inhibited the growth of carrots, parsnips, potatoes, table beets and rutabagas sown in the glasshouse. One year after the application of picloram, the growth of sweet corn and oats was reduced by about 20% while beans (*Phaseolus* sp.), parsnips and Swiss chard (*Beta vulgaris* var. cicla) failed to grow at all. Picloram residues 1055 days after application were 2.5 parts per billion (109) as determined by a bioassay using bean. P. 25. Test for picloram. A rapid, sensitive and specific fluorescence test for picloram was developed. Sulphuric acid 36 N solution was added to the dry residue in quartz tubes or on a white porcelain plate. Under short wavelength UV radiation, yellow fluorescence was observed. The test can also be carried out using glass test tubes and long wavelength UV radiation but this method is not so sensitive.

Agriculture Canada, Research Station, Regina. 1976. Research Branch Report 1975, pp. 265-272. P. 268. Herbicide behaviour in the environment. Results of investigations into the fate of herbicides in the environment are reported. The persistence of atrazine in Brown soils appeared to be related to Ca content and pH of the soil. The order of leachability of 3 uracil herbicides in a range of soil types was bromacil > terbacil > lenacil. Residue levels of 2,4-D of 0.002 and 0.017 $\mu\text{g}/\text{m}^3$ were detected in the air above Regina in June and July. The rate of volatilization of 2,4-D isooctyl ester from Asquith sandy loam soil was high for the first 24 h, after which time volatilization was negligible. The

degradation of C-2242 (chlortoluron) in steam-sterilized soil was negligible, indicating that microbiological processes are important for the breakdown of this herbicide. Residues from spring applications of benazolin, benzoylprop, alachlor, nitrofen, profluralin and picloram were detectable the following October while asulam had disappeared. Benzoylprop-ethyl, alachlor, nitrofen and profluralin were detected only in the top 5 cm of soil whereas residues of benazolin, picloram and the acid derivative of benzoylprop were observed at lower depths. In a study of the persistence of 4 herbicides in irrigation water, simazine was the most persistent, followed by atrazine, monuron and bromacil.

Agriculture Canada, Research Station, Regina. 1979. Research Branch Report, 1976-1978, pp. 325-333. Herbicide behaviour in the environment: herbicide residues in soils. In a 3-year field study several herbicides were applied in early May of each year and the residues remaining in the 0 to 5- and 5 to 10- cm soil depths were measured at 5, 13 and 17 months. Asulam, dicamba, bromoxynil, bromoxynil + MCPA, propanil, 2,4-D and 2,4,5-T were not carried over from one growing season to the next, when applications were made in May. Herbicides applied during the summer or autumn were sometimes carried over, especially if the soil was dry. Slight carry-over (5-15% of the original application) was noted with alachlor, atrazine, benazolin, benzoylprop-ethyl, diclofop-methyl, dichlobenil, dinitramine, EPTC, flamprop-methyl, tri-allate and trifluralin. Moderate carry-over (15-30%) was observed with linuron, nitrofen, picloram, profluralin and simazine. Persistence data with picloram was difficult to assess since the herbicide was leached readily. The rates of degradation of tri-allate and trifluralin were the same when the chemicals were applied alone or together.

Baarschers, W.H., J.G. Donnelly, and H.S. Heitland. 1988. Microbial toxicity of triclopyr and related herbicides. Toxicity Assessment. 3: 127-136. Microbial toxicity of triclopyr was measured with several microorganisms in comparison with 2,4-D and picloram. Growth inhibition of three fungi (*Trichoderma viride*, *Mortierella isabellina*, and *Saprolegnia parasitica*) was measured in terms of colony size on agar plates and in terms of cell counts for two algae (*Chlorella vulgaris* and *C. pyrenoidosa*). Dehydrogenase measurement by a direct 2-(4-iodophenyl)-3-(4-nitrophenyl)-5-phenyl tetrazolium chloride method was used for the bacteria *Pseudomonas pictorum* and *Arthrobacter globiformis*. Dose-response curves were determined to obtain EC50 values for triclopyr, 2,4-D, picloram, their commonly used amine salts, and the degradation products, 3,5,6-trichloro-2-pyridinol, 2,4-dichlorophenol and decarboxy picloram. Toxicities of triclopyr and 2,4-D were similar in most cases, and both compounds were more toxic than picloram. The 3 degradation products were substantially more toxic than the respective parent compounds. The algae were most sensitive and gave much lower EC50 values than the fungi and bacteria.

Baur, J.R., R.D. Baker, R.W. Bovey, and J.D. Smith. 1972. Concentration of picloram in the soil profile. Weed Science 20: 305-309. The concn. of picloram residues in a fine sandy loam soil was studied to a depth of 2.4 m for a

period of 2 years after the application of a rate of 1.12 kg/ha. Thirty days after application residues of 93 ppb and <5 ppb were recovered from the 0- to 15-cm and 46- to 122-cm soil depths respectively. After 6 months residues were between 5 and 10 ppb at the 0- to 183-cm level and <5 ppb at the 198- to 244-cm. depth. After one year residues to depths of 244 cm were <5 ppb. Residues one year after the application of picloram at 3.36 kg/ha either as polymerized spray or granules or conventional spray or granules were likewise sufficiently reduced to allow growth of most herbaceous species. Significantly greater residues occurred in soils treated with conventional spray rather than those treated with the polymerized spray. Likewise, conventional sprays resulted in higher soil residues than conventional granules during the early sampling period. Residue levels 180 days after treatment showed no significant differences between formulation.

Berezovskii, M. Ya. 1974. Residues of herbicides in plants and soil. Doklady Vsesoyuznoi Akademii Sel'skokhozyaistvennykh Nauk imeni V.I Lenina. 6: 16-18. Russian. Picloram at 2-2.5 kg/ha completely kills Russian knapweed [*Centaurea repens*] but residues persist in soil for >3 years. Although proso millet and maize are not sensitive to picloram at 1.5-2 kg/ha, picloram residues were found in these plants 3 years after the soil had been treated. These residues in tolerant crop plants are a potential health hazard to people and animals. Dicamba at 15-20 kg/ha was completely degraded in soil within 1 year but its metabolite 3,6-dichlorosalicylic acid persisted longer in soil and was detected in crop plants 2-3 years after application to soil. Although dicamba and its metabolite have a low toxicity to animals, the application of high rates of dicamba might lead to the accumulation of metabolites in crop products above the official tolerance level.

Berezovskii, M. Ya. and A.M. Krumzdorov 1974. Picloram residues in soils and plants. Doklady TSKhA. No. 180, II, 151-156. Russian. Trials were carried out in 1969-70 on permanent plots on a pale-chestnut, calcareous-solonchic, heavy loam soil in the low-rainfall area of the Stavropol' District. Picloram-potassium (as Tordon-22K) at 1.5-3 kg/ha was compared with dicamba-dimethylamine (as Banvel D) 10-15 kg/ha for the control of Russian knapweed [*Centaurea repens*] with application at the shooting stage. A little regrowth was noted at 2 years after the application of dicamba at 10-15 kg/ha whereas picloram 1.5-3 kg/ha still showed complete control after 3 years. Dicamba residues were determined by t.l.c. and picloram residues by a bioassay technique; [the herbicide is extracted from plant material by incubating the plant samples in soil and French beans are grown on this soil]. Picloram applications of 1.5-2 kg/ha left residues in the top 40 cm of soil for >4 years whereas dicamba was inactivated within 1 year. Although maize is relatively tolerant to picloram, residues 2 years after soil application accumulated in plants (especially leaves) and were not inactivated before harvest; residues in plants increased with the rate of the initial application. Picloram residues from applications of 1 kg/ha were detected in proso millet leaves 4 years after the

application to the soil. The use of picloram is recommended on uncropped land only or on patches of heavy infestation of *C. repens*.

Biggar, J.W. and M.W. Cheung. 1973. Adsorption of picloram

(4-amino-3,5,6-trichloropicolinic acid) on Panoche, Ephrata and Palouse soils: a thermodynamic approach to the adsorption mechanism.

Proceedings Soil Science Society of America 37: 863-868. The adsorption of picloram was studied on Panoche clay loam soil (pH 7.5, 0.9% o.m.) adjusted to pH 4.2 and 1.2, on Ephrata sandy loam soil (pH 7.2, 0.7% o.m.) and on Palouse silty loam soil (pH 5.9, 3% o.m.). The adsorption processes could be described by the Freundlich equation with Freundlich constants, K and 1/n, and percentage of adsorption at 25 deg C being, respectively, 0.21, 0.92 and 3-5.6% for the clay loam soil at pH 4.2; 2.5, 0.93 and 30% for the clay loam soil at pH 1.2; 0.172, 0.99 and 1.9-3.6% for the sandy loam soil; and 1.74, 0.92 and 26-33% for the silty loam soil. The standard free energy (ΔG deg kcal/mol), entropy (ΔS deg cal/mol per degree) and enthalpy (ΔH deg kcal/mol) associated with the adsorption processes were: respectively, -1.2, -14 and -5.3 for the clay loam soil at pH 4.2; -2.98, -59 and -20 for the clay loam soil at pH 1.2; -1.8, -24 and -9 for the sandy loam soil; and -3.11, -3.3 and -4.1 for the silty loam soil. Thermodynamic parameters were useful in assigning adsorption mechanisms to the four picloram-adsorbent-water systems. From summary.

Blackman, G.E., J.D. Fryer, A. Lang, and M. Newton. 1974. Persistence and disappearance of herbicides in tropical soils. The effects of herbicides in

South Vietnam Part B. Working papers. National Academy of Sciences.; Washington, DC; USA, 60 pp. Soil samples could be collected from only one of the forest areas in S. Vietnam that had been sprayed during the war, and could not be collected from alluvial soils. Further, sampling could not be repeated in the following year. However, supplementary experiments were carried out in the Philippines, and evaluations of persistence were made in different agricultural and forest soils (in S. Vietnam and the Philippines) as well as Mangrove soils. Findings were in excellent agreement with other research findings on herbicide persistence in soils. Only where herbicides (2,4-D, 2,4,5-T, picloram) were applied in very massive doses (2,4-D and 2,4,5-T at 1000 lb/acre and picloram 20 lb/acre) do they still persist in phytotoxic quantities. When Mangroves are applied at rates approaching 100 lb/acre of 2,4,-D and 2,4,5-T and more than or equal to 3 lb/acre of picloram, residues are unlikely to damage crops and have no effect on the establishment of seedlings of the major Mangrove species *Rhizophora apiculata* and *Ceripos tagal*. In areas subject to 1-2 herbicide missions, no phytotoxic residues could, in general, be detected after 18 months. Even where all of the spray reaches the ground (unintercepted by foliage), sensitive crops may be safely sown 4-6 wet months after the application of 2,4,-D + 2,4,5-T; resistant plants such as rice and maize may be safely sown 4-6 wet months after application of 2,4-D + picloram. It is concluded that claims that herbicides used during the war have

rendered the soil sterile, permanently or at least for prolonged periods, are without any foundation. [Cf. FA 35, 6161]

- Bondarev, V.S., Yu.Ya. Spiridonov, and V.G. Shestakov. 1986. Effect of sorption on rate of degradation of picloram in soil. Soviet Soil Science. 18: 58-65. Translated from Pochvovedenie (1985) No.7, 54-60.** The degradation of picloram in a soil enriched with activated charcoal is delayed because of increased sorption of the pesticide by the altered soil. The experimental data confirm that the model equations derived earlier can be used to describe the detoxification of picloram, which takes place chiefly in the soil solution.
- Bovey, R.W., F.R. Jr. Miller, J.R. Baur, and R.E. Meyer. 1975. Growth of sorghum and soybeans in picloram-treated soil [Herbicide residues]. J. Agron. 67: 433-436.** This study was carried out to determine the effect of picloram residues in the soil on the growth and dry matter production of sorghum cv. Topland and soybeans cv. Hill. Picloram-potassium at 1.12 kg/ha was incorporated into a Wilson clay loam soil at various intervals (from 1 1/2 to 26 months) prior to sowing the crops. Soil, sorghum and soybeans were analyzed for picloram content at time of harvest and germination tests were carried out with mature sorghum seed. Sorghum grown 12 months after the picloram application showed no reduction in plant stand, dry matter production, flowering or germination. No picloram was detected in sorghum seed produced by plants sown 6 or 12 months after the herbicide application. On the other hand, soybeans sown up to 6 months after the picloram application were completely killed and soybeans sown up to 14 months after the application showed a reduction in growth. Soybeans were sensitive to traces of picloram that were not detectable by gas chromatography 12 months after the herbicide treatment. It is recommended that sorghum should be grown not less than 1 year and soybeans not less than 2 years after an application of picloram at around 1.12 kg/ha.
- Brady, H.A. 1978. Picloram and dicamba persistence in forest environments [Pesticide residues in litter under *Quercus stellata*, toxicity to cucumbers]. Proc. South. Weed Sci. Soc. 28: 230-235.**
- Burgoyne, W., T. Tribble, and H.R. Ric. 1983. The persistence of picloram and 2,4-D in soils at latitudes north of 60° north. Weeds Today. 14: 10-11.** Analysis of soil samples taken during 1977-8 from a number of locations in Alaska showed that residues of up to 0.56 p.p.m. 2,4-D and 0.02 p.p.m. picloram were present 1 yr after spraying along service roads and railways. Extremes in rainfall and temp. in Alaska indicate special caution be taken in applying herbicides.
- Bush, P.B., Y.C. Berisford, J.W. Taylor, D.G. Neary, K.V. Miller, and J.E. Street. 1995. Operational monitoring of forest site preparation herbicides in the coastal plain: assessment of residues in perched water table. In, Herbicide-resistant crops: a bitter or better harvest? Proceedings of the 48th annual meeting of the Southern Weed Science Society, Memphis,**

Tennessee, USA, 16-18 January 1995., Southern Weed Science Society; Champaign, Illinois; USA. p.p115-120. Field trials were conducted during the spring of 1992 in Aiken, South Carolina on a fine loam in loblolly pine [*Pinus taeda*] clear-cut areas to assess the potential movement of Arsenal (imazapyr) at 1 lb/acre, Velpar (hexazinone) at 3 lb and Tordon + Garlon (picloram + triclopyr, resp.) at 2 + 4 lb to shallow groundwater. Monitoring wells were installed at depths of 4 and 8 feet where clay lenses were observed. Results showed significant lateral down-slope movement of picloram and hexazinone under saturated conditions when the slopes exceeded 2%. Triclopyr and imazapyr showed limited potential for lateral movement or movement to the 8 foot perched water table. Levels of hexazinone peaked at 2 months after application and decreased to non-detectable levels at 2 years post-application. The residue magnitude and rate of dissipation were affected by plot slope and position within the plot. Triclopyr and imazapyr were not as mobile or persistent in shallow wells as picloram and hexazinone.

Bussetti, S.G. de-, E.A. Ferreiro, S.G. De-Bussetti. 1996. Effect of picloram concentrations on residues in the soil. [Efecto de la concentracion de picloram sobre su residualidad en el suelo.]. Agrochimica. 40: 304-316. Spanish. Adsorption-desorption of picloram (applied at the recommended application rate) by ten soils of Bahia Blanca (Argentina) was studied. In order to show the effect of concentration on residuality, the N dissipation index is defined. It is possible to calculate - from adsorption isotherms - the number of times the soil should be changed by a new portion until adsorption is lowered to undetectable values. This N index show a good relation with some soil properties, the lower N values corresponding to acid soils with a good supply of organic matter and high cation exchange capacity.

Cessna, A.J., J. Waddington, and S. Bittman. 1989. Residues of 2,4-D and picloram in aspen poplar and soil after application with a roller. Canadian Journal of Plant Science. 69: 205-212. The use of wipers for herbicide application to brush regrowth in pastures was suggested for reducing damage to the forage understory. Estimates of picloram in the soil around the base of aspen poplar (*Populus tremuloides*) regrowth and of picloram and 2,4-D in poplar tissues were made 84 and 39 d, resp., after a roller application of the herbicides in a 7.3:1 w/w 2,4-D: picloram mixture. Bioassay revealed that 11-16% of the picloram applied reached the soil and that, when the herbicide mixture was applied at a high enough concn to kill the trees, sufficient picloram reached the soil around them to affect legume establishment. Chemical assay revealed that only about 2% or less of the picloram and 2,4-D remained in the poplar tissue and that >80% of this was in the leaves. These residues were unlikely to cause environmental problems because of the small quantities and the slow release from poplar tissue by leaching and decay. The remainder of the applied picloram and 2,4-D was unaccounted for and was assumed lost through metabolism and photochemical degradation.

Close, M.E., L. Pang, J.P.C. Watt, K.W. Vincent, and R. Naidu. 1998. Leaching of picloram, atrazine and simazine through two New Zealand soils. Special issue. Contaminants and the soil environment. Geoderma. 84: 45-63.

Picloram, atrazine, simazine, and bromide were applied to two sites, a Te Awa silt loam and a Twyford fine sandy loam, located in Hawkes Bay, New Zealand, in November 1993. Soil water concentrations were monitored at approximately monthly intervals using suction cup lysimeters over the following 640 days. Leaching of all chemicals below 1.1 m was observed at the Te Awa site whereas only bromide (400 days) and picloram (600 days) reached 1.3 m depth at the Twyford site: whereas atrazine and simazine only reached a depth of 0.4 m. Soil half lives and soil sorption coefficients (K_{oc}) for each pesticide were estimated by comparing the observed results with simulations using the GLEAMS model. Picloram was less mobile but more persistent than shown in previously quoted values. Atrazine and simazine, in contrast were more mobile and had the same level of persistence as quoted values. The greater mobility of the pesticides (smaller K_{oc}) at the Te Awa site was possibly a result of preferential flow.

Cseh, C. 1976. Residues of 3,6-dichloropicolinic acid, picloram and dicamba in the soil. [Residualidad en suelo del ácido 3,6-dichloropicolínico, picloram y dicamba, only]. Trabajos y Resúmenes, III Congreso Asociación Latinoamericana de Malezas "ALAM" y VIII Reunión Argentina de Malezas y su Control, "ASAM", Mar del Plata,. Vol 1, 211. Spanish. Stand and yields of soybeans following wheat, treated with various rates of 3,6-dichloropicolinic acid, picloram, dicamba and 2,4-D either 70 or 102 days before sowing the soybeans, were unaffected by residues from the herbicide treatments.

Dennis, D.S., W.H. Gillespie, R.A. Maxey, and R. Shaw. 1977. Accumulation and persistence of picloram (Tordon 10K) in surface water and bottom sediments in West Virginia. Archives of Environmental Contamination and Toxicology 6: 421-433. Ponds and streams in Braxton, Kanawha, Mason, Jackson and Hampshire counties, W. Virginia, were sampled to determine the accumulation, persistence and movement of picloram residues in surface waters and bottom sediments. The highest residue levels of 437 µg/litre in water and 657 µg/kg (dry wt.) in bottom sediments were detected within 1-3 wks after application of Tordon 10K (picloram-potassium 11.6%) pellets at 44.8 kg product/ha. Residue levels in water and sediments decreased with distance from application sites and time since application. From summary.

Deubert, K.H. 1985. Environmental impact of spot treatment on utility rights-of-way. Proceedings, 39th annual meeting of the Northeastern Weed Science Society. 218. Problems in studying the environmental impact of spot-applied herbicides are discussed. Field trials were conducted applying herbicides to ground cover and shrubs assuming 100% and 10% runoff during application based on 18.67 l concentrate/ha. Av. retention by the plants was 50%, while >80% of picloram, 2,4-D and triclopyr remained in the top 10 inch

soil layer. Contamination of ground water with herbicide residues was unlikely under these conditions.

- Donaldson, T.W. 1973. Phytotoxicity of picloram to wheat and lucerne in soil and nutrient solution. Proceedings of the 4th Asian-Pacific Weed Science Society Conference, Rotorua, 239-241.** The phytotoxicity of picloram to wheat and lucerne and the effect of soil type on toxicity were determined by growing the plants in nutrient solution and various soils containing known amounts of herbicide. From 30-40 times more picloram was required to reduce wheat growth by 50% (100 times more in red-brown loam soil) than was required for a similar reduction in lucerne growth. Toxicity to both crops was greatest in the nutrient solution and sandy loam soil and least in clay soil. Minimum concns. reducing crop growth were about 0.1 ppm. for wheat and 0.001 ppm. for lucerne. Picloram residues in soil must be reduced below these levels before wheat or lucerne could be grown without damage. From summary.
- Dowler, C.C., W. Forestier, and F.H. Tschirley. 1968. Effect and persistence of herbicides applied to soil in Puerto Rican forests. Weed Sci. 16: 45-50.**
- Ebbersten, S. 1972. Picloram (4-amino-3,5,6-trichloropicolinic acid). Studies concerning persistence in soil and plants and biological methods for determining picloram residues. [Pikloram (4-amino-3,5,6-trikloropikolinsyra). Studier av persistens i jord och växter samt metodstudier rörande biologisk bestämning av pikloramrester]. Uppsala, Institutionen för Växtodling, Lantbrukshögskolan 175 pp. Swedish English** This publication is divided into 2 main sections: 1. A literature survey including sections on (a) the effects of picloram on higher plants, soil micro-organisms and higher animals (mammals, birds and fish), (b) the persistence of picloram in plant tissue, soil and water and (c) methods for determining picloram residues. 2. Results of investigations carried out in Sweden during 1966-70 to study persistence and movement in the soil, determination of residues and the effects on following crops of wheat and potatoes.
- Esau, R. 1984. Effects of various herbicides on succeeding rotational crops. Twenty-first Annual Alberta Soil Science Workshop Proceedings. Farming for the future. pp. 220-224.** Duplicate trials were conducted at Brooks and Olds, Alberta, on Brown and Black Chernozemic soils, respectively. Selected crops were replanted the following season after herbicidal applications to evaluate the duration and effects of herbicidal residues. Linuron at 1.1 and 2.2 kg/ha and dicamba at 0.5 and 1.0 kg/ha did not produce any phytotoxic symptoms at Olds, although rapeseed was injured by a prior application of linuron at 2.2 kg/ha. Picloram at 26 and 52 g/ha, applied as Tordon 202-C produced significant injury, particularly to potatoes, beans, fababeans, alfalfa and peas at both locations. Picloram two years after application continued to cause crop injury, with more significant carryover at Olds than at Brooks.

Similarly, metribuzin applied at 0.5 and 1.0 kg/ha was more injurious at Olds; it injured mostly cruciferous crops and sugarbeets.

Formoso, F.A. 1981. Effect of picloram residues in the soil on the growth of forage legumes. [Incidencia de residuos de picloram en el suelo sobre el comportamiento de leguminosas forrajeras.]. Revista Tecnica Universidad de la Republica Facultad de Agronomia, Montevideo. 50: 9-21. Spanish.

Two experiments, one on black grumusol and the other on a sandy meadow soil, were conducted to determine the response of *Trifolium repens* (2 cultivars) *T. subterraneum* (3 cultivars), *Lotus corniculatus* and *Medicago polymorpha*, sown 5 months after application of Tordon 101 (picloram 60 g + 2,4-D 240 g) at 1, 2, 3, 4 and 5 litres/ha. Results indicate that many factors are involved including soil type and the presence or absence of plant cover. On the sandy soil, the highest herbicide rate caused 67% reduction in DM production by *T. subterraneum*, cv. Yarloop being the most susceptible. On the grumusol (silty clay soil) DM production by *M. polymorpha* was significantly reduced by Tordon 101 at 4 litres/ha in the presence of 71% plant cover. *T. repens* and *L. corniculatus* were not significantly affected on either soil type. Reduction in DM production occurred only in the first year of the legume crop and only at rates in excess of 3 litres/ha of the herbicide.

Fryer, J.D., P.D. Smith, and J.W. Ludwig. 1979. Long-term persistence of picloram in a sandy loam soil. Journal of Environmental Quality. 8: 83-86.

Picloram was applied to a ryegrass (*Lolium perenne*) sward at 0.05, 0.28 and 1.68 kg ai/ha in June 1967 and again in August of 1969 and 1970. Small amounts of residue were found in soil samples 1 year after application of the low and medium doses. At the highest rate, 5 to 6% of the amount applied was usually recovered 1 year after spraying. Following the final application this residue degraded slowly over 3 years. Analyses of the final samples (222 weeks after spraying) indicated that the residue had declined to about 0.5% of the total applied. In stratified soil samples, residues were found to the maximum sample depth of 90 cm 1 year after the initial application, but 69 weeks after the final application no residue was found below 30 cm. Crops grown on all plots in 1974 did not differ in yield. However, on the plots that had received the highest rate, leaf abnormalities were noted in beans and potatoes and color differences in kale.

Gallina, M.A. and G.R. Stephenson. 1992. Dissipation of [¹⁴C]glufosinate ammonium in two Ontario soils. Journal of Agricultural and Food Chemistry 40: 165-168. The degradation and mobility of glufosinate ammonium was evaluated in laboratory trials using 2 soils, Fox sandy loam and Guelph loam. Soil TLC analysis revealed that ¹⁴C-labelled glufosinate ammonium was slightly more mobile than amitrole and less mobile than picloram in both soils. Two glufosinate ammonium metabolites, 3-(methylphosphinyl)propionic acid (MPPA-3) and 2-(methylphosphinyl)acetic acid (MPAA-2), were more mobile than the parent herbicide in the Fox sandy loam. In the Guelph loam, the MPPA-3 metabolite was again more mobile than

the parent herbicide. However, the MPAA-2 metabolite was significantly less mobile than the parent herbicide. The adsorption coeff. for ^{14}C -labelled glufosinate ammonium in the Guelph loam and Fox sandy loam soils were 0.37 and 0.21, resp. Degradation studies showed that ^{14}C -labelled glufosinate ammonium was rapidly degraded to its MPPA-3 and MPAA-2, and eventually to $^{14}\text{CO}_2$. The half-life of glufosinate ammonium was between 3 and 7 d.

Gomez, C.A. and R. Riveros. 1975. Picloram residues in the soils of the Rio Sinu valley. Revista Comalfi. 2: 110-128. Spanish. Experiments were carried out in Colombia to study (1) the characteristic symptoms of picloram injury in 2 susceptible species, (2) a method for determining precisely the residues of picloram in soils and (3) the persistence of the compound in the climatic conditions of the Rio Sinu valley. Results showed that cucumber was a better test plant than soybean because not only is it sensitive to concns. in the soil as low as 5×10^{-3} $\mu\text{g}/100 \text{ g}$ of soil but it is not killed by concns. as high as 50 $\mu\text{g}/100\text{g}$. Plant height and leaf growth were found to be adequate parameters for determining picloram residues in these plants. Measurements should be made no later than 15 days after planting and supplemented by visual appraisal of toxicity symptoms. On clay soils in high rainfall conditions in the Rio Sinu valley no residues were detected 150 days after apply picloram at 3.2 kg/ha. From summary.

Grover, R. and G.G. Bowes. 1981. Picloram residue levels for the control of leafy spurge regrowth. Canadian Journal of Plant Science. 61: 661-664. The persistence of picloram in the soil was examined following a single application at 2.24 kg/ha or 4 annual applications at 0.56 kg/ha for the control of *Euphorbia esula*. The concn. of picloram in the upper 7.5 cm of soil decreased from 820 p.p.b. immediately after the application of 2.24 kg/ha to between 17 and 52 p.p.b. 3 years later. Picloram residues ranged from 45 to 165 p.p.b. during the 4 years of annual applications. The critical level of picloram in the soil to prevent *E. esula* re-establishment from seed was approx. 50 p.p.b.

Guenzi, W.D. and W.E. Beard. 1976. Picloram degradation in soils as influenced by soil water content and temperature. J. Environ. Qual. 5: 189-192.

Harrell, B.H. Jr. and T.J. Sheets. 1984. Persistence of low levels of picloram in some North Carolina soils and its effects on flue-cured tobacco. Proceedings, Southern Weed Science Society, 37th annual meeting. 1984, 120. In field studies at 3 sites in 1980-82, 0.02-25 g picloram/ha was applied before transplanting tobacco. Yield reductions in the 1st year were significant but no reductions occurred in subsequent years, although at one site plant injury from the high rate was visible 3 years after application. Effects on quality showed a similar pattern. In a laboratory experiment, scintillation spectrometry showed that most of the picloram absorbed by tobacco plants grown in a picloram solution accumulated in the leaves and that concn. >50 p.p.b. in leaves of green tobacco would make leaves unmarketable.

Helbert, S. 1990. Behaviour of four soil-active herbicides in a boreal podzol.

Forest Ecology and Management. 31: 125-152. The results of a field study of herbicide behaviour in an orthic humo-ferric podzol begun in the spring of 1983, on a south-facing slope near Gambo Pond, central Newfoundland, Canada, are presented. Dicamba, hexazinone, tebuthiuron and picloram were applied on four test plots within a clear-felled site of *Picea mariana* (black spruce). The LF, Ae, Bf, Bc and C soil horizons were sampled from 3 to 486 d after application, depending on herbicide. Residue analysis indicated the distribution of herbicides through the soil profile over time, also each herbicide's propensity to leach or persist. All herbicides leached to the Bf horizon, occasionally to the BC horizon, and rarely to the C horizon. More than 75% of residues detected per sample period were found to be from the organic surface layer. The LF horizon was an important residue sink, with 78, 83, 84 and 93% detected per sample period for dicamba, tebuthiuron, picloram and hexazinone, respectively. Ninety percent of dicamba, hexazinone and picloram disappeared in <486 d, whereas the point estimate for tebuthiuron fell outside the range of predictable values (>486 d). Fifty percent disappearance times were: 7-16 d picloram; 9-25 d dicamba; 123-186 d hexazinone; and >296 d tebuthiuron.

Hickman, M.V., C.G. Messersmith, and R.G. Lym. 1989. Picloram Release From Leafy Spurge (*Euphorbia-esula*) Roots In The Field. Weed Sci. 37: 167-174.

Leafy spurge (*E. esula*) was controlled (frequently >85%) by all concn of picloram applied by pipe wick, although control tended to increase as solution concn increased. Picloram release from roots was greater from plants treated in the flowering and seed-filling stages than from plants in the vegetative stage. Picloram release from roots was generally correlated with application rate, averaging 490, 820, and 1420 p.p.b.w. in soil for the 30, 60 and 120 g/litre application rates, resp. Picloram release from roots occurred rapidly with 86% of the picloram detected in the 0- to 13-cm soil depth present by 1 week after treatment. Picloram was detected at all soil depths (0-39 cm) sampled, but >84% was in the upper 13 cm and 8% was in both the 13- to 26- and 26- to 39-cm depths. Leafy spurge shoots emerged through a 7.5- and 15-cm depth of picloram-treated soil at concn up to 1000 p.p.b.w. within 14-21 days after the untreated control. Picloram soil residue had little effect on leafy spurge root growth.

Ismail, B.S. and K. Kalithasan. 1997. Effects of repeated application on persistence and downward movement of four herbicides in soil. Australian Journal of Soil Research. 35: 503-513.

The downward movement and persistence of picloram, terbuthylazine, alachlor, and pendimethalin were studied under field conditions in loamy soil in Malaysia. Picloram and alachlor were applied separately at 0.5 and 2.0 kg a.i./ha, respectively, while terbuthylazine and pendimethalin were each applied at 1.0 kg a.i./ha. Each herbicide was subjected to 2 experimental conditions: (i) the required amount of herbicide applied 2 times, and (ii) the required amount applied 6 times. The

presence of these herbicides in soil was assessed by bioassay techniques. Rice seed (*Oryza sativa*) and long bean (*Vigna sinensis* [*V. unguiculata*; cowpeas]) were used to assay pendimethalin and picloram, respectively, while cucumber (*Cucumis sativus*) was used for both alachlor and terbuthylazine. The results showed that both alachlor and picloram moved downward faster than terbuthylazine and pendimethalin. Both alachlor and picloram, but not terbuthylazine or pendimethalin, could be detected in 5-10 cm layer at 1 day after application (DAA). The phytotoxic residues of picloram, pendimethalin, terbuthylazine, and alachlor were detected in the 0-5 cm layer until 84, 56, 49, and 35 DAA (2 applications), respectively. However, after 6 applications, the phytotoxic residue of these herbicides in the top layer was reduced. The results show that pendimethalin was less mobile than the other herbicides. The half-lives of picloram, pendimethalin, terbuthylazine, and alachlor were 9.7, 6.4, 6.0, and 4.4 days, respectively, after 2 applications, but after 6 applications, the half-lives of these herbicides were shorter.

Johnsen, T.N. and W.L. Warskow. 1980. Effects of fall burning of chaparral woodland on soil residues of picloram. Weed Science. 28: 282-284. Residue of picloram aerially sprayed onto a central Arizona chaparral stand was markedly reduced in the surface 7.6 cm of soil by an autumn burn conducted 5 weeks later. Control of *Quercus turbinella* was also reduced. From summary.

Johnsen, T.N. Jr. 1980. Picloram In Water And Soil From A Semi Arid Pinyon Pinus-Edulis And Juniper Juniperus-Osteosperma Watershed. J. Environ. Qual. 9: 601-605. A mixture of picloram (4-amino-3,5,6-trichloropicolinic acid) at 2.8 kg acid equivalent (ae)/ha and 2,4-D (2 herbicides) at 5.6 kg acid equivalent/ha was aerially applied onto 113 ha of a 146 ha pinyon-juniper watershed (*J. osteosperma* and *P. edulis*, respectively), in north-central Arizona [USA]. Picloram residues in runoff water and soil were monitored. Picloram was detected in runoff water leaving the treated area for 30.5 mo. after application. The highest concentration, 320 ppb, was in the initial runoff after treatment. A total of 1.1% of the picloram applied left the treated area in runoff water. Picloram was not detected farther than 5.6 km downstream. The picloram concentration was relatively constant during runoff events unless water from snow melt or from an untreated area mixed with the runoff from the treated area. Less picloram came from an area with individually treated trees than from an area with broadcast application. Dip (grab), single-stage flood, or splitter-box water samples all gave comparable picloram contents from the same location with the same runoff event. Picloram was detected in the soils for 44 mo., mainly below the 45 cm depth down to bedrock at 122 cm.

Johnsen, T.N. Jr. and W.L. Warskow. 1980. Picloram dissipation in a small southwestern stream. Weed Sci. 28, 612-615. Picloram (4-amino-3,5,6-trichloropicolinic acid) injected directly into a small, central Arizona stream was lost by normal stream flow actions, such as the mixing of fast- and slow-moving water, and the interchange of surface and subsurface water in gravel and sand beds along the stream. Picloram was injected at a concentration of

6.26 ppmw; the maximum amount detected was 2.362 ppmw at 0.4 km downstream, 0.943 ppmw at 0.8 km, 0.316 ppmw at 1.6 km, 0.014 ppmw at 3.2 km, 0.001 ppmw at 6.4 km, and none further downstream. Picloram was detected near the limits of detection (0.001 to 0.004 ppmw) 2 days after injection at the 0.4-, 0.8-, and 1.6-km sites. In photodegradation tests, sunlight decomposed 57% of the picloram in containers after 8.8 h of exposure.

Jotcham, J.R., D.W. Smith, and G.R. Stephenson. 1989. Comparative persistence and mobility of pyridine and phenoxy herbicides in soil. Weed

Technology 3: 155-161. Bioassays with soyabeans and lentils were used to compare the persistence of 2,4,5-T, triclopyr and picloram in soil after applying 0.038, 0.38 and 3.8 kg/ha under field conditions. Soil samples were collected 1-269 days after spraying and were kept frozen until growth room bioassays were conducted. Triclopyr was slightly less persistent than 2,4,5-T, but neither herbicide was biologically active during the next season. At least 90% of picloram disappeared within 7 months, but its biological activity was more persistent than that of either triclopyr or 2,4,5-T. Nine months after treatment, neither lentils nor soyabeans could be grown in soil treated with picloram at 3.8 kg/ha. Triclopyr and 2,4-D had similar soil TLC mobilities in 4 different soils. Picloram was significantly more mobile than either triclopyr or 2,4,5-T, primarily due to its lower adsorption in the soils examined.

Kirkland, K.J. and C.H. Keys. 1979. The long-term effect of picloram and its residue on grain production and weed control. Weed Science. 27: 493-497.

The persistence of picloram applied annually at rates ranging from 0.02 to 0.07 kg/ha was measured each spring over an 8-year period. Picloram residue levels were in proportion to the rate of application. Picloram levels 12 and 24 months after application averaged 45% and 10%, respectively, of the level measured immediately after application. The control of *Polygonum convolvulus* was good, with populations declining significantly over the test period. Wheat growth and yields were not affected by picloram at rates of 0.035 kg/ha or less.

Kohl, R.A., C.G. Carlson, and S.G. Wangemann. 1994. Herbicide leaching potential through road ditches in thin soils over an outwash aquifer. Applied Engineering in Agriculture 10: 497-503.

Research was conducted to provide data on the leaching potential of 2,4-D and picloram applied to road ditches over shallow aquifers in South Dakota, USA. A comparison of soil profiles in the ditch and adjoining field indicated that an average of 0.3 m (1 ft) of soil was removed from road ditch soils, leaving very shallow soil profiles over the aquifer material. Cumulative infiltration of water into side slopes and ditch bottoms was measured on representative soils together with gravel road runoff to determine a water balance for the ditch. Undisturbed soil columns were brought into a greenhouse where leaching water was collected and analysed for the herbicides, which had been applied at recommended rates. The combination of extra leaching water from road runoff added to direct rainfall, and the naturally shallow soils that have been reduced in depth to build the roadbed resulted in two to five times the amount of water passing through to

groundwater than through adjoining fields. From 2 to 33% of the applied herbicides came through the undisturbed soil columns after the first storm event. The results indicate that caution should be exercised if the choice is made to use chemical methods of weed control in road ditches.

Krzyszowska, A.J., R.D Allen, and G.F. Vance. 1994. Assessment of the fate of two herbicides in a Wyoming rangeland soil: column studies. J. environ. qual.: American Society Of Agronomy 23: 1051-1058. Extensive use of dicamba (2-methoxy-3,6-dichlorobenzoic acid) and picloram (4-amino-3,5,6-trichloropicolinic acid) in arid Wyoming, along with large volumes of irrigation water used in some areas, has created a concern for the potential contamination of surface and groundwaters by these herbicides. Persistence and mobility of dicamba and picloram were investigated in a Wyoming rangeland soil using batch adsorption and soil column studies. The objectives of this study were to characterize soil chemical and physical properties that affect herbicide transport, examine herbicide sorption, model herbicide movement, and estimate degradation rate constants. Essentially no sorption of dicamba was detected; however, picloram sorption was greatest in the highest organic C content horizon. Both saturated (5.90, 2.96, and 0.82 kg ha⁻¹ dicamba and 1.85, 0.97, and 0.47 kg ha⁻¹ picloram) and unsaturated (2.76 and 1.00 kg ha⁻¹ for dicamba and picloram, respectively) column experiments were conducted. The herbicides and Br tracer (34, 38, 69, and 137 micrograms L⁻¹) were displaced through the soil columns using distilled water that was added in daily increments (60 mL d⁻¹). Degradation rate constants were calculated using both simple recovery fraction technique and by matching LEACHP-generated breakthrough curves to experimental data. For the two columns receiving intermediate application rates, anaerobic picloram dissipation was more rapid ($t_{1/2} = 19$ d) than for aerobic conditions ($t_{1/2} = 87$ d). The rate of dissipation of dicamba was approximately the same under aerobic and anaerobic conditions ($t_{1/2} = 15$ and 17 d in the saturated and unsaturated columns, respectively). Picloram and dicamba dissipation was more rapid at the lowest application rates, with $t_{1/2}$ of 13 and 10 d. At the highest application rates, $t_{1/2}$ of 23 and 17 d were measured for picloram and dicamba, respectively. Both herbicides were found to be highly mobile, with the mobility of picloram increasing at higher pore-water velocities.

Krzyszowska-Waitkus, A.J., R.D. Allen, G.F. Vance, R.Zhang, and D.E. Legg. 1999. A field lysimeter study to evaluate herbicide transport in a Wyoming irrigated pasture. Commun. soil sci. plant-anal. 30: 245-263. A field study was conducted to assess the fate and mobility of the herbicides dicamba and picloram in an irrigated pasture. The herbicides were applied at two application rates to four plots (two replicates) that contained soil-water collectors. Herbicide concentrations as a function of depth and application rate were evaluated statistically to determine if replicate data could be combined. Results indicated dicamba concentration variations were low, suggesting the mean value of the replicate plots could be compared; however, picloram

concentration variations were high, and the replicate plot data could not be combined. Half-time values for herbicide disappearance (time required for herbicide concentration to diminish from its maximum to half maximum levels), calculated from the arithmetic mean of the logistic equations, were useful in describing herbicide transport. Half-time values were dependent upon application rate, collector depth, pesticide type, and plot location. Dicamba applied at the low application rate was detected at 15 and 30 cm depths only, and was not detected throughout the entire study period (467 days) at deeper depths. Significant differences occurred between plots receiving the high dicamba application rate, which was attributed to permeability differences that affected herbicide migration in the soil profile. Picloram half-time values were also affected by soil organic carbon, which increased picloram adsorption. Differences in herbicide concentrations were observed within plots receiving the high picloram application rates, which was primarily attributed to spatial differences in hydraulic conductivity. Herbicide disappearance was most rapid at the shallow depth within plots receiving lower herbicide application rates.

Kuo, E.C.Y. 1973. The reaction of picloram and 2,4-D with montmorillonite clays and soils. Dissertation Abstracts International, B. 34: 952-953; 161 pp.

Mobility and adsorption of carboxyl-¹⁴C-labelled picloram and 2,4-D in 43 western soils, measured by t.l.c. and batch equilibrium techniques was correlated with soil pH, o.m. content and extractable aluminium. The multiple regression models developed predicted mobility and adsorption of both herbicides from these parameters in soils of pH <7. In two soils picloram mobility was reduced by activated charcoal. Picloram adsorption by H-montmorillonite increased with decreasing pH from 2.6 to 0. The adsorption of picloram by acid H-montmorillonite paralleled the picloram curve and the Freundlich isotherm. Acidified picloram, a derivative of 4-amino-pyridine, did not differ in absorption spectrum from its parent compound after acid treatments, thus indicating an absence of protonation. The picloram molecule could not accept an extra proton due to its dipolar nature, low basicity and the presence of strong electron withdrawing chloro and carboxylate functional groups. The reaction of picloram with H-montmorillonite increased the carbonyl stretching frequency, indicating a preferential interaction between annular nitrogen rather than the carbonyl oxygen of the picloram molecule with H-montmorillonite.

Kwong, K.F.N.K., G. Umrit, M. Nowbotsing, and A.K. Gopaul. 1999. Ground and surface water contamination by herbicide residues used in sugar cane fields in Mauritius. Sugar Cane. 3: 14-18.

Residues of nine herbicides, namely atrazine, diuron, hexazinone, 2,4-D, linuron, ioxynil, paraquat, oxyfluorfen and picloram, which are all used in weed control in sugarcane, were monitored at fortnightly intervals during 1995 and 1996 in ground and surface waters in Mauritius. The groundwater came from 20 boreholes representing the 10 main groundwater basins of Mauritius while the surface water was sampled at 25 locations along rivers forming part of the Grand River

North West catchment area. Only the residues of atrazine, hexazinone and diuron could be detected in the freshwater sources in Mauritius. More than 60% of the groundwater samples analysed (> 50% for river water) did not contain any detectable level of herbicide residue. Even when present, the levels of the residues were mostly within the range 0.05 to 0.5 ppb with their highest recorded concentrations rarely exceeding the maximum limits of 3 ppb atrazine, 14 ppb diuron and 210 ppb hexazinone recommended for drinking water sources in the 1991 Environment Protection Act of Mauritius or by the United States Environment Protection Agency. The frequency of appearance of the herbicide residues varied from site to site and was not related to the piezometric depth of the groundwater basin. High rainfall events had a greater impact than time of herbicide application on the appearance of herbicide residues in the ground and surface waters. It is suggested that no freshwater source in Mauritius is sheltered from possible contamination by these herbicides, but that the public fear and mistrust of herbicides are not justified as the level of herbicide residues in the water does not in general pose a risk to human health.

Lavy, T.L., J.D. Mattice, B.W. Skulman, E.E. Jr. Gbur, J.H. Massey, S.A. Senseman, and M.R. Barrett. 1997. Persistence of herbicides aged at three subsoil depths. Abstracts of Papers American Chemical Society. 214 (1-2): p ENVR 126.

Lavy, T.L., J.D. Mattice, J.H. Massey, B.W. Skulman, S.A. Senseman, E.E. Jr. Gbur, and M.R. Barrett. 1996. Long-term in situ leaching and degradation of six herbicides aged in subsoils. Journal of Environmental Quality. 25: 1268-1279. To assess the importance of degradation and leaching in the persistence of aged herbicide residues in subsoils, formulations of atrazine, metribuzin, metolachlor, picloram, 2,4-D, and alachlor were applied separately to two moist Arkansas, USA, subsoils (Typic Fragiudult and Typic Udipsamment) and buried for up to 3 years. The treated subsoils were placed in one of two storage container types, buried in situ at 30, 90, or 150 cm within the soil profile, and retrieved at 6 month intervals. Amounts of herbicide remaining in the subsoils were determined chromatographically. Use of two different types of storage containers allowed for comparison of the relative degradation and leaching occurring with time. Statistical evaluation of these data showed that significant early (less than 6 months after treatment) degradation occurred in 80% of 36 possible herbicide X soil depth X location combinations. Early leaching occurred between 30 and 50% of the time. Long-term degradation (greater than 6 months after treatment) occurred in 23 of 28 cases, while long-term leaching occurred in 7 cases. Slow degradation and notable leaching of picloram occurred at 90 and 150 cm at the loamy fine sand location. In addition, prolonged persistence of alachlor relative to metolachlor occurred in subsoils at both study locations.

Lym, R.G. and C.G. Messersmith. 1981. Perennial weed control in pasture using roller and wick applicators. Proceedings North Central Weed Control Conference, 36: 42-43. Picloram at 2 lb/acre broadcast and the same solution

(1:7.5 picloram:water, v:v), applied with a roller in September 1978 gave similar control of leafy spurge [*Euphorbia esula*] for 3 growing seasons. Control was about 10% better with the roller than with the wick applicator and the lowest solution to give adequate control was 1:3 picloram:water v:v. This solution gave 85 and 70% control of Canada thistle [*Cirsium arvense*] one year after treatment. A soil bioassay indicated that wick application of a 1:7 picloram:water solution and broadcast application of picloram at 2 lb/acre gave similar residues of 0.17 and 0.19 p.p.m. respectively 19 wk after application. Picloram at 1 lb/acre broadcast gave a residue of 0.03 p.p.m. which was similar to that from a wick application at 1:3 and roller applications at 1:1, 1:3 and 1:7 (v:v).

Lym, R.G. and C.G. Messersmith. 1987. Leafy spurge control and herbicide residue from annual picloram and 2,4-D application. J. Range Manage. 40: 194-198. Annual applications of picloram and picloram + 2,4-D and 2 applications of 2,4-D/year for 5 consecutive years was evaluated for *Euphorbia esula* control. The picloram treatments were evaluated for soil residue. The experiment was located at 2 sites in eastern North Dakota and 1 site in western North Dakota on various soil types. Picloram at 0.28, 0.42 and 0.56 kg/ha provided 48, 75 and 90% control of *E. esula* after 4 annual treatments, resp. Control increased to 85 and 91% when 2,4-D at 1.1 kg/ha was added to the annual treatment of picloram at 0.28 and 0.42 kg/ha, resp. 2,4-D with picloram at 0.56 kg/ha did not increase control compared with picloram alone. Picloram did not accumulate in the upper 15 cm of the soil profile and was generally not detected above the 2 p.p.b.w. level 12 months following each annual application. Greater picloram residue was found deeper in sandy than clay soil with high rather than low OM. Picloram at 500 and 250 p.p.b.w. was required to reduce *E. esula* seedling emergence and subsequent survival by 50%, resp. Picloram at 125 p.p.b.w. reduced regrowth from root segments of 4 lengths to near zero. Picloram at 8 to 32 p.p.b.w. stimulated seedling emergence compared with the control. Annual application of picloram at low rates gradually controlled *E. esula* but picloram soil residues were not high enough to control subsequent seed germination and shoot regrowth from roots.

Mabury, S.A. and D.G. Crosby. 1996. Pesticide reactivity toward hydroxyl and its relationship to field persistence. Journal of Agricultural and Food Chemistry 44: 1920-1924. To estimate the reactivity of organic pesticides toward hydroxyl, a standard competitor, p-nitroso-N,N-dimethylaniline (PNDA), competed with a particular compound for the radicals produced by the photolysis of hydrogen peroxide. The rate at which the pesticide competed with PNDA for hydroxyl determined its reactivity. Of 10 pesticides tested (atrazine, carbaryl, carbofuran, 2,4-D, hexazinone, MCPA, picloram, propanil and quinclorac) carbaryl was the most reactive, carbofuran and MCPA were of intermediate reactivity, and hexazinone was one of the least reactive. Experiments in irradiated field water, both in the laboratory and in sunlit rice

paddies in California, showed that pesticide dissipation rates followed the order of reactivity with hydroxyl radical.

MacDiarmid, B.N. 1975. Soil residues of picloram applied aerially to New Zealand brushweeds. Proceedings of the 28th New Zealand Weed and Pest Control Conference. 109-114. Following aerial spraying of gorse and manuka (*Leptospermum scoparium*), bioassays and field sowings of white clover showed that in 75% of locations treated, picloram residues had fallen within 15 months from 1.1 kg/ha to a level which allowed white clover establishment. Soil types varied in their absorption capacity. Picloram concentrations were highest in the top 0-75 mm of soil but did not differ between pasture and bare ground sites.

Marley, J.M.T. 1980. Persistence and leaching of picloram applied to a clay soil on the Darling Downs. Queensland Journal of Agricultural and Animal Science. 37: 15-25. Picloram (4-amino-3,5,6-trichloropicolinic acid) was applied at six rates (0, 23.3, 70, 210, 630 and 1890 g ha⁻¹) to a montmorillonitic clay soil. Rate of degradation of the herbicide and its vertical movement in the soil profile were determined by bioassays of field samples taken at four times (3.7, 7.4, 16.8 and 28.4 months) after application. Wheat, lucerne and soybeans were sown at various times following application to determine the effect of phytotoxic residues on the growth of these crops. At all four sampling times the zone of highest concentration of picloram was in the surface 15 cm of soil. Picloram was not detected below 30 cm. At selective weed control rates of 23.3 g ha⁻¹ and 70 g ha⁻¹ less than 10% of the applied picloram was present in the soil 7.4 months after application. At the latter rates, the growth of neither wheat nor lucerne was affected when planted 7.4 months after application.

McKinley, R.S. and G.P. Arron. 1987. Distribution of 2,4-D and picloram residues in environmental components adjacent to a treated right-of-way. Report / Ontario Hydro, Research Division ; no. 87-49-K. v, 27. Selective herbicide application to non-compatible tree species is an integral part of vegetation management of Ontario Hydro rights-of-way. Tordon 101 is presently being used to control the growth of non-compatible woody plant species (those which have the potential for interfering with power transmission) on rights-of-way in Northern and Eastern Ontario, where as 2,4-D and picloram is generally used in Southern Ontario. The study was conducted at two sites along the Des Joachims power corridor located along the eastern boundary of Algonquin Park, including a chain of 4 lakes whose watershed included part of the right-of-way. Sampling for residues in soil, vegetation lake water, sediment and representative fish and mammal species was conducted in areas adjacent to the right-of-way before herbicide treatment and at pre-selected times within a 22-month period after application.

McKone, C.E. and E.G. Cotterill. 1974. Extraction of picloram residues from a sandy loam soil. Bulletin of Environmental Contamination and Toxicology.

11: 3, 233-237. The recovery was examined of low levels of picloram (0.01 to 0.1 ppm.) at pH levels >7 from soil fortified in the laboratory and from the same soil containing residues from a dose of 1.5 lb/acre applied 67 weeks before sampling. A series of KOH concns. were prepared in 10% KCl as extractant. Aliquots were shaken with 25 g of the soil to give filtrate pH's in the range 7.2 to 11.6. The filtrate was acidified to adjust the pH to <2., partitioned into chloroform containing 5% ethanol (see WA 21, 477) and methylated with diazomethane. The methyl ester was determined using a 1.5 m X 4 mm (internal diam.) glass column packed with 1.5% XE 60 on Chromosorb W and fitted with a ⁶³Ni electron capture detector. Operating conditions were [temps. in deg C]: column 180, injection port 215, detector 300, carrier gas 80 ml/min oxygen-free N₂. The quantities of picloram extracted were below the limit of detection (0.001 ppm.) where the KOH solution was <pH 8. Above pH 8 the extractable picloram increased almost linearly to 0.038 ppm. at the highest pH. With the fortified soil recovery was obtained at all pH levels which ranged from 60% at pH 7.2 to 96% at pH 11.6. In another experiment using Ca(OH)₂ as extractant, selected as it conveniently buffered soils of varying pH to pH 12.4, recovery from soil fortified with picloram in the range 0.01 to 1 ppm. slightly exceeded 100%; Ca(OH)₂ (at pH 12.4) also accounted for a considerable increase in extractable picloram in field weathered residues compared with KOH at pH 9.35.

Meredith, P. 1996. Effects of picloram (Tordon (R)), clopyralid, triclopyr and chlorpyrifos on growth vigor, leaf form, pigmentation, yield specific gravity, tuber shape, and light sensitivity of potatoes. American Potato Journal. 73: 373.

Meru, S., K. Liber, K. Stonefield, K. Solomon, and G. Stephenson. 1990. Persistence And Lateral Movement Of 2,4-D And Picloram On Power Line Rights-Of-Way. Arch. Environ. Contam. Toxicol. 19: 572-577. Soil persistence and lateral movement of 2,4-D (2,4-dichlorophenoxy acetic acid) and picloram (4-amino-3,5,6-trichloropicolinic acid) were examined following their application as a stem-foliage spray for brush control on two power line rights-to-way. Ditches to collect runoff water were located 3, 10, 20, and 30 m downslope from the treated areas. Runoff water and soil samples were collected after 0.14, 0.43, 0.57, 1, 2, 4, 7, 8, 11, 15, 16, and 48 weeks and were analyzed for picloram and 2,4-D residues. Only 3 of 85 soil samples downslope from the target areas contained residues of 2,4-D, and only 1 of 85 down slope samples contained a detectable residue of picloram. Of 56 runoff water samples, only 11 contained 2,4-D residues and only 1 contained residues of picloram. The greatest distances downslope at which residues were detected in runoff water were 20 and 10 m for 2,4-D and picloram, respectively. No residues of either herbicide were recovered in soil or water at 15 weeks or 48 weeks after spraying. Despite normal rainfall frequency and amounts in the first several weeks after spraying in mid-June, significant runoff of either herbicide was not evident at either study site.

- Michael, J.L. and D.G. Neary. 1993. Herbicide dissipation studies in southern forest ecosystems. *Environmental Toxicology and Chemistry* 12: 405-410.** Results of research on the movement of hexazinone, imazapyr, picloram, and sulfometuron in first-order watersheds in the southern United States are presented. Herbicides contaminate surface waters to varying degrees, depending on application rate, method of application, product formulation, and site-specific characteristics. Highest concentrations are observed in streams in ephemeral pulses during the first three storm events after application. Streamside management zones greatly reduce the amount of herbicide entering streams from forestry applications. Soil persistence of herbicides is highly variable and a function of many site characteristics. Plant residues have been monitored and found to dissipate rapidly, with half-lives ≤ 40 d.
- Michael, J.L., D.G. Neary, and M.J.M. Wells. 1989. Picloram movement in soil solution and streamflow from a coastal plain forest. *Journal of Environmental Quality*. 18: 89-95.** Picloram (4-amino-3,5,6-trichloropicolinic acid) was aerially applied to a longleaf pine (*Pinus palustris*) site in the upper coastal plain of Alabama to control kudzu (*Pueraria lobata*). Pellets (10% a.i.) were spread at 56 kg ha⁻¹ on loamy sand (Typic Kanhapludult) soils. Picloram movement was monitored with mineral soil samples, tension-cup lysimeters, flow-proportional streamflow samplers, and discrete samplers. Picloram concentrations in the upper 15 cm of mineral soil peaked at 0.96 to 2.25 mg kg⁻¹ 25 days after application, depending on slope position, and declined to 0.13 to 0.29 mg kg⁻¹ 1 year later. In soil solution, picloram was detected at a depth of 0.4 m between 26 and 273 days after application. Only 4 of 15 lysimeters consistently contained detectable residues. Maximum picloram concentrations in soil solution were 130, 450, and 191 mg m⁻³ for ridge, midslope, and toe-slope positions, respectively. Downstream monitoring began 4 days after the herbicide application, and an initial concentration of 68 mg m⁻³ of picloram was detected. The maximum downstream concentration of 77 mg m⁻³ occurred 18 days after the application, immediately after the second storm event. Downstream concentrations dropped to <10 mg m⁻³ after 90 days and to <2 mg m⁻³ after 200 days. Following localized retreatment along the stream more than a year after the initial treatment, concentrations climbed again into the 20 to 30 mg m⁻³ range. Most of the initial off-site movement came from a perennial stream that had been inadvertently treated, but subsequently storm runoff was the largest contributor to stream contamination. Picloram residues in this stream were similar to those observed downstream, but they were higher (up to 241 mg m⁻³) and dropped faster to below 2 mg m⁻³ after 150 days.
- Neary, D.G., J.L. Michael, and J.A. Griffith. 1996. Herbicides - protecting long-term sustainability and water quality in forest ecosystems. *Second International Conference on Forest Vegetation Management, 1995. New Zealand Journal of Forestry Science*. 26: 241-264.** World-wide, sediment is the major water quality problem. The use of herbicides for controlling competing vegetation during stand establishment can be beneficial to forest

ecosystem sustainability and water quality by minimizing off-site soil loss, reducing on-site soil and organic matter displacement, and preventing deterioration of soil physical properties. Sediment losses from sites where competing vegetation is controlled by mechanical methods can be 1-2 orders of magnitude greater than natural losses from undisturbed watersheds. On a watershed basis, vegetation management techniques in general increase annual erosion by <7%. Herbicides do not increase natural erosion rates. Organic matter and nutrients that are critical to long-term site productivity can be removed off-site by mechanical vegetation-management techniques and fire, or redistributed on-site in a manner that reduces availability to the next stand. For several decades, research has been conducted on the fate of herbicides used in forestry in various watersheds throughout the southern and western USA, Canada, and Australia. This research has evaluated chemicals such as 2,4-D, glyphosate, hexazinone, imazapyr, metsulfuron methyl, picloram, sulfometuron methyl, tebuthiuron, and triclopyr. Losses in stream flow, and leaching to groundwater, have been evaluated. Field study data indicate that residue concentrations tend to be low, except where direct applications are made to ephemeral channels or streams, and do not persist for extended periods of time. Regional environmental impact statements in the USA demonstrate that forestry herbicide presence in surface and groundwater is not a significant risk to water quality or human health. They also clearly indicate that herbicides can greatly reduce water quality deterioration that is produced by erosion and sedimentation.

Neary, D.G., P.B. Bush, and J.L. Michael. 1993. Fate, dissipation and environmental effects of pesticides in southern forest: A review of a decade of research progress. *Environmental Toxicology and Chemistry* 12: 411-428.

Neary, D.G., P.B. Bush, C.K. McMahon, R.L. Cantrell, J.W. Jr. Taylor. 1988. Persistence of nine forest pesticides in the surface horizon of a typical quartzsammment soil of Ocala National Forest. *Proceedings, Soil and Crop Science Society of Florida*. 47: 127-134. 2,4-D, dicamba, dichlorprop, hexazinone, picloram and triclopyr were injected into turkey oak (*Quercus laevis*) at labelled rates for site preparation, and chlorpyrifos, fenitrothion, and lindane were sprayed onto sand pine (*Pinus clausa*) for bark beetle [scolytid] control. Soil persistence of these pesticides was evaluated. Initial concn in the A1 horizon of a Typic Quartzsammment were related to the application rates. Except for a soil-applied granular formulation of hexazinone, application of pesticides to the soil probably occurred primarily as a result of litterfall, crown leaching, stem washoff, and spillage. Peak concn of most herbicides in the A horizon occurred 2 months after application and ranged from 5.34 mg/kg for dichlorprop to 0.10 mg/kg for dicamba. The insecticide peak concn were reached between 5 and 8 months after application and ranged from 5.11 mg/kg (chlorpyrifos) to 1.54 mg/kg (fenitrothion). Secondary peaks of some pesticide residues were frequently detected in the A horizon 2 to 6 months after

application. Except for chlorpyrifos and lindane, concn were <0.40 mg/kg after 12 months. Persistence was generally in the order of chlorpyrifos > lindane > hexazinone > fenitrothion > dichlorprop > triclopyr > picloram > dicamba > 2,4-D. The results suggested that pesticide exposure of forest workers in dusty conditions and with max. soil pesticide concn would not be significant (<0.2% and 0.5% of the acceptable daily intake for herbicides and insecticides, resp.).

Neary, D.G., P.B. Bush, J.E. Douglass, and R.L. Todd. 1985. Picloram Movement In An Appalachian USA Hardwood Forest Watershed. J. Environ. Qual. 14: 585-592. Picloram (4-amino-3,5,6-trichloropicolinic acid) was applied at a rate of 5.0 kg ha⁻¹ acid equivalent to 4 ha of the 28-ha Watershed 19, Coweeta Hydrologic Laboratory in western North Carolina [USA]. The herbicide was broadcast manually as a pellet formulation (10% acid equivalent) in May 1978. The objective was to eliminate a poor-quality mixed oak overstory and rododendron (*Rhododendron maximum* L.)-laurel (*Kalmia latifolia* L.) understory prior to planting white pine (*Pinus strobus* L.). Picloram residues in samples from an Umbric Dystrochrept soil peaked in concentration in the upper 0.07 m at 11.58 mg kg⁻¹, had a half-life of about 4 weeks, and declined to near detection limits 28 weeks after application. Soil solution contained the highest picloram levels at 0.6 m (peak of 350 mg m⁻³). Picloram residues were detected in soil solution 1.2 m into the soil, but concentrations were < 25 mg m⁻³, and persisted for only 60 weeks. Intensive sampling to two springs detected trace levels for a period of 18 d. Only sporadic, low-level picloram residues were detected in streamflow from nested 10-ha and 28-ha watersheds during a 70-week period. Use of the herbicide picloram did not affect the quality of streamflow from Watershed 19 for domestic or agricultural purposes.

Newton, M., F. Roberts, A. Allen, B. Kelpas, D. White, and P. Boyd. 1990. Deposition and dissipation of three herbicides in foliage, litter, and soil of brushfields of southwest Oregon. J. Agric. Food Chem.: American Chemical Society. 38: 574-583. The herbicides 2,4-D ((2,4-dichlorophenoxy)acetic acid), triclopyr ([3,5,6-trichloro-2-pyridinyl)-oxy]acetic acid), and picloram (4-amino-3,5,6-trichloro-2-pyridinecarboxylic acid) were applied by helicopter to test grids in mountainous southwestern Oregon brushfields on shallow, rocky, clay loam soils. Herbicide concentrations were observed in crown twigs and foliage, browse twigs and foliage, litter, and soil. Initial deposits in the target area ranged from 61 to 115% (average 82%) of the nominal dosage, with coefficients of variation of 29-104%. Initial concentrations in crown foliage were 44-mg/kg for each kilogram per hectare applied; deposits on browse foliage and litter were 38% and 74%, respectively, of crown concentrations. Early after application, decreases were more rapid for salt formulations than for esters. After 79 days, decrease of all herbicides was slight in foliage, but continued in soil. Picloram disappeared most rapidly and was least mobile, followed by triclopyr and 2,4-D. Triclopyr and 2,4-D remained nearly constant in foliage through winter. Disappearance was rapid in litter.

- Norris, L.A. 1981. The behavior of herbicides in the forest environment and risk assessment. In, Weed control in forest management. Proceedings of the 1981 John S. Wright Forestry Conference. H.A. Holt and B.C. Fischer (Eds.). pp. 192-215.** US regulations for hazard assessment and the behaviour (movement, persistence and fate) of herbicides in the forest environment are discussed. The specific behaviour of 2,4-D, picloram, atrazine, MSMA, fosamine, glyphosate and hexazinone is reviewed.
- Pang, L., M.E Close, J.P.C. Watt, and K.W. Vincent. 2000. Simulation of picloram, atrazine, and simazine leaching through two New Zealand soils and into groundwater using HYDRUS-2D. J. contam. hydrol. Amsterdam : Elsevier Science B.V. 44: 19-46.**
- Peijnenburg, W.J.G.M., K.G.M. De Beer, H.A. Den Hollander, M.H.L. Stegeman, and H. Verboom. 1993. Kinetics, products, mechanisms and QSARs for the hydrolytic transformation of aromatic nitriles in anaerobic sediment slurries. Environ. Toxic. and Chem. 12: 1149-1161.** The degradation of several substituted benzonitriles was examined in anaerobic sediment-water systems under laboratory conditions. Formation of the corresponding benzoic acids was the main transformation process taking place. The pseudo-first-order rate constants of this process were shown to depend on both the chemical structure of the starting compound and the sediment characteristics. The starting compounds were selected with the aim of obtaining a maximum variation in chemical reactivity and physical properties, and the sediments were selected with the aim of assessing several environmental factors influencing the kinetics of transformation. Quantitative structure-activity relationships were developed for both ortho- and meta/para-substituted nitriles by relating pseudo-first-order disappearance rate constants for reductive hydrolysis of 27 aromatic nitriles in anoxic sediment slurries to some readily available molecular descriptors. The best correlations were obtained with the octanol/water partition coefficient of the nitriles and the summation of the inductive constants of the substituents as parameters. The correlations were strongly enhanced by taking into account the fraction of the compounds sorbed to the solid phase. Also it was found that upon correction for sorption, rate constants for reductive hydrolysis of three substituted benzonitriles obtained in six sediment samples did not differ significantly. Thus the obtained relationships may be used to calculate rates of transformation of given aromatic nitriles in given sediment systems.
- Perala, D.A. 1980. A provisional assessment of triclopyr herbicide for use in Lake States' forestry. US Department of Agriculture Forest Service Research Paper. No. FSRP-NC-180, 7 pp.** Triclopyr-triethylamine at 1.5-4.5 lb a.e./acre was applied alone or in combination with 2,4-D or Tordon 101 Mixture (tri-isopropanolamine salts of 2,4-D 2 lb + picloram 0.54 lb a.e./gal) at 2 lb + 0.5 lb a.e./acre in July 1975; white spruce (*Picea glauca*) was planted on 6 site preparation treatments in April 1976. Soil analyses in May 1976 showed that triclopyr and picloram residues were unlikely to be leached out of the topsoil high in OM content and that their rates of degradation were similar. The white

spruce planted in the spring following treatment was not damaged. *Betula papyrifera* and *Acer rubrum* were readily top-killed by triclopyr at 4.5 lb/acre and 6 lb/acre would probably kill *Quercus rubra* and *Tilia americana*. Tordon 101 was more effective against *Acer saccharum* and *Populus tremuloides*. Triclopyr mixtures with 2,4-D or Tordon 101 were not as effective as the individual herbicides applied alone at the same total rate. Tordon 101 reduced sprouting better than triclopyr. Triclopyr at rates of 1-2 lb a.e./acre proved highly effective and safe for the release of white spruce when sprayed 2-3 weeks after the completion of shoot growth.

- Ping, C.L., H.H. Cheng, and B.L. McNeal. 1975. Variations in picloram leaching patterns for several soils. Soil Science Society of America Proceedings. 39: 470-473.** Laboratory studies of picloram-potassium leaching under saturated conditions were conducted for 4 soils. Colorimetric analysis of picloram residues showed that leaching patterns could be related to variations in soil texture and pore uniformity for 3 soils from arid and semi-arid regions. Diffusion from conducting pores into adjacent micropores appeared to be the most plausible explanation of leaching patterns obtained for an oxisol of volcanic origin from Hawaii. Evidence supporting the presence of the postulated micropore structure in this topical soil was obtained from constancy in flow rate, from scanning electron micrographs and from picloram recovery at a reduced leaching rate. From summary.
- Ragab, M.T.H. 1974. Picloram [herbicides] persistence in sandy loam soils and effect of its residue on crops. Minutes, Can. Weed Comm. East Sect., 28th: 37-38.**
- Ragab, M.T.H. 1975. Residues of picloram in soil and their effects on crops. Can. J. Soil Sci. 55: 55-9.**
- Sahai, R., M. Chauhan, and S.S.S. Kushwaha. 1984. Verification of a theoretical model for pesticidal pollution. Sci. Total Environ. 35: 13-21.** Lin, Sahi and Eyring's model for the accumulation of pesticide residues in soil, which may relate to pollution by pesticides, has been further developed to estimate maximum pesticide residues in soil and vegetation as a function of time for different orders of pesticide decomposition reactions. The developed model has also been verified from some experimental data available in the literature on solbar, carbofuron, phorate, picloram, linuron and 2,4,5-T pesticides for first or second order reactions using correlation methods. From this model, the eventual persistence of pesticide residues in soil and vegetation may be predicted.
- Sassman, J., R. Pienta, M. Jacobs, and J. Cioffi. 1984. Pesticide background statements. Volume 1. Herbicides. Agriculture Handbook, United States Department of Agriculture, Forest Service. No.633, 1110pp.** This handbook begins with general information including sections on the USDA Forest Service, physical and chemical properties, toxicity, toxicity testing, relative toxicities, the fate and transport of pesticides in organisms, soil and water,

assessment of hazards and the assumptions made in the preparation of the data presented. This preliminary section is followed by the background statements on amitrole, atrazine, 2,4-D, 2,4-DP [dichlorprop], dalapon, dicamba, fosamine ammonium, glyphosate, hexazinone, picloram, simazine and triclopyr. Each background statement includes sections on general information such as physical and chemical properties and the normal use patterns, toxicity to various organisms, mutagenicity, fate in the environment and in organisms, use by the USDA Forest Service, exposure and hazard assessment.

Schroder, G.L. 1982. Herbicides in sugarbeets: spray drift; residues in soil; and chlorophyll fluorescence. Dissertation Abstracts International, B. 42: 10, 3908; 99 pp. In an evaluation of the effects of herbicide drift in sugar-beet, 2,4-D at 0.035-0.28 kg/ha tended to increase yields but reduced % sucrose at late stages. Dicamba at 0.018 kg/ha and picloram at 0.028 kg applied to 12-1f sugar-beet reduced percent sucrose but not the yield. All three herbicides increased storage losses. In a field evaluation, ethofumesate residues, 1 year after applying 1.12 kg/ha overall and 2.24 kg/ha as a banded treatment, reduced the wheat yield in 1977 on a silty clay soil. The yield was not reduced in 1978 on a loam soil, but residues from 4.48 and 8.96 kg/ha overall reduced the yield in 1979 on a clay soil. Crop tolerances of 4 crops to 4 p.p.m.w. in the glasshouse were sunflower > soybean > barley > wheat. In a study of the effects of herbicides on chlorophyll fluorescence, 10-5M diuron and 10-3M desmedipham inhibited uncoupled electron transport in isolated sugar-beet and redroot pigweed [*Amaranthus retroflexus*] chloroplasts. Max. electron transport inhibition was evident 4h after spraying sugar-beet with 1.1 kg diuron/ha. Max. [growth] inhibition occurred 8 and 24 h after spraying with 1.1 kg phenmedipham and desmedipham/ha, respectively. Max. fluorescence occurred within 6 and 8 h after spraying sugar-beet with diuron and phenmedipham, respectively.

Scifres C.F., R.W. Bovey, and M.G. Merkle. 1972. Variation in bioassay attributes as quantitative indices of picloram in soils. Weed Research. 12: 58-64. Symptom ratings were more effective than fresh wt. or oven-dry wt. of field beans or sunflowers to quantify ng amounts of picloram in river sand. Fresh wt., dry wt. or symptom ratings of soybeans effectively quantified ng quantities of picloram in river sand or sandy clay loam. From 92 to 97% of the variation in bioassay reaction was attributed to variation in picloram concn. with the species studied, except cucumber, for which the functional relationship log concn. versus symptom rating was developed. Results from gas-liquid chromatography (GLC) analyses and the sensitive bioassay methods were closely correlated but GLC demonstrated less inherent variability than the bioassay methods. By utilizing the proper functional relationship and indicator variable, regression analyses of bioassay reaction were used to determine picloram residues of 0-250 ng/g soil on a statistical basis. From summary.

Scifres, C.J., H.G. McCall, R. Maxey, and H. Tai. 1977. Residual Properties Of 2,4,5-T And Picloram In Sandy Rangeland Soils. Journal: J Environ Qual. 6:

36-42. Two watersheds were treated with 1 application of 2,4,5-T + picloram (1:1) at 1.12 kg/ha while 1 other watershed was treated for 2 consecutive yr at the same herbicide rates. Residues of 2,4,5-T were reduced to trace levels [< 10 ppb] in soils 7 days after application at 1 location, after 28 days at the 2nd, and after 56 days at the 3rd. Residues of 2,4,5-T were not detected below 15 cm and usually remained in the surface 2.5 cm of soil. Picloram was reduced to trace levels within 56 to 112 days after application, was not detected deeper than 60 cm, and was usually restricted to the surface 15 cm of soil. There was no evidence of subsurface lateral movement of either herbicide. Surface runoff water contained trace amounts of residue following storms for about 30 days after application. There was no evidence of residue carry over into the 2nd year after treatment in water, soils, or vegetation. Monitoring of cumulative residues in water, soils, and vegetation showed that about 75% of the picloram was dissipated from the ecosystem within 28 days after application and over 90% was lost after 112 days.

Scifres, C.J., R.R. Hahn, J.D. Colon, and M.G. Merkle. 1971. Picloram Persistence In Semi Arid Rangeland Soils And Water. Weed Science 19: 381-384.

Shannon, P.W. and J.M. Leslie. 1982. Chemical control of blackberry in Northland. Proceedings of the thirty-fifth New Zealand weed and pest control conference. M.J. Hartley, (Ed.). New Zealand Weed and Pest Control Society Inc.; Palmerston North; New Zealand pp.166-168. The use of 2,4,5-T, 2,4,5-T + picloram, glyphosate, fosamine and triclopyr for blackberry control was investigated. 2,4,5-T, 2,4,5-T + picloram or triclopyr gave near-complete cane knockdown 5-7 months after application in spring or autumn. Glyphosate or triclopyr gave the most regrowth suppression 1 yr after autumn application while 2,4,5-T + picloram gave the most regrowth suppression after spring application. None of the treatments completely killed the blackberry. Picloram residues in soil samples used for bioassay inhibited white clover seedling germination for up to 9 months following spraying. Soil residues of triclopyr caused little inhibition of white clover seedling germination after 3 months.

Shipman, R.D. and T.J. Prunty. 1988. Effects of herbicide residues on germination and early survival of red oak acorns. Proceedings, 42nd annual meeting of the Northeastern Weed Science Society. pp. 86-91. The response of greenhouse-grown *Quercus rubra* to several herbicides at 1, 2 and 4 times the manufacturer's recommended rate was studied under greenhouse conditions. Dicamba, 2,4-D, picloram, sulfometuron-methyl and triclopyr \pm picloram significantly reduced the percentage of germinating acorns. Picloram, sulfometuron-methyl and triclopyr significantly reduced seedling height. Glyphosate \pm non-ionic wetter, hexazinone and simazine had little or no effect on percentage germination or seedling height. However, hexazinone inhibited photosynthesis and eventually killed the seedlings. Soil type significantly affected herbicide availability and subsequent phytotoxicity.

- Sims, G.K., J.D. Wolt, R.G. Lehmann, J.P.E. Anderson (ed.), D.J. Arnold (ed.), F. Lewis (ed.), and L. Torstensson. 1992. Bioavailability of sorbed pesticides and other xenobiotic molecules. Proceedings of the international symposium on environmental aspects of pesticide microbiology, 17-21 August 1992, Sigtuna, Sweden. 159-164.** The relevance of degradation processes and sorption mechanisms in soil to bioavailability, and the effects of sorption on the degradation of weakly and strongly sorbed compounds are discussed. The results of many studies indicated that sorbed phase materials were not directly available to microorganisms in soil. Sorption effects on biodegradation were observed with strongly sorbed compounds that interacted with soil by either partitioning (naphthalene) or ionic interactions (diquat). Even weakly sorbed materials (pyridine, flumetsulam [N-(2,6-difluorophenyl)-5-methyl [1,2,4]triazolo[1,5a]pyrimidine-2-sulfonamide] and picloram) persisted longer when sorbed. It was concluded that interactions between sorption and biodegradation should be considered in modelling pesticide fate, and that the half-life of a compound in soil may best be treated as a variable (dependent upon sorption and possibly other factors), rather than a constant.
- Sirons, G.J., R. Frank, and R.M. Dell. 1977. Picloram residues in sprayed Macdonald-Cartier Freeway right-of-way. Bulletin of Environmental Contamination and Toxicology. 18: 526-533.** Tordon 101 (picloram + 2,4-D) was applied to the median and shoulder areas of the freeway in alternate years commencing May 1968. Soil core sampling for picloram residues commenced in May 1969 and continued for three years at seven sites along the freeway. While soil types on the shoulder differed between sites, the median was composed uniformly of clay or clay loam. The median soils showed uniform results, with little lateral movement but increased washout in areas adjacent to the gravel drainage line. The grass cover showed pronounced retention and uptake of picloram. Picloram showed high vertical mobility, and a three-year application cycle would reduce the risk of contamination of the surrounding area.
- Smetnik, A.A., V.S. Gorbato, Yu.Ya. Spiridonov, V.N. Kolupaeva, H. Brown (ed.), G.W. Cussans (ed.), M.D. Devine (ed.), S.O. Duke (ed.), C. Fernandez-Quintanilla (ed.), A. Helweg (ed.), R.E. Labrada (ed.), M. Landes (ed.), P. Kudsk (ed.), and JC Streibig. 1996. Movement of picloram, dicamba and chlorsulfuron in structured soils. In, Proceedings of the second international weed control congress, Copenhagen, Denmark, 25-28 June 1996: Vols. 1-4. 305-309.** Field studies were carried out during 1990-1992 in Russia to study the movement of picloram, dicamba and chlorsulfuron in a soddy-podzolic and Chernozem soil under different irrigation regimes. The greatest herbicide content was almost always found in the upper 5 cm soil layer. Residues of picloram, dicamba and chlorsulfuron did not contaminate the groundwater.

Smith, A.E. 1980. Persistence studies with [^{14}C] 2,4-D in soils previously treated with herbicides and pesticides. *Weed Research*. 20: 355-359. The persistence of ^{14}C -2,4-D at a rate equivalent to 1 kg/ha was compared under laboratory conditions in samples of heavy clay, sandy loam, and clay loam at 85% of field capacity moisture and 20 plus or minus 1 deg C which had either received no pre-treatment, or had been pre-treated for 7 days at the 2 mu g/g level with benzoylprop-ethyl, diclofop-methyl, dinitramine, flamprop-methyl, nitrofen, picloram, tri-allate, trifluralin, and a combination of tri-allate and trifluralin. The breakdown of ^{14}C -2,4-D was also studied in the same soils that had similarly received pre-treatments of 2 mu g/g of the cereal and seed dressing Vitaflo-DB (carbathiin + thiram + lindane), the insecticide, malathion, and a combination of Vitaflo-DB and malathion. In each soil type, the half-life of the 2,4-D was similar regardless of whether the soil had, or had not, received any pre-treatment, indicating that none of the chemicals investigated adversely affected the soil degradation of 2,4-D. From summary.

Smith, A.E., D. Waite, R. Grover, L.A. Kerr, L.J. Milward, and H. Sommerstad, 1988. Persistence And Movement Of Picloram In A Northern Saskatchewan Canada Watershed. *J. Environ. Qual.* 17: 262-268. In the summer of 1982, 477 ha of a weapons range in northern Saskatchewan were treated with a granular formulation of picloram (4-amino-3,5,6-trichloropicolinic acid) at a rate of 3.38 kg ha⁻¹ (a.i.). For the next 2 yr, the persistence of picloram was monitored in the soil at sites within and outside the treatment area. Picloram was monitored for a 3-yr period in the groundwater at off-target sites and in the surface waters and sediments of a creek and two lakes adjoining the treatment area. Extensive leaching of the herbicide was noted. After 14 months residues were recovered from the 60- to 90-cm soil depths, and after 22 months from the 90- to 120-cm soil layer. After 26 months between 138 and 396 g ha⁻¹ of picloram were recovered from the top 120-cm soil depth. Picloram was detected in the top 30 cm of soils, approximately 1 km from the treatment area, when sampled 14 and 22 months following the initial application. Picloram (0.25-83.3 .mu.g L⁻¹) was recovered after 35 months from groundwater samples collected at 120 cm from the same off-target sites. This transfer to nontreated sites was considered to result from a combination of blowing surface soil and groundwater movement from the treated area. Samples of surface waters taken from a lake approximately 1 km from the treatment zone indicated that picloram residues could be detected (0.1-1.15 .mu.g L⁻¹) in the falls of 1983 and 1984, but not in the summers of 1984 and 1985. Traces of picloram (0.14-0.39 .mu.g L⁻¹) were recovered in the fall of 1983 and summer of 1985 in creek waters situated approximately 300 m from the edge of the treatment area. Picloram was detected (12 .mu.g kg⁻¹) in only one lake sediment sample at one sampling period.

Spiridonov, Yu.Ya., V.G. Shestakov, Yu.M. Matveev, V.S. Bondarev, and G.S. Spiridonova. 1982. Effect of fertilizers on herbicidal activity of picloram and its persistence in soil. *Agrokhimiya*.2: 100-105. Russian. Application of

FYM alone and with NPK to a dernopodzolic soil decreased the herbicidal activity of picloram and increased its absorption by soil and degradation.

- Vallee, J.C., C. Martin, and G. Vansuyt. 1975. Picloram persistence after weed control in crops. Compte Rendu de la 8e Conference du COLUMA. 71-78. French.** Serious injury in some tobacco and vegetable (lettuce, pea, tomato etc.) crops in France has been caused by picloram residues both in the soil and in straw. Experiments were, therefore, conducted to investigate picloram persistence. Residues were found in straw from cereals treated with 0.16 to 0.32 kg/ha especially when the straw was decomposing. Every 100 g of straw treated with 0.16 kg/ha contained 5-20 μ g of picloram while 100 g of straw treated with 0.32 kg/ha contained 50-100 μ g. Residues in soil were lower but persistence was prolonged in soils rich in o.m. Tobacco plants were used as bioassay material, being highly susceptible to picloram at concns. as low as 10⁻¹⁰. Results showed that the use of straw for compost and the ploughing-in of straw before sowing dicotyledonous crops involves considerable risk.
- Vore, R.E. and H.P. Alley. 1982. Soil persistence--picloram and dicamba Herbicides, Weed control, Wyoming. Res. J. Univ. Wyo. Agric. Exp. Stn., The Station. 172: 137-147.**
- Watson, V.J., P.M. Rice, and E.C. Monnig. 1989. Environmental fate of picloram used for roadside weed control. Journal of Environmental Quality 18: 198-205.** The herbicide picloram (4-amino-3,5,6- trichloro-2-pyridine carboxylic acid) was applied to control spotted knapweed (*Centaurea maculosa* Lam.) in the northern Rockies to determine persistence in soils and vegetation, losses by photodegradation, rainfall induced migration, and potential contamination of surface and groundwater. Two sites were selected to represent best case and worst case conditions (within label restrictions) for on-site retention of picloram. A valley bottom terrace was treated with 0.28 kg/ha of picloram in the spring of 1985, and sampled over the following 445 d. In the spring of 1986, 1.12 kg/ha of picloram was applied to both sides of a minimal construction logging road extending 4 km along a stream (102 to 815 m³) that drains a granitic upper mountain watershed. Of the 17.1 km² watershed, 0.15% (2.5 ha) was sprayed. Vegetation, soils, surface water, and groundwater near the road were sampled during the 90 d following application. At the valley bottom site, 36, 13, and 10.5% of the picloram applied persisted after 90, 365, and 445 d, respectively. At the mountain watershed site, 78% persisted after 90 d, and picloram was not detected in the surface or groundwaters during the 90 d following application. Depending on the timing of delivery, as little as 1% or less of the application could have been detected after delivery to the stream. Loss by photodegradation during the first 7 d after treatment was important at both sites.
- Welp, G. 1989. Solubility and availability of environmental chemicals depending on soil characteristics. [Löslichkeit und Bioverfügbarkeit von Umweltchemikalien in Boden unterschiedlichen Stoffbestandes.]**

Mitteilungen der Deutschen Bodenkundlichen Gesellschaft. 59: 43-52.

German. The influence of the adsorption and solubility characteristics of chemicals on the microbial toxicity of potential soil pollutants was investigated with reference to the role of soil characteristics in the availability of such chemicals. Topsoil samples were collected from 18 sites in order to obtain a large variability. Organic carbon content ranged from 0.9-11.4%, clay from 2-41%, and pH (CaCl₂) from 3.5-7.8. Fourteen chemicals were tested, including Hg, PCP, Cd, 2,4,5-T, Picloram, phenol and DDT. The microbial toxicity was correlated with the water solubility of substances and also with soil chemical characteristics, namely absorption capacity and pH. The composition of soil solution can influence the availability of Hg, Pb and some organic compounds through complexation.

ENVIRONMENTAL FATE - WATER

- Abramova, K.A., T.D. Panasyuk, E.A. Nikanorova, and V.F. Vasil'chenko. 1975. Picloram behaviour in water, soil and plants. Materialy 10go Mezhdunarodnogo Simpoziuma Stran-Chlenov SEV, Pushchino, SSSR. Vol. 2: 98-100. Russian.** Field trials in 1968-73 on a dark-chestnut soil in a region of inadequate rainfall showed that 1 kg picloram/ha persisted in the top 40 cm of soil for 46 months and 2% of the amount originally applied was recovered from the top 80 cm of soil. Picloram residues in plants growing on treated soil amounted to 6 mg/kg found in proso millet straw and 0.2 mg/kg found in the grain. Maize plants growing in pot soil containing 1.5 mg picloram/kg accumulated 83 mg picloram/kg during 6 months. Cereal plants assimilated 1-3% of the applied amount and maize up to 10% with adequate moisture and dense sowing. In trials in 400-g capacity pots, 2 ml picloram/pot completely killed French beans and tomatoes and 4 ml/pot inhibited sunflower growth by 50%.
- Bovey, R.W., E. Burnett, C. Richardson, M.G. Merkle, J.R., and W.G. Knisel. 1974. Occurrence of 2,4,5-T and picloram in surface runoff water in the Blacklands of Texas. J. Environ. Qual. 3: 61-4.**
- Bush, P.B., Y.C. Berisford, J.W. Taylor, D.G. Neary, K.V. Miller, and J.E. Street. 1995. Operational monitoring of forest site preparation herbicides in the coastal plain: assessment of residues in perched water table. In, Herbicide-resistant crops: a bitter or better harvest? Proceedings of the 48th annual meeting of the Southern Weed Science Society, Memphis, Tennessee, USA, 16-18 January 1995., Southern Weed Science Society; Champaign, Illinois; USA. p.p115-120.** Field trials were conducted during the spring of 1992 in Aiken, South Carolina on a fine loam in loblolly pine [*Pinus taeda*] clear-cut areas to assess the potential movement of Arsenal (imazapyr) at 1 lb/acre, Velpar (hexazinone) at 3 lb and Tordon + Garlon (picloram + triclopyr, resp.) at 2 + 4 lb to shallow groundwater. Monitoring wells were installed at depths of 4 and 8 feet where clay lenses were observed. Results showed significant lateral down-slope movement of picloram and hexazinone under saturated conditions when the slopes exceeded 2%. Triclopyr and imazapyr showed limited potential for lateral movement or movement to the 8 foot perched water table. Levels of hexazinone peaked at 2 months after application and decreased to non-detectable levels at 2 years post-application. The residue magnitude and rate of dissipation were affected by plot slope and position within the plot. Triclopyr and imazapyr were not as mobile or persistent in shallow wells as picloram and hexazinone.
- Cavalier, T.C., T.L. Lavy, and J.D. Mattice 1989. Assessing Arkansas ground water for pesticides: methodology and findings. Ground Water Monitoring Review. 9: 159-166.** During 1985-1987, 119 wells, springs and municipal drinking water supplies throughout Arkansas were monitored for the presence

of acifluorfen, alachlor, aldicarb, atrazine, benomyl, cyanazine, cypermethrin, 2,4-D, dichlorprop, diuron, fenvalerate, fluometuron, hexazinone, linuron, metolachlor, permethrin, picloram and propanil. Not every sample was analyzed for every pesticide. Overall, results indicated that the pesticides were not present in the ground water samples studied. Detectable concentrations of alachlor, atrazine and metolachlor were found in one irrigation well at 5.5, 5.8, and 6.9 $\mu\text{g/litre}$, resp. However, since previous and subsequent sampling failed to detect these compounds, their presence is attributed to a localized spill or handling error rather than agricultural application.

Cessna, A.J., R. Grover, L.A. Kerr, and M.L. Aldred. 1985. A multiresidue method for the analysis and verification of several herbicides in water. J. of Agric. and Food Chem. 33: 504-507. An analytical method for determining and verifying residues of both neutral and acidic herbicides in water is presented. Acidic herbicides were derivatized by using diazomethane. Recoveries of MCPA, bromoxynil, 2,4-D, dicamba, picloram, tri-allate and trifluralin from distilled water at fortification levels of 0.1-1 ng/l ranged from 80 to 117%. Except for MCPA, all herbicide residues could be verified by using 2 different detector modes. The method was used successfully in a preliminary study to monitor herbicide residues in irrigation return flow waters.

Commission of the European Communities. 1978. Environment and quality of life. Final reports on research sponsored under the first environmental research programme. Commission of the European Communities.; Luxembourg. 460pp. The projects reported on include one concerned with mutagenicity of pesticides, including herbicides (Pp. 177-182) and one on the ecological effects of water pollutants, mentioning picloram and 2,4-D (Pp. 254-264). The last section of the book deals with the establishment of a data bank on environmental chemicals (including a number of herbicides).

Dennis, D.S., W.H. Gillespie, R.A. Maxey, and R. Shaw. 1977. Accumulation and persistence of picloram (Tordon 10K) in surface water and bottom sediments in West Virginia. Archives of Environmental Contamination and Toxicology 6: 421-433. Ponds and streams in Braxton, Kanawha, Mason, Jackson, and Hampshire Counties, West Virginia, were sampled to determine the accumulation, persistence, and movement of picloram residues in surface waters and bottom sediments. The highest residue levels of 437 $\mu\text{g/L}$ in water and 657 $\mu\text{g/kg}$ dry weight basis (243 $\mu\text{g/kg}$ wet weight basis) in bottom sediments were detected within one to three weeks after application of picloram (Tordon 10K) pellets at the rate of 44 . 8 product kg/ha. Residue levels in water and sediments decreased with distance from application sites and time since application.

Donald D.B. and J. Syrgiannis. 1995. Occurrence of pesticides in prairie lakes in Saskatchewan in relation to drought and salinity. Journal of Environmental Quality 24: 266-270. Prairie lakes are critical breeding, staging, and feeding habitat for a variety of shorebirds and waterfowl, and

lower trophic levels in these habitats could be affected by agricultural pesticides. Following the severe drought of 1988 in Saskatchewan, concentration of 11 pesticides were determined in water, sediment, and zooplankton in 10 permanent and nine semipermanent lakes (those lakes that did not have standing water in 1988). The detection frequency for lindane, alpha-HCH, and 2,4-D in water was 57, 70, and 78%, respectively, with the maximum concentration 0.011, 0.004, and 0.43 $\mu\text{g/L}$, respectively. Triallate was detected in 39% of sediment samples and 54% of zooplankton samples at a maximum concentration of 31 and 10.2 $\mu\text{g/kg}$, respectively. When the lakes were grouped by salinity, detection frequencies of these pesticides were significantly higher in brackish lakes, which tended to be semipermanent ($N = 6$, mean specific conductance 3100 $\mu\text{S/cm}$) than in saline lakes, which tended to be permanent ($N = 6$, mean specific conductance 60 900 $\mu\text{S/cm}$). Other pesticides were detected in 10 to 20% of samples (diclofop-methyl, atrazine, MPCA, dicamba, and bromoxynil) or not at all (trifluralin and picloram). With one exception, pesticide concentrations in these lakes were below those levels that might be deleterious to aquatic life, suggesting that these pesticides have not affected the food of avifauna at these lakes.

Forsyth, D.J., P.A. Martin, and G.G. Shaw. 1997. Effects of herbicides on two submersed aquatic macrophytes, *Potamogeton pectinatus* L. and *Myriophyllum sibiricum* Komarov, in a prairie wetland. *Environmental Pollution* 95: 259-268. Clopyralid, picloram, 2,4-D and a mixture of 2,4-D plus picloram, (Tordon 202C) were added to the water of 1 m square enclosures in a prairie wetland in Saskatchewan, Canada to produce concentrations of 0.01 and 0.1 mg active ingredient litre⁻¹. Effects on the submersed macrophytes, *Potamogeton pectinatus* and *Myriophyllum sibiricum*, were monitored by taking repeated measurements of plant weight, flower and tuber production and inspecting for injuries at 30 and 60 days after application. Clopyralid did not inhibit weight gain (growth) in either species, but stimulated growth and flowering by *M. sibiricum* at 0.01 mg litre⁻¹ and tuber production by *P. pectinatus* at both rates. The low rate of 2,4-D stimulated flowering by *M. sibiricum* and tuber production by *P. pectinatus*, whereas the high rate inhibited growth of *M. sibiricum* and injured both species. Picloram did not affect growth of either species, but injured *M. sibiricum* at both concentrations and inhibited flowering at 0.1 mg litre⁻¹. Tordon 202C at 0.1 mg litre⁻¹ caused reduced growth and flowering in *M. sibiricum* and injured both species; 0.01 mg litre⁻¹ also injured *M. sibiricum*. Mortality resulted only from Tordon 202C and 2,4-D. Field data are lacking to assess the extent to which submerged macrophytes in prairie ponds are exposed to harmful concentrations of herbicide from aerial spraying, drift from ground application, runoff or wind erosion of soil.

Frank, R., G.J. Sirons, and B.D. Ripley. 1979. Herbicide contamination and decontamination of well waters in Ontario, Canada, 1969-78. *Pesticides Monitoring Journal*. 13: 120-127. Over the 10-year period 1969-78, the waters of 237 wells were analysed because of contamination from herbicide

spillage in or near the well, complaints of impaired water flavour or injury to seedling plants moistened with the well water. Herbicides were identified in 159 wells: 98 had a single herbicide, 46 had two, 12 had three, one had four, and another had five separate herbicides contributing to the contamination. Wells were grouped according to the mode of entry of the contaminant. Entry occurred most commonly as an aerial spray drift or in runoff. Serious contaminations were caused by spillage of herbicide concentrates and spray solutions in or around the well. Twenty-four of the contaminated wells were further investigated to determine the persistence of the contaminant and how to remove it. Some wells were decontaminated adequately to allow reuse within nine weeks, others required three years and yet others had to be abandoned. Particularly persistent contaminants were aminotriazole, dinoseb, and picloram. From summary.

Gear J.R., J.G. Michel, and R. Grover. 1982. Photochemical degradation of picloram. Pesticide Science. 13: 189-194. The rate of photochemical degradation of aqueous solutions of picloram under UV light was measured by five different methods of analysis. These were chosen to assay the loss of picloram, dechlorination, alteration or loss of the aromatic amino group, loss of aromaticity and decarboxylation. The initial rate and mean rate of reaction were determined in each case and their relationship to each other was used to assess the significance of that particular reaction to the overall degradation of picloram and its early degradation products. Results suggest that dechlorination is the major photochemical process, with decarboxylation, loss of aromaticity and deamination all being significant subsequent reactions. From summary

Haas, R.H., G.O. Hoffman, and M.G. Merkle. 1970. Persistence of picloram in natural water sources. Tex. Agr. Exp. Sta. Consolidated. Progr. Rep. 2801-2828: 86-90.

Huston, P.L. and J.J. Pignatello. 1999. Degradation of selected pesticide active ingredients and commercial formulations in water by the photo-assisted Fenton reaction. Water Research 33: 1238-1246. The destruction of pesticide active ingredients (AI) and commercial formulations in acidic aqueous solution with the catalytic photo-Fenton, Fe(III)/H₂O₂/UV, advanced oxidation process has been studied. The AI are alachlor, aldicarb, atrazine, azinphos-methyl, captan, carbofuran, dicamba, disulfoton, glyphosate, malathion, methoxylchlor, metolachlor, picloram and simazine. Complete loss of pure AI occurred in most cases in <30 min under the following conditions: 5.0 X 10⁻⁵ M Fe(III), 1.0 X 10⁻² M H₂O₂, T = 25.0degreeC, pH 2.8 and 1.2 X 10¹⁹ quanta l⁻¹ s⁻¹ with fluorescent blacklight UV irradiation (300-400 nm). Considerable mineralization over 120 min occurred in most cases as evidenced by the appearance of inorganic ions and the decline in total organic carbon (TOC) of the solution. Intermediate products such as formate, acetate and oxalate appeared in early stages of degradation in some cases. Observed rate constants calculated from initial rates varied by a factor of <aprx3. The commercial products. Furadan (AI, carbofuran), Lasso 4EC (AI, alachlor) and Lasso

Microtech (AI, alachlor) were also tested. The "inert ingredients" (adjuvants) present in these products had no effect (Furadan), a slight effect (Lasso 4EC), or a strong effect (Lasso Microtech) on the rate of degradation of the AI. Lasso Microtech, in which the AI is micro-encapsulated in a polymeric shell wall microsphere, required slightly elevated temperatures to effect removal of alachlor in a timely manner. The results show that many pesticides and their commercial formulations in dilute aqueous solution are amenable to photo-Fenton treatment.

Johnsen, T.N. Jr. 1980. Picloram In Water And Soil From A Semi Arid Pinyon Pinus-Edulis And Juniper Juniperus-Osteosperma Watershed. J. Environ. Qual. 9: 601-605. A mixture of picloram (4-amino-3,5,6-trichloropicolinic acid) at 2.8 kg acid equivalent (ae)/ha and 2,4-D (2 herbicides) at 5.6 kg acid equivalent/ha was aerially applied onto 113 ha of a 146 ha pinyon-juniper watershed (*J. osteosperma* and *P. edulis*, respectively), in north-central Arizona [USA]. Picloram residues in runoff water and soil were monitored. Picloram was detected in runoff water leaving the treated area for 30.5 mo. after application. The highest concentration, 320 ppb, was in the initial runoff after treatment. A total of 1.1% of the picloram applied left the treated area in runoff water. Picloram was not detected farther than 5.6 km downstream. The picloram concentration was relatively constant during runoff events unless water from snow melt or from an untreated area mixed with the runoff from the treated area. Less picloram came from an area with individually treated trees than from an area with broadcast application. Dip (grab), single-stage flood, or splitter-box water samples all gave comparable picloram contents from the same location with the same runoff event. Picloram was detected in the soils for 44 mo., mainly below the 45 cm depth down to bedrock at 122 cm.

Johnsen, T.N., Jr., and W.L. Warskow. 1980. Picloram dissipation in a small southwestern stream. Weed Sci. 28: 612-615. Picloram (4-amino-3,5,6-trichloropicolinic acid) injected directly into a small, central Arizona stream was lost by normal stream flow actions, such as the mixing of fast- and slow-moving water, and the interchange of surface and subsurface water in gravel and sand beds along the stream. Picloram was injected at a concentration of 6.26 ppmw; the maximum amount detected was 2.362 ppmw at 0.4 km downstream, 0.943 ppmw at 0.8 km, 0.316 ppmw at 1.6 km, 0.014 ppmw at 3.2 km, 0.001 ppmw at 6.4 km, and none further downstream. Picloram was detected near the limits of detection (0.001 to 0.004 ppmw) 2 days after injection at the 0.4-, 0.8-, and 1.6-km sites. In photodegradation tests, sunlight decomposed 57% of the picloram in containers after 8.8 h of exposure.

Johnson, J.E. 1971. The Public Health Implications of Widespread Use of the Phenoxy Herbicides and Picloram (Paper presented at the Symposium on Possible Public Health Implications of Widespread Use of Herbicides, American Institute of Biological Sciences, 1970) Bioscience. 21: 899-905. The possible public health implications of widespread use of the phenoxy herbicides and picloram are discussed. Of concern are 2,4-dichlorophenoxy-

acetic-acid (2,4-D) (94757), 2,4,5-trichlorophenoxy- acetic-acid (2,4,5-T) (93765), 2-(2,4,5-trichlorophenoxy)-propionic-acid (silvex) (93721), and 4-amino-3,5,6-trichloro-picolinic-acid (picloram) (1918021) - the phenoxies because of widespread use, picloram, 2,4,5-T and 2,4-D because of their use as military defoliants. Literature on the subject is reviewed. There is very little human exposure to phenoxy herbicides through food. Tolerances for each herbicide for various crops proposed to the Federal Drug Administration are given. Air and water are, however, potential sources of exposure of man. Levels of residues in controlled spraying of pond water are given. The reported teratogenic effects of 2,4,5-T are discussed. Experimental studies are related which discount such effects. Acute oral toxicities are given for herbicides. It is concluded that the widespread use of phenoxy herbicides has produced no demonstrable evidence of potential harm to man. The most widely used, 2,4-D and 2,4,5-T, are degraded and do not bioconcentrate. These materials have been shown to be comparatively well tolerated in a variety of test systems. Man is not exposed to harmful concentrations. Impurities, such as the chlorodibenzo-p-dioxins, can be an important factor, but can be controlled by proper manufacturing.

Kohl, R.A., C.G. Carlson, and S.G. Wangemann. 1994. Herbicide leaching potential through road ditches in thin soils over an outwash aquifer. *Applied Engineering in Agriculture* 10: 497-503. Research was conducted to provide data on the leaching potential of 2,4-D and picloram applied to road ditches over shallow aquifers in South Dakota, USA. A comparison of soil profiles in the ditch and adjoining field indicated that an average of 0.3 m (1 ft) of soil was removed from road ditch soils, leaving very shallow soil profiles over the aquifer material. Cumulative infiltration of water into side slopes and ditch bottoms was measured on representative soils together with gravel road runoff to determine a water balance for the ditch. Undisturbed soil columns were brought into a greenhouse where leaching water was collected and analysed for the herbicides, which had been applied at recommended rates. The combination of extra leaching water from road runoff added to direct rainfall, and the naturally shallow soils that have been reduced in depth to build the roadbed resulted in two to five times the amount of water passing through to groundwater than through adjoining fields. From 2 to 33% of the applied herbicides came through the undisturbed soil columns after the first storm event. The results indicate that caution should be exercised if the choice is made to use chemical methods of weed control in road ditches.

Kwong, K.F., N.K., G. Umrit, M. Nowbotsing, and A.K. Gopaul. 1999. Ground and surface water contamination by herbicide residues used in sugar cane fields in Mauritius. *Sugar Cane*. 3: 14-18. English. Spanish. Residues of nine herbicides, namely atrazine, diuron, hexazinone, 2,4-D, linuron, ioxynil, paraquat, oxyfluorfen and picloram, which are all used in weed control in sugarcane, were monitored at fortnightly intervals during 1995 and 1996 in ground and surface waters in Mauritius. The groundwater came from 20

boreholes representing the 10 main groundwater basins of Mauritius while the surface water was sampled at 25 locations along rivers forming part of the Grand River North West catchment area. Only the residues of atrazine, hexazinone and diuron could be detected in the freshwater sources in Mauritius. More than 60% of the groundwater samples analysed (> 50% for river water) did not contain any detectable level of herbicide residue. Even when present, the levels of the residues were mostly within the range 0.05 to 0.5 ppb with their highest recorded concentrations rarely exceeding the maximum limits of 3 ppb atrazine, 14 ppb diuron and 210 ppb hexazinone recommended for drinking water sources in the 1991 Environment Protection Act of Mauritius or by the United States Environment Protection Agency. The frequency of appearance of the herbicide residues varied from site to site and was not related to the piezometric depth of the groundwater basin. High rainfall events had a greater impact than time of herbicide application on the appearance of herbicide residues in the ground and surface waters. It is suggested that no freshwater source in Mauritius is sheltered from possible contamination by these herbicides, but that the public fear and mistrust of herbicides are not justified as the level of herbicide residues in the water does not in general pose a risk to human health.

Lym, R.G., and C.G. Messersmith. 1986. Survey for picloram in wells and streams in North Dakota. Proceedings of the Western Society of Weed Science.

Vol.39, 85. A survey of wells and streams in 10 counties in North Dakota showed the presence of picloram in 5 wells which were within 1 mile of areas treated for *Euphorbia esula* control in 5 counties. Picloram levels ranged from trace to 12.4 p.p.b. Picloram was also found in Des Lacs and Souris rivers in Ward county but not in the Heart river.

Lym, R.G., and C.G. Messersmith. 1988. Survey of picloram in North Dakota groundwater. Weed Technology. 2: 217-222. This is the text of a paper given at a symposium on groundwater contamination by herbicides, at the Weed Science Society's annual meeting, held on 4 Feb. 1987 at St. Louis, Missouri. Wells and streams in 10 North Dakota counties were surveyed for picloram, the major herbicide used to control *Euphorbia esula* in the state. Three rivers and 144 wells were sampled in 1985. Picloram concn ranged from <0.1 to 6 p.p.b. in 2 rivers. An additional 44 wells were sampled in 1986; they were located within 2 km of the 5 wells where picloram was detected in 1985. Picloram concn in 1986 ranged from non-detectable to 6.7 p.p.b. in the original contaminated wells and was 0.97 p.p.b. in water from one of the additional 44 wells. Picloram concn in the river water was lower in 1986 than in 1985 but was detected farther downstream. All contaminated wells were within 1.5 km of an area treated for *E. esula*, but picloram had been spilled accidentally or misapplied near all but one of the wells. The concn detected were at least 100 times below suggested tolerance levels of water.

Mayes, M.A. and G.R. Oliver. 1985. An aquatic hazard assessment: Picloram. In Aquatic Toxicology And Hazard Assessment. Eighth Symposium. Bahner,

R.C. and D.J. Hansen (eds). Spec. Tech. Publ. Am. Soc. Test. Mater., No. 891, pp. 253-269. Picloram (4-amino-3,5,6-trichloropicolinic acid) exhibits herbicidal activities on broadleaf weeds and woody plants. The runoff potential of picloram is normally limited to less than 5% of the applied chemical removed from the site in runoff waters. Picloram is relatively nontoxic to freshwater fishes, with acute LC sub(50) values for technical acid ranging from 4.3 mg/L for lake trout (*Salvelinus namaycush*) to 55.3 mg/L for fathead minnows (*Pimephales promelas* Rafinesque). Freshwater invertebrates show similar susceptibility to technical picloram with acute LC sub(50) values ranging from 27 mg/L for *Gammarus lacustris* to 68.3 mg/L for *Daphnia magna*. The most sensitive marine invertebrate tested is the eastern oyster (*Crassostrea virginica*) with $18 > \text{EC sub}(50) < 32$ mg/L when exposed to a potassium salt formulation of picloram. Because of its relatively low toxicity to aquatic organisms and low potential for substantial quantities to enter the aquatic environment, picloram is not expected to present a hazard to the aquatic environment.

McKinley, R.S. and G.P. Arron. 1987. Distribution of 2,4-D and picloram residues in environmental components adjacent to a treated right-of-way. Report / Ontario Hydro, Research Division ; no. 87-49-K. v, 27. Selective herbicide application to non-compatible tree species is an integral part of vegetation management of Ontario Hydro rights-of-way. Tordon 101 is presently being used to control the growth of non-compatible woody plant species (those which have the potential for interfering with power transmission) on rights-of-way in Northern and Eastern Ontario, whereas 2,4-D and picloram is generally used in Southern Ontario. The study was conducted at two sites along the Des Joachims power corridor located along the eastern boundary of Algonquin Park, including a chain of 4 lakes whose watershed included part of the right-of-way. Sampling for residues in soil, vegetation lake water, sediment and representative fish and mammal species was conducted in areas adjacent to the right-of-way before herbicide treatment and at pre-selected times within a 22-month period after application.

Mehnert, E., S.C. Schock, M.L. Barnhardt, M.E. Caughey, S.F.J. Chou, W.S. Dey, G.B. Dreher, C. Ray. 1995. The occurrence of agricultural chemicals in Illinois' rural private wells: results from the pilot study. Ground Water Pub. Co. 15: 142-149. Water samples from 240 private wells in rural Illinois were collected over one year and analyzed for 39 agricultural chemicals. Sampling was conducted to provide preliminary information to refine a plan for a statewide survey of the agricultural chemical contamination of rural private wells. Wells were sampled according to a stratified random sampling plan that included four classes of depth to the uppermost aquifer material and two classes of well type. Depth to uppermost aquifer material was defined as the depth from ground surface to a geologic material that, if saturated, could be used as an aquifer. Occurrence, defined as the presence of one or more target analytes in a well water sample above some specified concentration, was shown to be higher

in large-diameter bored or dug wells than in small-diameter drilled wells. For small-diameter wells, occurrence generally decreased as the depth to the uppermost aquifer material increased. In addition, depth to the uppermost aquifer material could be used to predict the occurrence of some individual agricultural chemicals, such as nitrate and atrazine, but could not be used to predict the occurrence of picloram or pesticides in small-diameter wells. Of the 39 target analytes, 10 were detected at concentrations exceeding their respective minimum reporting levels. Nitrate and atrazine were the only compounds found at concentrations exceeding their respective maximum contaminant levels (MCLs) or U.S. EPA lifetime health advisory limits (HALs). A nonparametric statistical technique, contingency table analysis, identified factors associated with the occurrence of agricultural chemicals in three of the five study areas. Elevated specific conductance (greater than or equal to 500 micromhos/cm) of the sampled water was strongly associated with the occurrence of agricultural chemicals. This association was common to all three study areas analyzed. Identification of the source of the specific conductance could help identify the dominant pathway for transport of agricultural chemicals to ground water.

- Meru, S., K. Liber, K. Stonefield, K. Solomon, and G. Stephenson. 1990. Persistence And Lateral Movement Of 2,4-D And Picloram On Power Line Rights-Of-Way. Arch. Environ. Contam. Toxicol. 19: 572-577.** Soil persistence and lateral movement of 2,4-D (2,4-dichlorophenoxy acetic acid) and picloram (4-amino-3,5,6-trichloropicolinic acid) were examined following their application as a stem-foliage spray for brush control on two power line rights-to-way. Ditches to collect runoff water were located 3, 10, 20, and 30 m downslope from the treated areas. Runoff water and soil samples were collected after 0.14, 0.43, 0.57, 1, 2, 4, 7, 8, 11, 15, 16, and 48 weeks and were analyzed for picloram and 2,4-D residues. Only 3 of 85 soil samples downslope from the target areas contained residues of 2,4-D, and only 1 of 85 down slope samples contained a detectable residue of picloram. Of 56 runoff water samples, only 11 contained 2,4-D residues and only 1 contained residues of picloram. The greatest distances downslope at which residues were detected in runoff water were 20 and 10 m for 2,4-D and picloram, respectively. No residues of either herbicide were recovered in soil or water at 15 weeks or 48 weeks after spraying. Despite normal rainfall frequency and amounts in the first several weeks after spraying in mid-June, significant runoff of either herbicide was not evident at either study site.
- Meyer, R.F. and A. Ulmer. 1989. Eddy County ground water pilot survey. North Dakota Farm Research. 46: 23-27.** Ground water quality surveys were carried out during the summer of 1988 in Eddy County, North Dakota, USA to determine the herbicide picloram and nitrate-N concentrations. Inorganic analysis showed nitrate-N levels above 10 ppm at two locations and picloram levels in two wells to be 3.56 and 2.32 ppb.
- Michael, J.L. and D.G. Neary. 1993. Herbicide dissipation studies in southern forest ecosystems. Environmental Toxicology and Chemistry 12: 405-410.**

Results of research on the movement of hexazinone, imazapyr, picloram, and sulfometuron in first-order watersheds in the southern United States are presented. Herbicides contaminate surface waters to varying degrees, depending on application rate, method of application, product formulation, and site-specific characteristics. Highest concentrations are observed in streams in ephemeral pulses during the first three storm events after application. Streamside management zones greatly reduce the amount of herbicide entering streams from forestry applications. Soil persistence of herbicides is highly variable and a function of many site characteristics. Plant residues have been monitored and found to dissipate rapidly, with half-lives < 40 d.

Michael, J.L., D.G. Neary, and M.J.M. Wells. 1989. Picloram movement in soil solution and streamflow from a coastal plain forest. Journal of Environmental Quality. 18: 89-95. Picloram (4-amino-3,5,6-trichloropicolinic acid) was aerially applied to a longleaf pine (*Pinus palustris*) site in the upper coastal plain of Alabama to control kudzu (*Pueraria lobata*). Pellets (10% a.i.) were spread at 56 kg ha⁻¹ on loamy sand (Typic Kanhapludult) soils. Picloram movement was monitored with mineral soil samples, tension-cup lysimeters, flow-proportional streamflow samplers, and discrete samplers. Picloram concentrations in the upper 15 cm of mineral soil peaked at 0.96 to 2.25 mg kg⁻¹ 25 days after application, depending on slope position, and declined to 0.13 to 0.29 mg kg⁻¹ 1 year later. In soil solution, picloram was detected at a depth of 0.4 m between 26 and 273 days after application. Only 4 of 15 lysimeters consistently contained detectable residues. Maximum picloram concentrations in soil solution were 130, 450, and 191 mg m⁻³ for ridge, midslope, and toe-slope positions, respectively. Downstream monitoring began 4 days after the herbicide application, and an initial concentration of 68 mg m⁻³ of picloram was detected. The maximum downstream concentration of 77 mg m⁻³ occurred 18 days after the application, immediately after the second storm event. Downstream concentrations dropped to <10 mg m⁻³ after 90 days and to <2 mg m⁻³ after 200 days. Following localized retreatment along the stream more than a year after the initial treatment, concentrations climbed again into the 20 to 30 mg m⁻³ range. Most of the initial off-site movement came from a perennial stream that had been inadvertently treated, but subsequently storm runoff was the largest contributor to stream contamination. Picloram residues in this stream were similar to those observed downstream, but they were higher (up to 241 mg m⁻³) and dropped faster to below 2 mg m⁻³ after 150 days.

Morre, D.J. 1974. Brush control along agricultural drainage ditches. Environmental safety and efficacy of herbicide formulations. Tech. Rep. - Purdue Univ. Water Resour. Res. Cent. 49: 108 pp.

Murphy, E.C. and E.A. Greene. 1992. The occurrence of picloram (Tordon) and 2,4-D in groundwater in the Denbigh Sand Hills, McHenry County, North Dakota. Report of investigation (North Dakota Geological Survey) no. 95, 40 p.

- Neary, D.G., J.E. Douglass, and W. Fox. 1979. Low picloram concentrations in streamflow resulting from forest application of Tordon-10K. Proceedings of the 32nd Annual Meeting of the Southern Weed Science Society. 182-197.** Tordon-10K (picloram-potassium 10% pellets) were applied to 4 ha of a watershed at Franklin, N. C., to prepare a low-quality hardwood stand for planting eastern white pine (*Pinus strobus*). The herbicide was applied in May 1978 at 5 kg a.i./ha. Although application was followed by dry weather conditions, 76% of the overstorey plants and 95% of the rhododendron (*Rhododendron sp.*) and laurel (*Kalmia latifolia*) in the understorey were initially affected. Probably because of drought, only 30% of the overstorey and 20% of the understorey plants were killed. During the first 5 months after application, soil solution at 30 cm contained <10 p.p.b. picloram until heavy rains in Aug.; then, a peak of 174 p.p.b. was measured. At 60 cm, picloram peaked 2 months later at 179 p.p.b. In the soil solution sampled at 120 cm, picloram concns. never exceeded 3 p.p.b. Picloram was only detected twice (late June and early July) in streamflow, and the max. concn. was only 8 p.p.b. After heavy rains in Aug. totalling nearly 290 mm, no picloram was detected in streamflow. No major leaching of anions or cations has been evident in soil solution or streamflow. On the basis of this early data obtained during an intermittently dry summer, it is concluded that well-controlled applications of Tordon-10K made to ridges and upper slopes should not produce any significant pollution of streams draining the deep soil systems of the southern Appalachians. From summary.
- Neary, D.G., J.L. Michael, and J.A. Griffith. 1996. Herbicides - protecting long-term sustainability and water quality in forest ecosystems. Second International Conference on Forest Vegetation Management, 1995. New Zealand Journal of Forestry Science. 26: 241-264.** World-wide, sediment is the major water quality problem. The use of herbicides for controlling competing vegetation during stand establishment can be beneficial to forest ecosystem sustainability and water quality by minimizing off-site soil loss, reducing on-site soil and organic matter displacement, and preventing deterioration of soil physical properties. Sediment losses from sites where competing vegetation is controlled by mechanical methods can be 1-2 orders of magnitude greater than natural losses from undisturbed watersheds. On a watershed basis, vegetation management techniques in general increase annual erosion by <7%. Herbicides do not increase natural erosion rates. Organic matter and nutrients that are critical to long-term site productivity can be removed off-site by mechanical vegetation-management techniques and fire, or redistributed on-site in a manner that reduces availability to the next stand. For several decades, research has been conducted on the fate of herbicides used in forestry in various watersheds throughout the southern and western USA, Canada, and Australia. This research has evaluated chemicals such as 2,4-D, glyphosate, hexazinone, imazapyr, metsulfuron methyl, picloram, sulfometuron methyl, tebuthiuron, and triclopyr. Losses in stream flow, and leaching to

groundwater, have been evaluated. Field study data indicate that residue concentrations tend to be low, except where direct applications are made to ephemeral channels or streams, and do not persist for extended periods of time. Regional environmental impact statements in the USA demonstrate that forestry herbicide presence in surface and groundwater is not a significant risk to water quality or human health. They also clearly indicate that herbicides can greatly reduce water quality deterioration that is produced by erosion and sedimentation.

Neary, D.G., P.B. Bush, and J.L. Michael. 1993. Fate, dissipation and environmental effects of pesticides in southern forest: A review of a decade of research progress. *Environmental Toxicology and Chemistry* 12: 411-428.

Neary, D.G., P.B. Bush, J.E. Douglass, and R.L. Todd. 1985. Picloram Movement In An Appalachian USA Hardwood Forest Watershed. *J. Environ. Qual.* 14: 585-592. Picloram (4-amino-3,5,6-trichloropicolinic acid) was applied at a rate of 5.0 kg ha⁻¹ acid equivalent to 4 ha of the 28-ha Watershed 19, Coweeta Hydrologic Laboratory in western North Carolina [USA]. The herbicide was broadcast manually as a pellet formulation (10% acid equivalent) in May 1978. The objective was to eliminate a poor-quality mixed oak overstory and rododendron (*Rhododendron maximum* L.)-laurel (*Kalmia latifolia* L.) understory prior to planting white pine (*Pinus strobus* L.). Picloram residues in samples from an Umbric Dystrochrept soil peaked in concentration in the upper 0.07 m at 11.58 mg kg⁻¹, had a half-life of about 4 weeks, and declined to near detection limits 28 weeks after application. Soil solution contained the highest picloram levels at 0.6 m (peak of 350 mg m⁻³). Picloram residues were detected in soil solution 1.2 m into the soil, but concentrations were < 25 mg m⁻³, and persisted for only 60 weeks. Intensive sampling to two springs detected trace levels for a period of 18 d. Only sporadic, low-level picloram residues were detected in streamflow from nested 10-ha and 28-ha watersheds during a 70-week period. Use of the herbicide picloram did not affect the quality of streamflow from Watershed 19 for domestic or agricultural purposes.

Norris, L.A. 1981. The behavior of herbicides in the forest environment and risk assessment. *In*, Weed control in forest management. *Proceedings of the 1981 John S. Wright Forestry Conference*. H.A. Holt and B.C. Fischer (Eds.). pp. 192-215. US regulations for hazard assessment and the behaviour (movement, persistence and fate) of herbicides in the forest environment are discussed. The specific behaviour of 2,4-D, picloram, atrazine, MSMA, fosamine, glyphosate and hexazinone is reviewed.

Nutter, W.L., T. Tkacs, P.B. Bush, and D.G. Neary. 1984. Simulation of herbicide concentrations in stormflow from forested watersheds. *Water Resources Bulletin* 20: 851-857. The breakpoint rainfall hydrology and pesticide options of the field scale model CREAMS (Chemicals, Runoff, and Erosion from Agricultural Management Systems) were used to predict average concentrations

of hexazinone in stormflow from four forested watersheds in the upper Piedmont region of Georgia. Predicted concentrations were compared with measured concentrations recorded over a 13-month period. CREAMS accurately predicted hexazinone concentrations in the initial stormflow events which also contained the highest concentrations. The model underestimated the hexazinone concentrations in stormflow two months and greater following pesticide applications. In a companion study, the daily rainfall option of the CREAMS model was used to evaluate the relative risk associated with the maximum expected concentration of hexazinone, bromacil, dicamba, and triclopyr in stormflow from small forested watersheds. The model predicted the following order of potential residue appearance in stormflow: bromacil > triclopyr > hexazinone > picloram > dicamba. Subsurface movement of residues via interflow and deep leaching losses are not simulated by the version of CREAMS used in these studies.

Pang, L., M.E Close, J.P.C. Watt, and K.W. Vincent. 2000. Simulation of picloram, atrazine, and simazine leaching through two New Zealand soils and into groundwater using HYDRUS-2D. J. contam. hydrol. Amsterdam : Elsevier Science B.V. 44: 19-46.

Peterson, H.G., C Boutin, P.A. Martin, K.E. Freemark, N.J. Ruecker, and M.J. Moody. 1994. Aquatic phyto-toxicity of 23 pesticides applied at expected environmental concentrations. Aquatic Toxicol. 28: 275-292. Environment Canada uses an Expected Environmental Concentration (EEC) in evaluating the hazard of pesticides to nontarget aquatic organisms. This concentration is calculated by assuming an overspray of a 15 cm deep waterbody at the label application rate. The EEC of pesticides is then related to the EC50 (concentration causing a 50% reduction in a chosen toxicity endpoint) for a given aquatic test organism. At present, the use of an uncertainty factor is suggested in the literature if only a few species are tested because of important interspecific differences in pesticide sensitivity. The phytotoxicity of the EEC of 23 different pesticides to ten algae (24 h inhibition of ¹⁴C uptake) and one vascular plant (7-day growth inhibition) was determined in an effort to examine the question of interspecific sensitivity and its relation to the development of pesticide registration guidelines. Chemicals included five triazine herbicides (atrazine, cyanazine, hexazinone, metribuzin, and simazine), four sulfonyleurea herbicides (chlorsulfuron, metsulfuron-methyl, ethametsulfuron-methyl, triasulfuron), two phenoxyalkane herbicides (2,4-D and MCPA), two pyridine herbicides (picloram and triclopyr), a substituted urea, an amine derivative, and an imidazolinone herbicide (tebuthiuron, glyphosate and imazethapyr, respectively), a bipyridylium (diquat), a hydroxybenzonitrile (bromoxynil), an aldehyde (acrolein) and an acetanilide (metolachlor) herbicide, as well as two carbamate insecticides (carbofuran and carbaryl) and a triazole derivative fungicide (propiconazole). Test organisms were selected based on ecological relevance and present use in test protocols. Organisms included green algae (*Scenedesmus quadricauda* and *Selenastrum capricornutum*), diatoms

(*Nitzschia* sp. and *Cyclotella meneghiana*), cyanobacteria (*Microcystis aeruginosa*, *Oscillatoria* sp., *Pseudoanabaena* sp., *Anabaena inaequalis* and *Aphanizomenon flos-aquae*) and a floating vascular plant, duckweed (*Lemna minor*). The five triazine herbicides, acrolein and diquat inhibited the carbon uptake of all algae, diatoms and cyanobacteria by more than 50%. Two other pesticides, carbaryl and tebuthiuron, caused more than 50% inhibition in 90% of the algae tested. Nine of the 23 pesticides, five of which were triazine herbicides, were therefore highly phytotoxic to algae. Twelve pesticides inhibited growth of duckweed by more than 50%. Once again, all five of the triazine herbicides were among this group, as well as three sulfonyleurea herbicides and acrolein, diquat, metolachlor and tebuthiuron. Duckweed was the most sensitive organism tested, being equally affected by all pesticides causing algal phytotoxicity (with the exception of carbaryl), as well as being acutely affected by sulfonyleurea herbicides. Green algae were least sensitive to diquat; diatoms and one cyanobacterium were the only organisms that showed sensitivity to glyphosate. Through testing the phytotoxicity of a variety of agricultural pesticides to a wide range of algal taxa, it is evident that there are considerable differences in sensitivity among species and that the use of an uncertainty factor is necessary to provide an acceptable margin of safety in evaluating the hazard presented by these chemicals to the aquatic environment.

Sassman, J., R. Pienta, M. Jacobs, and J. Cioffi. 1984. Pesticide background statements. Volume 1. Herbicides. Agriculture Handbook, United States Department of Agriculture, Forest Service. No.633, 1110pp. This handbook begins with general information including sections on the USDA Forest Service, physical and chemical properties, toxicity, toxicity testing, relative toxicities, the fate and transport of pesticides in organisms, soil and water, assessment of hazards and the assumptions made in the preparation of the data presented. This preliminary section is followed by the background statements on amitrole, atrazine, 2,4-D, 2,4-DP [dichlorprop], dalapon, dicamba, fosamine ammonium, glyphosate, hexazinone, picloram, simazine and triclopyr. Each background statement includes sections on general information such as physical and chemical properties and the normal use patterns, toxicity to various organisms, mutagenicity, fate in the environment and in organisms, use by the USDA Forest Service, exposure and hazard assessment.

Scifres, C.J., H.G. McCall, R. Maxey, and H. Tai. 1977. Residual Properties Of 2,4,5-T And Picloram In Sandy Rangeland Soils. Journal: J Environ Qual. 6: 36-42. Two watersheds were treated with 1 application of 2,4,5-T + picloram (1:1) at 1.12 kg/ha while 1 other watershed was treated for 2 consecutive yrs at the same herbicide rates. Residues of 2,4,5-T were reduced to trace levels [< 10 ppb] in soils 7 days after application at 1 location, after 28 days at the 2nd, and after 56 days at the 3rd. Residues of 2,4,5-T were not detected below 15 cm and usually remained in the surface 2.5 cm of soil. Picloram was reduced to trace levels within 56 to 112 days after application, was not detected deeper than 60 cm, and was usually restricted to the surface 15 cm of soil. There was no

evidence of subsurface lateral movement of either herbicide. Surface runoff water contained trace amounts of residue following storms for about 30 days after application. There was no evidence of residue carry over into the 2nd year after treatment in water, soils, or vegetation. Monitoring of cumulative residues in water, soils, and vegetation showed that about 75% of the picloram was dissipated from the ecosystem within 28 days after application and over 90% was lost after 112 days.

Scifres, C.J., R.R. Hahn, J.D. Colon, and M.G. Merkle. 1971. Picloram Persistence In Semi Arid Rangeland Soils And Water. Weed Science 19: 381-384.

Shukla, S., S. Mostaghimi, V.O. Shanholtz, and M.C. Collins. 1998. A GIS-based modeling approach for evaluating groundwater vulnerability to pesticides. J. Am. Water Resour. Assoc. 34: 1275-1293. The Attenuation Factor (AF), a screening model, was used to evaluate the relative degree of vulnerability of groundwater to pesticide contamination in Louisa County, Virginia. For evaluating the contamination potential of pesticides, three scenarios of pesticide leaching represented by high, moderate, and low cases of degradation and sorption in the soil were considered. Data layers were overlaid within a Geographic Information System (GIS) for spatial computation of AF for the actual and 2m groundwater depths. This spatial database was divided into five contamination potential categories namely high, medium, low, very low, and unlikely, based on the numerical values of the AF for each cell (1/9 ha). The results for the three most mobile pesticides are presented in this paper. The performance of the AF model was evaluated by comparing its predicted results with the field data from an experimental watershed. The AF model was able to identify most of the frequently detected pesticides in the watershed. A sensitivity analysis was also performed. The results of this study provide information about the potential groundwater threat by pesticides to the citizens and decision-makers in the County and can be used for formulating an appropriate land use management plan to protect the groundwater quality.

Smith, A.E., D. Waite, R. Grover, L.A. Kerr, L.J. Milward, and H. Sommerstad, 1988. Persistence And Movement Of Picloram In A Northern Saskatchewan Canada Watershed. J. Environ. Qual. 17: 262-268. In the summer of 1982, 477 ha of a weapons range in Saskatchewan were treated with a granular formulation of picloram (4-amino-3,5,6-trichloropicolinic acid) at a rate of 3.38 kg ha⁻¹ (a.i.). For the next 2 yrs, the persistence of picloram was monitored in the soil at sites within and outside the treatment area. Picloram was monitored for a 3-yr period in the groundwater at off-target sites and in the surface waters and sediments of a creek and two lakes adjoining the treatment area. Extensive leaching of the herbicide was noted. After 14 months residues were recovered from the 60- to 90-cm soil depths, and after 22 months from the 90- to 120-cm layer. After 26 months between 138 and 396 g ha⁻¹ of picloram were recovered from the top 120-cm soil depths. Picloram was detected in the top 30 cm of soils, approximately 1 km from the treatment area, when sampled 14 and 22 months following the initial application. Picloram (0.25-88.3 µg

L-1) was recovered after 35 months from groundwater samples collected at 120 cm from the same off-target sites. This target to nontreated sites was considered to result from a combination of blowing surface soil and groundwater movement from the treated area. Samples of surface waters taken from a lake approximately 1 km from the treatment zone indicated that picloram residues could be detected (0.1-1.15 µg L⁻¹) in the autumns of 1983 and 1984, but not in the summers of 1984 and 1985. Traces of picloram (0.14-0.39 µg L⁻¹) were recovered in the autumn of 1983 and summer of 1985 in creek waters situated approximately 300 m from the edge of the treatment area. Picloram was detected (12 µg kg⁻¹) in only one lake sediment at one sampling period.

Task Force on Water Quality Guidelines (Canada). 1990. Canadian water quality guidelines : updates, March, 1990 : appendix VI. Inland Waters

Directorate, Water Quality Branch, 67 pp. Update to the Canadian Water Quality Guidelines, giving guidelines for amounts of picloram, metribuzin and cyanazine in raw water for drinking, recreational water, freshwater for aquatic life, agricultural uses, and industrial water supplies. Background information on uses and production, sources and pathways, environmental concentrations, and forms and fates in the aquatic environment are also included.

Trotter, D.M., R.A. Kent, and M.P. Wong. 1990. Canadian water quality guidelines for picloram. Environment Canada, Inland Waters Directorate, Water Quality Branch, . v, 62 p.

This report summarizes a literature review on the uses, fate, and effects of picloram (herbicide) on raw water for drinking water supply, freshwater aquatic life, agricultural water uses, recreational water quality and aesthetics, and industrial water supplies. Water quality guidelines for the protection of specific water uses are recommended in this report.

Watson, V.J., P.M. Rice, and E.C. Monnig. 1989. Environmental fate of picloram used for roadside weed control. Journal of Environmental Quality 18: 198-205.

The herbicide picloram (4-amino-3,5,6- trichloro-2-pyridine carboxylic acid) was applied to control spotted knapweed (*Centaurea maculosa* Lam.) in the northern Rockies to determine persistence in soils and vegetation, losses by photodegradation, rainfall induced migration, and potential contamination of surface and groundwater. Two sites were selected to represent best case and worst case conditions (within label restrictions) for on-site retention of picloram. A valley bottom terrace was treated with 0.28 kg/ha of picloram in the spring of 1985, and sampled over the following 445 d. In the spring of 1986, 1.12 kg/ha of picloram was applied to both sides of a minimal construction logging road extending 4 km along a stream (102 to 815 m³) that drains a granitic upper mountain watershed. Of the 17.1 km² watershed, 0.15% (2.5 ha) was sprayed. Vegetation, soils, surface water, and groundwater near the road were sampled during the 90 d following application. At the valley bottom site, 36, 13, and 10.5% of the picloram applied persisted after 90, 365, and 445 d, respectively. At the mountain watershed site, 78% persisted after 90 d, and picloram was not detected in the surface or groundwaters during the 90 d following application. Depending on the timing of delivery, as little as 1% or

less of the application could have been detected after delivery to the stream. Loss by photodegradation during the first 7 d after treatment was important at both sites.

- Wood, J.A. and D.H.J. Anthony. 1997. Herbicide contamination of prairie springs at ultratrace levels of detection. J. environ. qual. American Society Of Agronomy. v. 26: 1308-1318.** Natural springs provide an opportunistic subject for assessing aquifer contamination. To determine the frequency and level of aquifer contamination by herbicides in the Canadian prairie, a study of natural springs draining small surficial aquifers a few hectares in area was carried out in southern Saskatchewan. All but one of the aquifers investigated received herbicide applications either for agricultural purposes or brush control. Elevated tritium isotope activities (10-60 TU) confirmed recent recharge of these aquifers. No wells were present on these aquifers. Therefore, the possibility of contamination by direct entry down wells was eliminated from the study. Large volume extraction technology permitted detections of herbicides at ng L⁻¹ levels. This is the first study of herbicides in natural springs in Canada. Herbicides were detected in 23% of samples collected. The most frequently detected analyses being atrazine (6-chloro-N²-ethyl-N⁴-(isopropyl) -1,3,5-triazine-2,4-diamine), picloram (4-amino-3,5,6-trichloropicolinic acid) and 2,4-D ((2,4-dichlorophenoxy)acetic acid), with detections in 12, 7, and 7% of samples collected, respectively. The results show that shallow aquifer contamination occurs in the absence of wells. However, the levels detected were in the ng L⁻¹ (ppt) range, which is much less than levels commonly reported in most well surveys. None of the herbicide concentrations exceeded any guidelines for drinking water, livestock, irrigation, and aquatic life including Canadian, Provincial, World Health Organization, and USEPA guidelines.
- Yufu, S and J.J. Pignatello. 1993. Activation of hydrogen peroxide by iron(II) chelates for abiotic degradation of herbicides and insecticides in water. J. Agric. and Food Chem. 41: 308-312** Degradation of selected pesticides was carried out in water at pH 6 using hydrogen peroxide and soluble Fe(III) chelates of picolinic acid, gallic acid, or rhodizonic acid as catalysts and with or without near-UV irradiation. The catalysts were selected on the basis of an earlier screening. Without UV light, transformation of baygon, carbaryl, picloram, 2,4-D, 2,4,5-T, and atrazine was complete within a few minutes to about 2 h. Trifluralin reacted slowly. Ring- and carboxy-labeled (¹⁴C)-2,4-D and ringlabeled (¹⁴C)-2,4,5-T were 70-80% mineralized to ¹⁴CO⁻² in 2-4 h. Ring-labeled (¹⁴C)atrazine yielded no ¹⁴CO⁻². UV light accelerated degradation by the above chelates, as well as by thermally inactive oxalate and citrate chelates. UV acceleration is most likely due to charge-transfer photoreduction of the chelate to give Fe(II), which then reacts with H⁻²O⁻² to generate hydroxyl radical in the Fenton reaction. These reactions are potentially useful for detoxifying pesticide wastes.

FISH & AMPHIBIANS

- Donald D.B. and J. Syrgiannis. 1995. Occurrence of pesticides in prairie lakes in Saskatchewan in relation to drought and salinity. *Journal of Environmental Quality* 24: 266-270.** Prairie lakes are critical breeding, staging, and feeding habitat for a variety of shorebirds and waterfowl, and lower trophic levels in these habitats could be affected by agricultural pesticides. Following the severe drought of 1988 in Saskatchewan, concentration of 11 pesticides were determined in water, sediment, and zooplankton in 10 permanent and nine semipermanent lakes (those lakes that did not have standing water in 1988). The detection frequency for lindane, alpha-HCH, and 2,4-D in water was 57, 70, and 78%, respectively, with the maximum concentration 0.011, 0.004, and 0.43 $\mu\text{g/L}$, respectively. Triallate was detected in 39% of sediment samples and 54% of zooplankton samples at a maximum concentration of 31 and 10.2 $\mu\text{g/kg}$, respectively. When the lakes were grouped by salinity, detection frequencies of these pesticides were significantly higher in brackish lakes, which tended to be semipermanent ($N = 6$, mean specific conductance 3100 $\mu\text{S/cm}$) than in saline lakes, which tended to be permanent ($N = 6$, mean specific conductance 60 900 $\mu\text{S/cm}$). Other pesticides were detected in 10-20% of samples (diclofop-methyl, atrazine, MPCA, dicamba, and bromoxynil) or not at all (trifluralin and picloram). With one exception, pesticide concentrations in these lakes were below those levels that might be deleterious to aquatic life, suggesting that these pesticides have not affected the food of avifauna at these lakes.
- Ebbersten, S. 1972. Picloram (4-amino-3,5,6-trichloropicolinic acid). Studies concerning persistence in soil and plants and biological methods for determining picloram residues. [Picloram (4-amino-3,5,6-trikloropikolinsyra). Studier av persistens i jord och växter samt metodstudier rörande biologisk bestämning av pikloramrester]. Uppsala, Institutionen för Växtodling, Lantbrukshögskolan 175 pp.** **Swedish English** This publication is divided into 2 main sections: 1. A literature survey including sections on (a) the effects of picloram on higher plants, soil micro-organisms and higher animals (mammals, birds and fish), (b) the persistence of picloram in plant tissue, soil and water and (c) methods for determining picloram residues. 2. Results of investigations carried out in Sweden during 1966-70 to study persistence and movement in the soil, determination of residues and the effects on following crops of wheat and potatoes.
- Fogels, A. and J.B. Sprague. 1977. Comparative short-term tolerance of zebrafish, flagfish, and rainbow trout to five poisons including potential reference toxicants. *Water Res.*, 11: 811-817.** Zebrafish (*Brachydanio rerio*) and flagfish (*Jordanella floridae*) were evaluated as potential standard species for aquatic bioassays in Canada by comparing their short-term tolerance to that of

rainbow trout (*Salmo gairdneri*). When threshold or 10-day LC SUB-50 's for rainbow trout were assigned a value of 1 . 0, corresponding values for zebrafish and flagfish were respectively: copper sulfate, 1 . 6, 7 . 2; sodium pentachlorophenate, 4 . 7, 7 . 6; phenol, 2 . 5, 3 . 1; picloram, 1 . 6, 0 . 55; and dodecyl sodium sulfate, 2 . 8, 2 . 4. On the average, zebrafish were 2 . 6 times as tolerant as trout, and flagfish 4 . 2 times. Ratios of zebrafish/trout LC SUB-50 's were considerably less variable than flagfish/trout LC SUB-50 's. Considering the known variable response of rainbow trout and a maximum ratio of only 7 . 6 for exotic/trout LC SUB-50 's, responses of zebrafish and flagfish were judged not sufficiently different from those of rainbow trout to discount either exotic species from further consideration as a potential standard test-fish. As a reference toxicant, sodium pentachlorophenate presented difficulties with analysis and availability. Dodecyl sodium sulfate (DSS) showed no threshold of acute lethality for trout and 5-yr-old DSS had about one-third the toxicity of 1-yr old DSS. Phenol met all criteria considered for a reference toxicant.

Gallagher, E.P. and R.T. Di Giulio. 1991. Effects of 2,4-dichlorophenoxyacetic acid and picloram on biotransformation, peroxisomal and serum enzyme activities in channel catfish (*Ictalurus punctatus*). Toxicology Letters. 57: 65-72. Channel catfish (*Ictalurus punctatus*) exposed to a mixture of picloram and 2,4-dichlorophenoxyacetic acid (2,4-D) for 10 days displayed increased activities of hepatic ethoxyresorufin O-deethylase (EROD), decreased serum chloride concentrations and decreased liver body weight ratios. These changes were not observed in fish exposed to either compound alone. Neither compound, nor their mixture, increased hepatic peroxisomal catalase or lauroyl CoA oxidase activities. The results of this study indicate that 10-day exposure of 2,4-D or picloram does not induce peroxisomal enzymes in channel catfish; however, exposure to a mixture of 2,4-D and picloram may cause physiological effects to catfish not observed with either compound alone.

Garten, C.T. Jr. and J.R. Trabalka. 1983. Evaluation of models for predicting terrestrial food chain behavior of xenobiotics. Environmental Science and Technology 17: 10, 590-595. Results from an extensive literature review were used to evaluate the capabilities of existing simple empirical bioaccumulation models proposed for terrestrial vertebrates and fish. Generic application of such models appeared to be unsuitable; bioaccumulation in mammals and birds was very weakly correlated or uncorrelated with xenobiotic (exotic organic chemicals) bioaccumulation factors from fish tests (r^2 values were 0.09-0.43). The problem of wrongly classifying a compound, on the basis of physicochemical data, as not having a high bioaccumulation potential (e.g. methyl mercuric chloride) is discussed. Nontoxic substances were also given high bioaccumulation potentials by the screening model. Av. log-transformed bioaccumulation factors for xenobiotics such as buthidazole, dicamba, fenoprop, picloram, 2,4-D and other herbicides are tabulated for 6 mammal groups, fish, poultry and small birds. Other types of pesticide are also included in the data.

Johnson, C.R. 1978. Herbicide toxicities in the mosquito fish, *Gambusia affinis*.

Proc. R. Soc. Queensl. 89: 25-27. Mosquito fish, *G. affinis*, were exposed to a range of concentrations of eleven herbicides. From data obtained through static bioassay, the Median Tolerance Limit was calculated for each intoxicant. Considerable variation was found in toxicity to *G. affinis* with the various herbicides, ranging from 0.35 ppm for 96 h exposure to fenoprop to 19.0 g/l for 96 hour exposure to 2,2-DPA. Fenoprop, sodium arsenite, and picloram, respectively, were most toxic and the least toxic compounds tested were amitrole-T and 2,2-DPA.

Lorz, H.W., S.W. Glenn, R.H. Williams, C.M. Kunkel, L.A. Norris, and R.R.

Loper. 1979. Effects of selected herbicides on smolting of Coho salmon.

Report, US Environmental Protection Agency. No. EPA-600-3-79-071, 103 pp. The 96-h LC50 values of several herbicides to yearling coho salmon

(*Oncorhynchus kisutch*) were determined. All 96-h tests were conducted under static conditions at 10 deg C in freshwater of alkalinity and hardness 70-83 mg and 85-93 mg/litre (CaCO₃), respectively. Acrolein and dinoseb were the most toxic of 12 water-soluble herbicides tested, having LC50 values of 68 and 100 µg/litre, respectively. Atrazine, diquat and picloram were moderately toxic in freshwater (10-30 mg/litre). Fish exposed to Amitrole-T (aminotriazole + ammonium thiocyanate), diquat and paraquat in freshwater all exhibited dose-dependent effects in subsequent sea-water entry tests. Other herbicides produced little or no dose-related mortality when fish were challenged with sea-water. No effects on the (Na, K)-stimulated ATPase activity of the gills were observed with any herbicide. The effect of sublethal concns. of Tordon 101 (2,4-D + picloram), dinoseb and diquat on migratory disposition was tested by releasing herbicide-exposed salmon into a natural stream; only diquat had a significant effect. Hence, under normal (field) application acrolein and dinoseb could affect survival of all life stages of salmonids if water from treated irrigation ditches were released into the stream or river without sufficient holding or detoxifying time. The use of diquat at recommended treatment levels could reduce downstream migration of smolts and possibly affect their survival in sea-water. All other herbicide formulations tested appeared to have no effect on smolting of yearling coho salmon; however, atrazine has been shown to affect growth of young salmonids and survival of invertebrates at very low concns. Examination of the effects of herbicides on other life stages of coho salmon or of different formulations of the herbicides might produce considerably different results. From summary.

Mayes, M.A. and D.C. Dill. 1984. The Acute Toxicity Of Picloram Picloram Potassium Salt And Picloram Tri Iso Propanolamine Salt To Aquatic Organisms. Environ. Toxicol. Chem.3: 263-270.

Mayes, M.A. and G.R. Oliver. 1985. An aquatic hazard assessment: Picloram. In Aquatic Toxicology And Hazard Assessment. Eighth Symposium. Bahner, R.C. and D.J. Hansen (eds). Spec. Tech. Publ. Am. Soc. Test. Mater., No. 891, pp. 253-269. Picloram (4-amino-3,5,6-trichloropicolinic acid) exhibits

herbicidal activities on broadleaf weeds and woody plants. The runoff potential of picloram is normally limited to less than 5% of the applied chemical removed from the site in runoff waters. Picloram is relatively nontoxic to freshwater fishes, with acute LC sub(50) values for technical acid ranging from 4.3 mg/L for lake trout (*Salvelinus namaycush*) to 55.3 mg/L for fathead minnows (*Pimephales promelas Rafinesque*). Freshwater invertebrates show similar susceptibility to technical picloram with acute LC sub(50) values ranging from 27 mg/L for *Gammarus lacustris* to 68.3 mg/L for *Daphnia magna*. The most sensitive marine invertebrate tested is the eastern oyster (*Crassostrea virginica*) with $18 > \text{EC sub}(50) < 32$ mg/L when exposed to a potassium salt formulation of picloram. Because of its relatively low toxicity to aquatic organisms and low potential for substantial quantities to enter the aquatic environment, picloram is not expected to present a hazard to the aquatic environment.

- Mayes, M.A., D.L. Hopkins, and D.C. Dill. 1987. Toxicity of picloram (4-amino-3,5,6-trichloropicolinic acid) to life stages of the rainbow trout. Bulletin of Environmental Contamination and Toxicology. 38: 653-660.** In laboratory tests of the toxicity of picloram to rainbow trout (*Salmo gairdneri*) estimated 96 h and 196 h LC50s for approx. 90-day-old fish were 15.6 and 14 mg/litre, resp. Sublethal effects such as surface breathing, lack of schooling behaviour and loss of equilibrium were observed at concn down to 10.9 mg/litre. Larvae exposed to picloram showed significant reductions in survival at 2.02 mg/litre and reductions in length and wt at concn down to 0.88 mg. It was concluded that under present use guidelines picloram does not constitute an acute or chronic hazard to aquatic life.
- McKinley R.S. and G.P. Arron. 1987. Distribution of 2,4-D and picloram residues in environmental components adjacent to a treated right-of-way. Report / Ontario Hydro, Research Division ; no. 87-49-K. v, 27 p.** Selective herbicide application to non-compatible tree species is an integral part of vegetation management of Ontario Hydro rights-of-way. Tordo n 101 is presently being used to control the growth of non-compatible woody plant species (those which have the potential for interfering with power transmission) on rights-of-way in Northern and Eastern Ontario, where as 2,4-D and picloram is generally used in Southern Ontario. The study was conducted at two sites along the Des Joachims power corridor located along the eastern boundary of Algonquin Park, including a chain of 4 lakes whose water shed included part of the right-of-way. Sampling for residues in soil, vegetation lake water, sediment and representative fish and mammal species was conducted in areas adjacent to the right-of-way before herbicide treatment and at pre-selected times within a 22-month period after application.
- Morre, J.D. 1974. Brush control along agricultural drainage ditches. Environmental safety and efficacy of herbicide formulations. Tech. Rep. - Purdue Univ. Water Resour. Res. Cent. Vol.49, 108 pp.**

- Sassman, J., R. Pienta, M. Jacobs, and J. Cioffi. 1984. Pesticide background statements. Volume 1. Herbicides. Agriculture Handbook, United States Department of Agriculture, Forest Service. No.633, 1110pp.** This handbook begins with general information including sections on the USDA Forest Service, physical and chemical properties, toxicity, toxicity testing, relative toxicities, the fate and transport of pesticides in organisms, soil and water, assessment of hazards and the assumptions made in the preparation of the data presented. This preliminary section is followed by the background statements on amitrole, atrazine, 2,4-D, 2,4-DP [dichlorprop], dalapon, dicamba, fosamine ammonium, glyphosate, hexazinone, picloram, simazine and triclopyr. Each background statement includes sections on general information such as physical and chemical properties and the normal use patterns, toxicity to various organisms, mutagenicity, fate in the environment and in organisms, use by the USDA Forest Service, exposure and hazard assessment.
- Slyn'ko, Yu.V. 1987. Effect of Tordon 22K on the morphogenesis and gene pool of *Brachiodanio rerio* (Cyprinidae). Embryotoxic and teratogenic effects. Soviet Journal of Ecology. 18: 47-50.** Exposure of *B. rerio* roe to Tordon 22K (K salts of 2,4-D + picloram) at 4-16 mg/litre delayed larval hatching, reduced the growth rate of larvae and substantially increased the number of aberrant larvae. Larvae which hatched from treated roe showed increased levels of emergence, the first peak of which coincided with the start of motor activity and resorption of the yolk sac, the second with transition to external feeding and organization of morphofunctional reorganization of the pre-fry stage.
- Task Force on Water Quality Guidelines (Canada). 1990. Canadian water quality guidelines : updates, March, 1990 : appendix VI. Inland Waters Directorate, Water Quality Branch, 67 pp.** Update to the Canadian Water Quality Guidelines, giving guidelines for amounts of picloram, metribuzin and cyanazine in raw water for drinking, recreational water, freshwater for aquatic life, agricultural uses, and industrial water supplies. Background information on uses and production, sources and pathways, environmental concentrations, and forms and fates in the aquatic environment are also included.
- Trotter, D.M., R.A. Kent, and M.P. Wong. 1990. Canadian water quality guidelines for picloram. Environment Canada, Inland Waters Directorate, Water Quality Branch, v, 62 p.** This report summarizes a literature review on the uses, fate, and effects of picloram (herbicide) on raw water for drinking water supply, freshwater aquatic life, agricultural water uses, recreational water quality and aesthetics, and industrial water supplies. Water quality guidelines for the protection of specific water uses are recommended in this report.
- United States Department of the Interior Fish and Wildlife Service, Columbia, Missouri. 1979. Acute toxicity of benomyl, trifluralin and picloram to freshwater organisms. Columbia National Fisheries Research Laboratory: Annual report of research highlights, 1978, pp.1.** The fungicide benomyl was more toxic to fish and freshwater invertebrates than either trifluralin or

picloram. Trifluralin was more toxic to rainbow trout than channel catfish and picloram was slightly more toxic to young channel catfish than to rainbow trout. The results suggest that contamination of aquatic habitats by these chemicals during spawning could reduce the survival of young fish.

Woodward, D.F. 1979. Assessing the hazard of picloram to cutthroat trout. J.

Range Manage. 32: 230-232. Water concentrations of picloram, comparable with those reported from field investigations, were used to simulate field exposures of cutthroat trout (*Salmo clarki*) to the herbicide. Picloram increased fry mortality in concentrations greater than 1,300 g/l and reduced fry growth in concentrations above 610 g/l. The chemical had no adverse effect on fry in concentrations below 290 g/l. However, if persistent rainfall were to occur, resulting in continuous loss of picloram in runoff, the maximum allowable concentration might be much lower than 290 g/l.

Woodward, D.F. 1982. Acute toxicity of mixtures of range management herbicides to cutthroat trout. Journal of Range Management. 35: 539-540. Six

different paired mixtures of dicamba, picloram, 2,4-D butyl ester, 2,4-D isooctyl ester, and 2,4-D propylene glycol butyl ether ester were tested with cutthroat trout (*Salmo clarki*). Except for 2,4-D isooctyl ester, the LC50's resulting from mixtures of 2,4-D esters and picloram were lower than LC50's of those herbicides tested individually. Dicamba and 2,4-D isooctyl ester were the least toxic individually and mixtures of dicamba or 2,4-D isooctyl ester with the other herbicides tested did not result in increased toxicity. Results reflect the importance of using combination exposures in determining the biological significance of the simultaneous occurrence of more than one herbicide in surface waters.

HUMAN TOXICOLOGY

Anonymous. 1991. Picloram. IARC Monographs on the Evaluation of Carcinogenic Risks to Humans, Vol. 53: Occupational Exposures in Insecticide Application, and Some Pesticides, pages 481-493. The carcinogenicity of the systemic herbicide picloram (1918021) was examined and reviewed. Data on chemical structure, production and uses, and residue occurrences and limits in foods were presented. There was no available data on the carcinogenicity of picloram to humans, but tests for carcinogenicity were carried out in mice and rats by dietary administration. Tumor incidence was not increased in mice following administration of 2500 to 10,000mg/kg picloram for 1 to 79 weeks. Rat studies using 5000 to 20,000mg/kg for 39 to 41 weeks indicated increased incidence of liver cell tumors in males and also in females (separate studies). The incidence of C-cell adenomas of the thyroid was increased in females. There was no induction of chromosomal aberrations in mouse marrow cells in-vivo or in human cells; however, mitotic recombination was seen in yeast. Human studies on subjects aged 41 to 51 years dosed with 0.5 and 5mg/kg orally or applied dermally showed poor absorption through the skin, but good absorption when ingested. High renal clearance of unchanged picloram suggested that active renal tubular secretion was important for excretion. Studies on reproductive and developmental effects using rabbits, and eggs of mallard and hen showed little effect except at high doses. No mutations were induced in the *Drosophila* or *Salmonella* assays. Picloram was not classifiable as a human carcinogen at this time.

Burroughs, B.L., C.S. Johnson, and V.F. Garry. 1996. In vitro micronucleus response of commercial chlorophenoxy herbicides and adjuvants. Environmental and Molecular Mutagenesis 27: p 11.

Bush, P.B., D.G. Neary, C.K. McMahon, and J.W. Jr. Taylor. 1987. Suitability of hardwoods treated with phenoxy and pyridine herbicides for use as firewood. Archives of Environmental Contamination and Toxicology. 16: 333-341. Potential exposure to pesticide residues resulting from burning wood treated with phenoxy and pyridine herbicides was assessed. Wood samples from trees treated with 2,4-D, dicamba, dichlorprop, picloram and triclopyr contained variable amounts of parent compound residues at 4, 8 and 12 months after application. At the time of the latter sampling, residues of 2,4-D, dicamba and picloram were <2.1 mg/kg FW. Mean residue concn of triclopyr and dichlorprop were 3.5 and 13.0 mg/kg, resp. In a laboratory experiment, slow combustion released relatively stable compounds such as 2,4-D, dicamba and dichlorprop in significant amounts. Rapid combustion greatly enhanced decomposition of 2,4-D, dicamba, dichlorprop, picloram and triclopyr. It was suggested that a well-developed fire in a wood stove or fireplace with active flaming combustion and temp. of 800-1000°C should result in >95% thermal decomposition of the herbicides examined in this study. Burning of

herbicide-treated wood under smouldering conditions could result in very low levels of herbicide residue in ambient indoor air but the exposure levels are <0.3% of the threshold limit value for 2,4-D and triclopyr. The exposure was also more than 3 orders of magnitude lower than the established acceptable daily intakes for these products.

Commission of the European Communities. 1978. Environment and quality of life. Final reports on research sponsored under the first environmental research programme. Commission of the European Communities;

Luxembourg. 460pp. The projects reported on include one concerned with mutagenicity of pesticides, including herbicides (Pp. 177-182) and one on the ecological effects of water pollutants, mentioning picloram and 2,4-D (Pp. 254-264). The last section of the book deals with the establishment of a data bank on environmental chemicals (including a number of herbicides).

Hall, J.C., R.J.A. Deschamps, K.K. Krieg. 1989. Immunoassays for the detection of 2,4-D and picloram in river water and urine. J. Agric. Food Chem. 37: 981-984.

Jacobi H., G. Leier, I. Witte. 1996. Correlation of the lipophilicity of xenobiotics with their synergistic effects on DNA synthesis in human fibroblasts. Chemosphere. 32: 1251-1259. The binary combination effects on DNA synthesis of human fibroblasts were investigated using 2,4-D with 15 xenobiotics of different chemical substance classes. Results were compared with previous investigations on cell growth. Each of the 15 chemicals tested at their no effect concentrations (NOEC's) increased the effects of 2,4-D on DNA synthesis. Thereby, the EC-20 value of 2,4-D was reduced by approximately 40% in the combinations. The NOEC's of the xenobiotics used in the combinations varied by a factor of 1,600 and depended strongly on the lipophilicity of the agents combined with 2,4-D. A significant statistical correlation of $r = 0.90$ was found between the NOEC's of the 15 combined xenobiotics and their lipophilicity. The combination effects on DNA synthesis were similar to those on cell growth. The regression lines of the relationship between the NOEC's and lipophilicity in both assays showed only slight differences in the slopes. This is an additional confirmation of our hypothesis on a facilitated uptake of 2,4-D in the binary combinations.

Johnson, J.E. 1971. The Public Health Implications of Widespread Use of the Phenoxy Herbicides and Picloram. Bioscience, Vol. 21, No. 17, (Paper presented at the Symposium on Possible Public Health Implications of Widespread Use of Herbicides, American Institute of Biological Sciences, 1970) pages 899-905. The possible public health implications of widespread use of the phenoxy herbicides and picloram are discussed. Of concern are 2,4-dichlorophenoxy-acetic-acid (2,4-D) (94757), 2,4,5-trichlorophenoxy-acetic-acid (2,4,5-T) (93765), 2-(2,4,5-trichlorophenoxy)-propionic-acid (silvex) (93721), and 4-amino-3,5,6-trichloro-picolinic-acid (picloram) (1918021) - the phenoxies because of widespread use, picloram, 2,4,5-T and 2,4-D because of

their use as military defoliants. Literature on the subject is reviewed. There is very little human exposure to phenoxy herbicides through food. Tolerances for each herbicide for various crops proposed to the Federal Drug Administration are given. Air and water are, however, potential sources of exposure of man. Levels of residues in controlled spraying of pond water are given. The reported teratogenic effects of 2,4,5-T are discussed. Experimental studies are related which discount such effects. Acute oral toxicities are given for herbicides. It is concluded that the widespread use of phenoxy herbicides has produced no demonstrable evidence of potential harm to man. The most widely used, 2,4-D and 2,4,5-T, are degraded and do not bioconcentrate. These materials have been shown to be comparatively well tolerated in a variety of test systems. Man is not exposed to harmful concentrations. Impurities, such as the chlorodibenzo-p-dioxins, can be an important factor, but can be controlled by proper manufacturing.

Lavy, T.L., J.D. Mattice, and L.A. Norris. 1985. Absorbed dose comparisons for forest workers applying 2,4-D, dichlorprop and picloram. Abstracts of Papers, 189th American Chemical Society National Meeting, PEST 126.

The absorbed dose of 2,4-D and picloram received by ground workers applying Weedone 170 and Tordon 101-R in the forest was measured by urine analysis. Eighty workers engaged in their normal work activities cooperated in the study in which the exposure levels resulting from 4 different application techniques were compared. Knapsack applicators spraying a 50:50 mixture of 2,4-D and dichlorprop showed excretion rates and amounts of 2,4-D and dichlorprop to be similar. The major portion of the total picloram excreted occurred within the first 24 h. Relatively low amounts of picloram excreted agree with earlier studies which showed <1% absorption of dermally applied picloram. Picloram which occasionally entered the body orally appeared to be excreted at the same rate at that which entered dermally. Evaluation of the ratio of 2,4-D to picloram excreted for workers receiving all of their exposure dermally with those who received both oral and dermal doses provide field evidence that dermal absorption of 2,4-D far exceeds dermal absorption of picloram.

Lavy, T.L., L.A. Norris, J.D. Mattice, and D.B. Marx. 1987. Exposure of forestry ground workers to 2,4-D, picloram and dichlorprop. Environmental Toxicology and Chemistry. 6: 209-224. Urine samples from 80 forest workers applying 2,4-D + dichlorprop or picloram in Arkansas, Mississippi and Oklahoma showed that absorbed doses of herbicide were below the no observed effect level. Knapsack and hypohatchet operators received higher absorbed doses than those using injection bar and hack-and-squirt methods. The absorbed dose of dichlorprop and picloram ranged in both cases from undetectable to 0.18 and 0.02 mg/kg body wt, resp. During application, operators of knapsack sprayers following customary practices as well as those taking all feasible precautions received a higher dose of 2,4-D (0.04-0.24 mg/kg) when their clothing became saturated with spray, dew or perspiration than those in other crews.

- McMahon, C.K. and P.B. Bush. 1992. Forest worker exposure to airborne herbicide residues in smoke from prescribed fires in the southern United States. *American Industrial Hygiene Association Journal*. 53: 265-272.** A field validation study was conducted at 2 sites in Georgia in 1988 to measure the breathing zone concn of smoke-suspended particulate matter (SPM), herbicide residues and carbon monoxide (CO) during 14 operational fires. Smoke was monitored at sites burned within 30-169 d after treatment with labelled rates of forestry herbicides containing the a.i. imazapyr, triclopyr, hexazinone and picloram. Personal monitors and area monitors employing glass fibre filters and polyurethane foam collection media were used. No herbicide residues were detected in the 140 smoke samples from the 14 fires, even though the sensitivity of the monitoring methods was in the 0.1-4.0 µg/m³ range (several hundred to several thousand times less than any established occupational exposure limit for herbicides). Concn, however, were highly variable, depending on fire conditions and the location of personnel. Worker respirable (2.3-µm particle cut-off point) SPM concn varied between 0.2 and 3.7 mg/m³. Exposure periods depended on fire size, and ranged from 1.2 to 6.3 h. Area monitors that were replaced in high-density smoke zones had total SPM concn of between 2.0 and 45 µg/m³. CO breathing zone concn ranged from <6 to 30 ppm/h while the fires were being worked on (well below the Occupational Safety and Health Administration permissible exposure limit of 35 ppm/h when normalized to an 8-h work shift).
- McMahon, C.K., P.B. Bush, and T.G. Rials. 1994, Evaluation of worker respiratory exposure to herbicide residues in prescribed fire smoke: a preliminary report. Symposium on current research in the chemical sciences. Third Annual Southern Station Chemical Sciences Meeting, Alexandria, Louisiana, 1990. General Technical Report Southern Forest Experiment Station, USDA Forest Service., No. SO-101, 37-41.** Concentrations of smoke particles, herbicide residues and carbon monoxide were measured during 14 operational site-preparation prescribed fires on forest sites in Georgia which had been treated with labelled rates of imazapyr, triclopyr, hexazinone or picloram 30-169 days before burning.
- Monnig, E. 1992. Pesticides and human health: the complexities of risk. *Western Wildlands*. 18: 27-32.** A brief account is given on how people perceive risks, with reference to the health risk posed by pesticides. Herbicides used frequently in the USA, such as 2,4-D, picloram, dicamba, clopyralid and glyphosate, are used as examples to highlight short-comings in the U.S. Environment Protection Agency's toxicity data requirements for pesticides.
- Nolan R.J., N.L. Freshour, P.E. Kastl, and J.H. Saunders. 1984. Pharmacokinetics Of Picloram In Male Volunteers. *Toxicol. Appl. Pharmacol.* 76: 264-269.** The fate of picloram (4-amino-3,5,6-trichloropicolinic acid), an active ingredient in TORDON brand herbicides, was defined in 6 healthy male volunteers following single oral doses of 5.0 and 0.5 mg/kg, and a dermal dose

of 2.0 mg/kg. Picloram was administered orally as the sodium salt in grape juice. The dermal dose was applied to the volunteers' backs as the free acid dissolved in ethanol. Picloram was rapidly absorbed from the gastrointestinal tract ($t_{1/2}$ [half-life] = 20 min) and rapidly excreted unchanged in the urine. Over 90% of the oral dose was recovered as unchanged picloram in the urine excreted through 72 h; most of the dose (> 75%) was excreted within 6 h and the remainder was excreted with an average $t_{1/2}$ of 27 h. Picloram was slowly absorbed through the skin ($t_{1/2}$ = 12 h) and, based on the quantity of picloram excreted in the urine, only a small fraction (0.2%) of the picloram applied to the skin was absorbed. Picloram, because of its rapid excretion, had a low potential to accumulate in man during repeated or prolonged exposures. Picloram was poorly absorbed through human skin and it was not likely that acutely toxic quantities were absorbed by this route.

Sassman, J., R. Pienta, M. Jacobs, and J. Cioffi. 1984. Pesticide background statements. Volume 1. Herbicides. Agriculture Handbook, United States Department of Agriculture, Forest Service. No.633, 1110pp. This handbook begins with general information including sections on the USDA Forest Service, physical and chemical properties, toxicity, toxicity testing, relative toxicities, the fate and transport of pesticides in organisms, soil and water, assessment of hazards and the assumptions made in the preparation of the data presented. This preliminary section is followed by the background statements on amitrole, atrazine, 2,4-D, 2,4-DP [dichlorprop], dalapon, dicamba, fosamine ammonium, glyphosate, hexazinone, picloram, simazine and triclopyr. Each background statement includes sections on general information such as physical and chemical properties and the normal use patterns, toxicity to various organisms, mutagenicity, fate in the environment and in organisms, use by the USDA Forest Service, exposure and hazard assessment.

Schulz, C.O., P.K. LaGoy, and M.B. Paxton. 1986. Reviewing the literature on the health effects of phenoxy herbicides and associated dioxins. In, Chlorinated Dioxins And Related Compounds. O. Hutzinger. W. Crummett, F.W. Karasek, E. Merian, G. Reggiani, M. Reissinger, and S. Safe (eds.). Chemosphere. 15: 9-12, 2099-2102. This review covers all the available scientific information on the health effects of phenoxy herbicide formulation, phenoxy herbicide active ingredients, polychlorinated dibenzo-p-dioxin impurities, cacodylic acid, and picloram. Also included are scientific studies on the absorption, distribution, metabolism, and excretion of these substances in mammals. Unpublished reports that are in the public domain are covered in the review. The review does not include information on analytical methodology, analytical results, or information on environmental distribution and fate.

Schulz, C.O., S.A. Segal, and W.D. Reichardt. 1990. Review of literature on herbicides, including phenoxy herbicides and associated dioxins. Chemosphere. 20: 7-9, 1001-1004. A synopsis is presented of the published and unpublished scientific literature (between 1985 and 1988) relevant to the human health effects of 2,4-D, 2,4,5-T, cacodylic acid and picloram, and of the

chlorinated dibenzo-p-dioxins and dibenzofurans that contaminated formulations of the herbicides sprayed in Vietnam. Three tables provide information on the type and volume of literature, the nature of exposed groups or individuals and the category of injury resulting from exposure. It is concluded that the literature neither confirms nor denies the presence of lasting adverse health effects attributable to herbicide exposure in Vietnam.

Task Force on Water Quality Guidelines (Canada). 1990. Canadian water quality guidelines : updates, March, 1990 : appendix VI. Inland Waters Directorate, Water Quality Branch, 67 pp. Update to the Canadian Water Quality Guidelines, giving guidelines for amounts of picloram, metribuzin and cyanazine in raw water for drinking, recreational water, freshwater for aquatic life, agricultural uses, and industrial water supplies. Background information on uses and production, sources and pathways, environmental concentrations, and forms and fates in the aquatic environment are also included.

US Environmental Protection Agency. Health and Ecological Criteria Division. 1992. Drinking water criteria document for picloram. U.S. Environmental Protection Agency Washington, D.C., 1 v. (various pagings).

Witte, I., H. Jacobi, and U. Juhl-Strauss. 1995. Correlation of synergistic cytotoxic effects of environmental chemicals in human fibroblasts with their lipophilicity. Chemosphere 31: 4041-4049. Synergistic interactions between 2,4-D (94757) and environmental chemicals on in-vitro 2,4-D cytotoxicity and the influence of lipophilicity of the compounds were investigated. GM-05757 cells were incubated with 2,4-D (used as its dimethylammonium salt) in binary combinations with dimethyl-sulfoxide (67685), ethanol (64175), dichloroacetic-acid (79436), nitriloacetic-acid (139139), 4-chloroaniline (106478), picloram (1918021), 4-chlorophenol (106489), chloroflurenol (2536314), 2,4,6-trichlorophenol (88062), tributylamine (102829), pentachlorophenol (87865), or dicofol (115322) for 1 hour (hr). All compounds were used at concentrations previously determined not to have induced any growth inhibition (NOECs), measured as the ratio of cells counted immediately after exposure ended to those counted 48hr after exposure ended. The concentrations of 2,4-D and the other chemicals alone and in combination causing a 20% decrease in cell growth (EC20) were determined. Associations between the EC20s of the combinations and their lipophilicity, as indicated by the logarithm of the octanol/water partition coefficient, were examined by logistic regression techniques. All compounds enhanced the toxicity of 2,4-D, as evidenced by decreases in the EC20. Except in the case of nitriloacetic-acid, the decreases in the EC20 were similar, varying from 43.3 to 60.7% over that of 2,4-D alone. Combined exposure to 2,4-D plus nitriloacetic-acid reduced the EC20 by 10.6% compared to that of 2,4-D alone. Except for tributylamine, the decreases in EC20 produced by the combined exposures were strongly correlated with their lipophilicity. The correlation coefficient was reduced if tributylamine was included in the analysis. The authors conclude that all chemicals may exhibit synergistic toxic effects when combined at nontoxic doses with dissimilar

compounds. The strength of the correlation appears to be related to lipophilicity. This correlation may reflect the ability of lipophilic compounds to damage the cell membrane which then facilitates and enhances uptake of hydrophilic agents.

Wood, J.A. and D.H.J. Anthony. 1997. Herbicide contamination of prairie springs at ultratrace levels of detection. J. environ. qual. American Society Of Agronomy. v. 26: 1308-1318. Natural springs provide an opportunistic subject for assessing aquifer contamination. To determine the frequency and level of aquifer contamination by herbicides in the Canadian prairie, a study of natural springs draining small surficial aquifers a few hectares in area was carried out in southern Saskatchewan. All but one of the aquifers investigated received herbicide applications either for agricultural purposes or brush control. Elevated tritium isotope activities (10-60 TU) confirmed recent recharge of these aquifers. No wells were present on these aquifers. Therefore, the possibility of contamination by direct entry down wells was eliminated from the study. Large volume extraction technology permitted detections of herbicides at ng L⁻¹ levels. This is the first study of herbicides in natural springs in Canada. Herbicides were detected in 23% of samples collected. The most frequently detected analyses being atrazine (6-chloro-N²-ethyl-N⁴ (isopropyl) -1,3,5-triazine-2,4-diamine), picloram (4-amino-3,5,6 trichloropicolinic acid) and 2,4-D ((2,4-dichlorophenoxy)acetic acid), with detections in 12, 7, and 7% of samples collected, respectively. The results show that shallow aquifer contamination occurs in the absence of wells. However, the levels detected were in the ng L⁻¹ (ppt) range, which is much less than levels commonly reported in most well surveys. None of the herbicide concentrations exceeded any guidelines for drinking water, livestock, irrigation, and aquatic life including Canadian, Provincial, World Health Organization, and USEPA guidelines.

MAMMALIAN TOXICOLOGY

Adams, S.L., S.T. Horvat, A.E. Irwin, R.W. Junkin, N.M. Koreman, and B.R. Blakley. 1991. The Effects Of Tordon 202c Exposure On Urethan-Induced Lung Adenoma Formation In Female Cd-1 Mice. *Veterinary And Human Toxicology* 33: 209-211.

Blakley, B.R. 1997. Effect of Roundup and Tordon 202C herbicides on antibody production in mice. *Veterinary and Human Toxicology*. 39: 204-206.
Female CD-1 mice were exposed to Tordon 202C (2,4-D and picloram) or Roundup (glyphosate) in drinking water for 26 d at concentrations ranging from 0 to 0.42% or from 0 to 1.05%, respectively. The mice were inoculated with sheep red blood cells to produce a T-lymphocyte, macrophage dependent antibody response on day 21 of the herbicide exposure period. Tordon 202C dosing reduced weight gain and water consumption at the 0.42% level of exposure. Roundup exposure did not alter weight gain or water consumption. Antibody production was unaffected by Roundup dosing, suggesting that Roundup is unlikely to cause immune dysfunction under normal application conditions. In contrast, all levels of Tordon 202C exposure reduced antibody production by as much as 45%. The immunosuppressive activity of Tordon 202C was associated with levels more than 12X the normal application level, although it was not determined which component of the formulation was responsible for the immunosuppressive effect. The presence of immune alteration subsequent to exposure to Tordon 202C at levels marginally above the normal application levels suggests that chronic exposure to Tordon 202C in the environment has the potential to alter immune function.

Blakley, P.M., J.S. Kim, and G.D Firneisz. 1989. Effects Of Paternal Subacute Exposure To Tordon 202c On Fetal Growth And Development In Cd-1 Mice. *Teratology* 39: 237-242. Male CD-1 mice were exposed to Tordon 202c (a picloram and 2,4-D combination herbicide) in the drinking water at concentrations of 0.21, 0.42, and 0.84% solutions for 60 days prior to mating with untreated females. Subsequently there was no exposure to Tordon 202c during gestation. Fetal weight and crown-rump length were reduced in the highest dosage group. The incidence of malformed fetuses (e.g., ablepharon, cleft palate, and unilateral agenesis of the testes) was increased in the middle dosage group while the incidence of fetuses with variants was increased in the lowest (e.g., an extra pair of ribs) and the highest dosage groups (e.g., incomplete ossification of the skeleton). The frequency of pregnancy failure was increased in the middle dosage group. Indices of paternal toxicity included increased lethality and decreased water consumption in the highest dosage group and increased relative spleen weights in the lowest and middle dosage groups. The results suggest paternally mediated reproductive toxicity.

Blakley, P.M., J.S. Kim, and G.D. Firneisz. 1989. Effects Of Gestational Exposure To Tordon 202c On Fetal Growth And Development In Cd-1 Mice. *J*

Toxicol Environ Health 28: 309-316. The teratogenic effects of Tordon 202c, a picloram and 2,4-D combination formulation, are unknown. Pregnant CD-1 mice were exposed to Tordon 202c in the drinking water at concentrations of 0.10, 0.21, and 0.42% from d 6 to 15 of gestation. Fetal growth parameters, including body weight and crown-rump length, were reduced in a dose-dependent manner, as was placental weight. The incidence of dead fetuses/resorptions and malformed fetuses (especially cleft palate) was increased in the highest dosage group. A subtle indication of maternal toxicity was noted in the highest dosage group as evidenced by decreased water consumption and increased relative liver weight. The present study suggests that Tordon 202c is embryotoxic and teratogenic in CD-1 mice when administered during organogenesis.

Brooks, J.J., J.L. Rodrigue, M.A. Cone, K.V. Miller, B.R. Chapman, A.S. Johnson, and M.B. Edwards. 1995. Small mammal and avian communities on chemically-prepared sites in the Georgia sandhills. Proceedings of the Eighth Biennial Southern Silvicultural Research Conference, Alabama, 1994., USDA Forest Service. No. SRS-1, 21-23. The effects of 3 forestry herbicide site preparation treatments (hexazinone, picloram + triclopyr, and imazapyr) on small mammal and avian communities were compared at pre-treatment, and 1, 2, and 3 years post-treatment in the Sandhills physiographic region of Marion County, Georgia. Few differences in small mammal capture rates occurred among treatments. Capture rates declined immediately following site preparation, but returned to pre-treatment levels by 18 months post-treatment. The greatest winter avian abundance occurred at 3 years post-treatment; however, no differences in winter avian abundance were observed among treatments. In year 3 post-treatment, summer birds favouring forest edge + scrub habitats were higher on hexazinone-treated sites. Summer avian abundance was strongly associated with residual woody vegetation.

Burroughs, B.L., C.S. Johnson, and V.F. Garry. 1996. In vitro micronucleus response of commercial chlorophenoxy herbicides and adjuvants. Environmental and Molecular Mutagenesis 27: p 11.

Chaturvedi, A.K. 1993. Biochemical and toxicological studies on the mixtures of three commonly used herbicides in mice. Archives of Environ. Contamin. and Toxicol. 24: 449-454. Herbicidal-mixtures have not been adequately studied in biological systems. Therefore, mixtures of three commonly-used herbicides were evaluated. Alachlor (AL), atrazine (AT), picloram (PI), AL+AT, AT+PI, PI+AL and AL+AT+PI, at 10 ppm (in drinking water) of each herbicide were provided to mice for 30, as well as for 90, days ad libitum; these herbicides and mixtures, at 100 mg/kg (in corn oil) of each herbicide, were also given to additional groups of mice by oral intubation daily for 21 days. In the 30-day test, the spleen/body weight ratios on Day 31 with respect to the control were increased in the AT (53%) and AL+AT (44%) groups. Decreases in the body weights were noted in the treated groups after Day 31 during the 90-day test. Serum glutamic-pyruvic transaminase (SGPT), glutamic-oxalacetic

transaminase (SGOT) and alkaline phosphatase activities with AL+AT+PI were elevated by 36-92% on Day 91; SGPT (34%) and SGOT (73%) activities were increased with AL. During the 21-day oral intubation study, the mouse body weights in the mixture groups were generally lower than the control ($p < 0.05$). The liver/body weight ratios were elevated in all groups (16-38%); the spleen/body weight ratio increased with PI (50%). The kidney/body weight ratios were high with PI+AL and AL+AT+PI ($p < 0.05$). Excluding AT, the pentobarbital-induced sleep was less (51-77%) in the herbicide-treated groups. Also, necrosis of individual and small groups of hepatocytes was noted with the mixtures. The hepatic metabolism of aniline, amidopyrine, phenacetin, and/or benzo(a)pyrene in both 21- and 90-day tests was generally high in the herbicide-treated groups ($P < 0.05$). Findings from this study reveal that these herbicidal-mixtures have the potential to cause hepatotoxicity and stimulate the liver xenobiotic-metabolizing enzymes in mice.

Chaturvedi, A.K., L.M. Radke, K. Gholami, I.E. Berg, and G. Padmanabhan. 1989. Toxicity Of Alachlor At Atrazine At And-Or Picloram Pi In Mice. 73rd Annual Meeting Of The Federation Of American Societies For Experimental Biology, New Orleans, Louisiana, Usa, March 19-23., Faseb (Fed Am Soc Exp Biol) J 3 (4). A1189.

Ebbersten, S. 1972. Picloram (4-amino-3,5,6-trichloropicolinic acid). Studies concerning persistence in soil and plants and biological methods for determining picloram residues. [Picloram (4-amino-3,5,6-trikloropikolinsyra). Studier av persistens i jord och växter samt metodstudier rörande biologisk bestämning av pikloramrester]. Uppsala, Institutionen för Växtodling, Lantbrukshögskolan 175 pp. Swedish English. This publication is divided into 2 main sections: 1. A literature survey including sections on (a) the effects of picloram on higher plants, soil micro-organisms and higher animals (mammals, birds and fish), (b) the persistence of picloram in plant tissue, soil and water and (c) methods for determining picloram residues. 2. Results of investigations carried out in Sweden during 1966-70 to study persistence and movement in the soil, determination of residues and the effects on following crops of wheat and potatoes.

Garten, C.T. Jr. and J.R. Trabalka. 1983. Evaluation of models for predicting terrestrial food chain behavior of xenobiotics. Environmental Science and Technology 17: 10, 590-595. Results from an extensive literature review were used to evaluate the capabilities of existing simple empirical bioaccumulation models proposed for terrestrial vertebrates and fish. Generic application of such models appeared to be unsuitable; bioaccumulation in mammals and birds was very weakly correlated or uncorrelated with xenobiotic (exotic organic chemicals) bioaccumulation factors from fish tests (r^2 values were 0.09-0.43). The problem of wrongly classifying a compound, on the basis of physicochemical data, as not having a high bioaccumulation potential (e.g. methyl mercuric chloride) is discussed. Nontoxic substances were also given

high bioaccumulation potentials by the screening model. Av. log-transformed bioaccumulation factors for xenobiotics such as buthidazole, dicamba, fenoprop, picloram, 2,4-D and other herbicides are tabulated for 6 mammal groups, fish, poultry and small birds. Other types of pesticide are also included in the data.

Gorzinski S.J., K.A. Johnson, R.A. Campbell, and T.D. Landry. 1987. Dietary Toxicity Of Picloram Herbicide In Rats. J Toxicol Environ Health 20: 367-378. The toxicity of orally administered technical-grade picloram was evaluated in male and female Fischer 344 rats. Dietary dose levels were up to 2000 mg/kg body weight (bw).cntdot.d for 2 wk, 500 mg/kg bw.cntdot.d for 13 wk, or 200 mg/kg bw.cntdot.d for 12 mo. Routine indices of toxicity were evaluated at all of the respective time periods. Body weight, food consumption, clinical chemistries, urinalyses, and hematological determinations were considered unaffected by treatment. The only treatment-related effect, regardless of the duration of exposure, was in the liver of both male and female rats. This was generally manifested as an increase in the liver-to-body weight ratio and slight hypertrophy and pallor of the centrilobular hepatocytes. These effects were consistently present in rats receiving 1000 mg/kg bw.cntdot.d for 2 wk, 300 mg/kg bw.cntdot.d for 13 wk, or 200 mg/kg bw.cntdot.d for 6 or 12 mo. Similar effects were marginally evident for rats receiving 500 mg/kg bw.cntdot.d, 150 mg/kg bw.cntdot.d for 13 wk, or 60 mg/kg bw.cntdot.d for 6 or 12 mo. At 60 mg/kg bw.cntdot.d, the effects were not progressive from 6 to 12 mo. The no-observable-effect level (NOEL) was 20 mg/kg bw.cntdot.d for male and female rats fed picloram for 12 mo.

Hayes J.R, LW. Condie, J.F. Borzelleca. 1986. Acute 14-Day Repeated Dosing And 90-Day Subchronic Toxicity Studies of Potassium Picloram. Fundam. Appl. Toxicol. 7(3): 464-470. Potassium picloram was administered either by gavage (acute studies) or in drinking water to male and female Sprague-Dawley-derived rats (14-day and 90-day studies). The acute oral LD50 was 950 mg/kg (812-1120) for males and 686 mg/kg (599-786) for females. Depression, prostration, ataxia, tremors, and convulsions preceded death. There were no consistent biologically significant compound-related effects in rats that received 60, 190, or 600 mg potassium picloram/kg/day for 14 days. In the subchronic study, rats received 60, 190, 600 or 1070 mg potassium Picloram/kg/day in drinking water for 90 consecutive days. There were only 4 male and 2 female survivors out of 20 rats of each sex at the 1070 mg/kg dose and 16 male and 18 female survivors at the 600 mg/kg dose. Mortality was dose dependent. Administration of picloram appeared to exacerbate renal and hepatic lesions commonly noted in rats of this age. For example, at levels up to 1070 mg/kg mild lesions in the kidney of treated rats, especially in males at 600 mg/kg, were noted. Also noted were an increased incidence of mononuclear liver foci in male rats that received 190 and 600 mg/kg and an increased severity of mononuclear liver foci in females that received 600 mg/kg. There were no other consistent biologically significant compound-related effects. No specific organ

site toxicity could be identified in these studies. Toxicity from exposure to picloram in drinking water is apparently low.

- Kosterov, V.M. and V.V. Ermakov. 1980. Determination of picloram in organs and tissues of animals Herbicide. Khim-Sel'sk-Khoz. Moskva, "Khimia". v. 13: 55-57. Russian.**
- McKinley, R.S. and G.P. Arron. 1987. Distribution of 2,4-D and picloram residues in environmental components adjacent to a treated right-of-way. Report / Ontario Hydro, Research Division ; no. 87-49-K v, 27.** Selective herbicide application to non-compatible tree species is an integral part of vegetation management of Ontario Hydro rights-of-way. Tordon 101 is presently being used to control the growth of non-compatible woody plant species (those which have the potential for interfering with power transmission) on rights-of-way in Northern and Eastern Ontario, where as 2,4-D and picloram is generally used in Southern Ontario. The study was conducted at two sites along the Des Joachims power corridor located along the eastern boundary of Algonquin Park, including a chain of 4 lakes whose watershed included part of the right-of-way. Sampling for residues in soil, vegetation lake water, sediment and representative fish and mammal species was conducted in areas adjacent to the right-of-way before herbicide treatment and at pre-selected times within a 22-month period after application.
- Miller, K.V. and Chapman B.R. 1995. Responses of vegetation, birds and small mammals to chemical and mechanical site preparation, In, FRI Bulletin, No 192; Popular Summaries from Second International Conference on Forest Vegetation Management. R.E. Gaskin and J.A. Zabkiewicz (eds). New Zealand Forest Research Institute, Rotorua, New Zealand. p 146-148 1995**
- Nolte, K.R. and T.E. Fulbright. 1997. Plant, small mammal, and avian diversity following control of honey mesquite. Journal of Range Management 50: 205-212.** A field trial was conducted in the Welder Wildlife Foundation Refuge, Texas, on a mesquite-mixed grass community dominated by *Prosopis glandulosa* (honey mesquite), interspersed with chaparral (e.g. *Acacia smallii*, *Celtis pallida* and *Zanthoxylum fagara*) and grasses (*Stipa leucotricha*, *Panicum obtusum* and *Setaria leucopila*), to investigate the effects of herbicide application to *P. glandulosa* on community plant and vertebrate species richness and diversity. A 1:1 mixture of triclopyr + picloram was applied to three 13 ha plots during 1992 and to 3 additional plots in 1993. Mesquite and forb canopy cover in the zone \leq 1 m from the soil surface were lower within treated plots than in control plots in both years. Grass canopy cover did not differ between herbicide-treated plots and control plots. Vegetation species richness and evenness, Shannon's index, beta diversity and the proportion of rare plant species did not differ between controls and sites treated during 1992 and 1993. Rodent and avian relative frequency, richness and diversity were not significantly different in 1992 on herbicide treatment plots and untreated

controls. It is suggested that the application of triclopyr + picloram in mesquite-mixed grass communities in the Texas Coastal Bend does not significantly reduce plant and vertebrate species richness and diversity within the first 2 years after treatment.

Oakes D.J. and J.K. Pollak. 1999. Effects of a herbicide formulation, Tordon 75D(R), and its individual components on the oxidative functions of mitochondria. *Toxicology* 136: 41-52. This investigation evaluates the toxicity of a herbicide formulation, as well as testing its active and other components (other components comprise all components of Tordon 75D(R) excluding the active components: i.e. the solvents, triisopropanolamine and diethyleneglycol monoethyl ether, a silicone defoamer and a proprietary surfactant, polyglycol 26-2). The results showed that Tordon 75D(R) (a mixture of the triisopropanolamine salts of 2,4-dichlorophenoxy acetic acid (2,4-D) and 4-amino-3,5,6-trichloropicolinic acid (picloram) and its other components) impaired the oxidative functions of submitochondrial particles (SMPs). The effective concentrations that caused 50% inhibition of SMP activity (EC50S) for Tordon 75(R) were in the low micromolar range for 2,4-D and picloram in the presence of the other components, while in the absence of the other components exposure to 136 times higher concentrations of the triisopropanolamine forms of 2,4-D and picloram administered as a mixture were required to inhibit the oxidative functions of SMPs. Tordon 75(R) also significantly decreased the respiratory control ratio of intact rat liver mitochondria. The results show that the toxic effects of Tordon 75(R) on SMPs (at the EC50) and intact rat liver mitochondria were not due to any additive or synergistic actions of a mixture of its active and other components, but rather were caused solely by the proprietary surfactant. Since mitochondria are responsible for over 90% of the energy production in all eukaryotic organisms, the use of the SMP assay provides a convenient in vitro assay for evaluating cellular toxicity and can be regarded as an informative screening assay when designing chemical products which contain mixtures of chemicals.

Ogryzkov, S.E., L.P. Gontsova, V.I. Cherkasova, and G.R. Kas'yanenko. 1988. Clinical and morphological assessment of effect of picloram in wheat grain on laboratory animals. *Sov. Agric. Sci.* New York, N.Y. : Allerton Press.. (12) p. 48-51. English, Russian.

Pereira L.F., A.P. Campello, and O. Silveira. 1994. Effect of Tordon 2,4-D 64/240 Triethanolamine BR on the Energy Metabolism of Rat Liver Mitochondria. *Journal of Applied Toxicology* 14: p 21-26. Tordon herbicide, which is a mixture of 4-amino-3,5,6-trichloropicolinic acid (picloram) and 2,4-dichlorophenoxyacetic acid (2,4-D), depresses the phosphorylation efficiency of the rat liver mitochondria, as inferred from the decrease of the respiratory control coefficient and the ADP/O ratios when NAD⁺-dependent substrates were used; NADH oxidase and NADH cytochrome c reductase were also inhibited, without any effect on the other enzymatic complexes of the respiratory chain. Tordon (66.2 nmol picloram + 270 nmol 2,4-D mg⁻¹ protein)

affected the amplitude of swelling induced by glutamate, succinate, (N,N,N',N'-tetramethyl-p-phenyldiamine + sodium ascorbate and ATP. These results characterize an interaction of Tordon with complex I of the respiratory chain and also a partial collapse of the proton motive force of the mitochondrial inner membrane without affecting its elasticity.

Ralphs, M.H., G.D. Manners, and D.R. Gardner. 1998. Toxic alkaloid response to herbicides used to control tall larkspur. *Weed Science* 46: 116-119.

Herbicides have been used to control tall larkspur (*Delphinium barbeyi*) to prevent cattle deaths by this weed. As there is some evidence that tall larkspur may become more toxic and more palatable during the desiccation process following herbicide treatment, a series of studies were conducted to measure toxic alkaloid concentration in tall larkspur following treatment with metsulfuron, picloram and glyphosate. Herbicides were applied to larkspur plants grown in a greenhouse (1990), to field (Salina, Utah) plots infested with larkspur (1993) and to individual larkspur plants in the field (1995). Leaves were harvested up to 14 or 28 days following treatment and toxic alkaloids were measured. Metsulfuron increased toxic alkaloid concentration in the 1990 greenhouse study and in 1993 field plot studies, and increased both concentration and absolute amount of toxic alkaloids in 1995 individual plant treatments. Alkaloids in plants treated with picloram either remained unchanged or declined slightly in all 3 studies and were similar to control plants. In the 1995 study, glyphosate caused the relative concentration of alkaloids to increase as the plants desiccated, but the absolute amount of alkaloids was similar to control plants. Picloram and glyphosate did not reduce alkaloid concentration; thus, the risk of poisoning remains until plants desiccate. Metsulfuron increased alkaloid concentration, thus increasing the risk of poisoning. Cattle should not be allowed to graze sprayed areas until larkspur desiccates and withers.

Robens, J.F. 1978. Tests For Possible Carcinogenicity Of 20 Pesticides In Osborne Mendel Rats And B-6c-3f-1 Mice. *Toxicology And Applied* 45:236.

Sassman, J., R. Pienta, M. Jacobs, and J. Cioffi. 1984. Pesticide background statements. Volume 1. Herbicides. *Agriculture Handbook, United States Department of Agriculture, Forest Service. No.633, 1110pp.* This handbook begins with general information including sections on the USDA Forest Service, physical and chemical properties, toxicity, toxicity testing, relative toxicities, the fate and transport of pesticides in organisms, soil and water, assessment of hazards and the assumptions made in the preparation of the data presented. This preliminary section is followed by the background statements on amitrole, atrazine, 2,4-D, 2,4-DP [dichlorprop], dalapon, dicamba, fosamine ammonium, glyphosate, hexazinone, picloram, simazine and triclopyr. Each background statement includes sections on general information such as physical and chemical properties and the normal use patterns, toxicity to various organisms, mutagenicity, fate in the environment and in organisms, use by the USDA Forest Service, exposure and hazard assessment.

- Schulz, C.O., P.K. LaGoy, and M.B. Paxton. 1986. Reviewing the literature on the health effects of phenoxy herbicides and associated dioxins. In, Chlorinated Dioxins And Related Compounds [5th International Symposium on Chlorinated Dioxins and Related Compounds, Bayreuth (FRG) , 1985 Sep 16-19.] O. Hutzinger, W. Crummett, F.W. Karasek, E. Merian, G. Reggiani, M. Reissinger, and S. Safe (eds.). Chemosphere vol. 15, no. 9-12, pp. 2099-2102.** This review covers all the available scientific information on the health effects of phenoxy herbicide formulation, phenoxy herbicide active ingredients, polychlorinated dibenzo-p-dioxin impurities, cacodylic acid, and picloram. Also included are scientific studies on the absorption, distribution, metabolism, and excretion of these substances in mammals. Unpublished reports that are in the public domain are covered in the review. The review does not include information on analytical methodology, analytical results, or information on environmental distribution and fate.
- Schulz, C.O., S.A. Segal, and W.D. Reichardt. 1990. Review of literature on herbicides, including phenoxy herbicides and associated dioxins. Chemosphere. 20: 7-9, 1001-1004.** A synopsis is presented of the published and unpublished scientific literature (between 1985 and 1988) relevant to the human health effects of 2,4-D, 2,4,5-T, cacodylic acid and picloram, and of the chlorinated dibenzo-p-dioxins and dibenzofurans that contaminated formulations of the herbicides sprayed in Vietnam. Three tables provide information on the type and volume of literature, the nature of exposed groups or individuals and the category of injury resulting from exposure. It is concluded that the literature neither confirms nor denies the presence of lasting adverse health effects attributable to herbicide exposure in Vietnam.
- Smith, R.A. and D. Lewis. 1988. A potpourri of pesticide poisonings in Alberta in 1987. Veterinary and Human Toxicology. 30: 118-120.** Brief case histories are given of poisoning by: carbofuran in dogs, cats, ducks and cattle; lindane, carboxin and thiram in cattle; lindane and carboxin in cattle and a dog; phorate in pigs; chlordane in a dog; picloram in sheep; and 4-aminopyridine in racing pigeons. Simple extraction procedures and a gas chromatography mass spectrometry system were used for diagnosis.
- Stott, W.T., K.A. Johnson, T.D. Landry, S.J. Gorzinski, and F.S. Cieszlak. 1990. Chronic Toxicity And Oncogenicity Of Picloram In Fischer 344 Rats. J Toxicol Environ Health 30: 91-104.** The chronic toxicity and oncogenicity of the herbicide picloram was studied in male and female Fischer 344 rats administered 0, 20, 60, or 200 mg/kg.cntdot.d technical-grade picloram via their feed for 2 yr. A comprehensive set of in-life and clinical pathology parameters was measured and an extensive list of tissues was examined grossly and by light microscopy from control and treatment groups of animals. The primary treatment-treated effect observed in the study was hepatocellular swelling and altered tinctorial properties in the central regions of the liver lobules of both sexes of rats ingesting 60 or 200 mg/kg.cntdot.d picloram. Males were more affected than females. Increases in liver weights accompanied these changes in

both sexes of rats ingesting the high dose level of picloram. All other histopathologic lesions observed were typical of those that normally occur in aged Fischer 344 rats. There were no treatment-related increases in the incidence of any particular tumor type or in total tumors. No treatment-related effects were observed in rats ingesting 20 mg/kg.cntdot.d of the test material.

Trotter, D.M., R.A. Kent, and M.P. Wong. 1990. Canadian water quality guidelines for picloram. Environment Canada, Inland Waters Directorate, Water Quality Branch, . v, 62 p. This report summarizes a literature review on the uses, fate, and effects of picloram (herbicide) on raw water for drinking water supply, freshwater aquatic life, agricultural water uses, recreational water quality and aesthetics, and industrial water supplies. Water quality guidelines for the protection of specific water uses are recommended in this report.

Zakharik, N.V. 1985. Quality of meat from sheep with chronic poisoning by Tordon 22K herbicide (picloram-potassium). Veterinarnaya Nauka Proizvodstvu. 23: 196-198. Russian. Picloram potassium was not toxic for 5 sheep when given at 1, 5 or 25 mg/kg body weight daily for 3 months. Meat from sheep slaughtered 5 and 10 days after the final dose contained more amino and ammonia nitrogen than usual and had a high pH and an unpleasant smell upon boiling. Meat from sheep killed 15 or 30 days after the final dose seemed to be normal.

AVIAN TOXICOLOGY

- Brooks, J.J., J.L. Rodrigue, M.A. Cone, K.V. Miller, B.R. Chapman, A.S. Johnson, and M.B. Edwards. 1995. Small mammal and avian communities on chemically-prepared sites in the Georgia sandhills. Proceedings of the Eighth Biennial Southern Silvicultural Research Conference, Alabama, 1994., USDA Forest Service. No. SRS-1, 21-23.** The effects of 3 forestry herbicide site preparation treatments (hexazinone, picloram + triclopyr, and imazapyr) on small mammal and avian communities were compared at pre-treatment, and 1, 2, and 3 years post-treatment in the Sandhills physiographic region of Marion County, Georgia. Few differences in small mammal capture rates occurred among treatments. Capture rates declined immediately following site preparation, but returned to pre-treatment levels by 18 months post-treatment. The greatest winter avian abundance occurred at 3 years post-treatment; however, no differences in winter avian abundance were observed among treatments. In year 3 post-treatment, summer birds favouring forest edge + scrub habitats were higher on hexazinone-treated sites. Summer avian abundance was strongly associated with residual woody vegetation.
- Ebbersten, S. 1972. Picloram (4-amino-3,5,6-trichloropicolinic acid). Studies concerning persistence in soil and plants and biological methods for determining picloram residues. [Pikloram (4-amino-3,5,6-trikloropikolinsyra). Studier av persistens i jord och växter samt metodstudier rörande biologisk bestämning av pikloramrester]. Uppsala, Institutionen för Vaxtodling, Lantbrukshogskolan 175 pp. Swedish English.** This publication is divided into 2 main sections: 1. A literature survey including sections on (a) the effects of picloram on higher plants, soil micro-organisms and higher animals (mammals, birds and fish), (b) the persistence of picloram in plant tissue, soil and water and (c) methods for determining picloram residues. 2. Results of investigations carried out in Sweden during 1966-70 to study persistence and movement in the soil, determination of residues and the effects on following crops of wheat and potatoes.
- Miller, K.V. and Chapman B.R. 1995. Responses of vegetation, birds and small mammals to chemical and mechanical site preparation, In, FRI Bulletin, No 192; Popular Summaries from Second International Conference on Forest Vegetation Management. R.E. Gaskin and J.A. Zabkiewicz (eds). New Zealand Forest Research Institute, Rotorua, New Zealand. p 146-148 1995**
- Nolte, K.R. and T.E. Fulbright. 1997. Plant, small mammal, and avian diversity following control of honey mesquite. Journal of Range Management 50: 205-212.** A field trial was conducted in the Welder Wildlife Foundation Refuge, Texas, on a mesquite-mixed grass community dominated by *Prosopis glandulosa* (honey mesquite), interspersed with chaparral (e.g. *Acacia smallii*,

Celtis pallida and *Zanthoxylum fagara*) and grasses (*Stipa leucotricha*, *Panicum obtusum* and *Setaria leucopila*), to investigate the effects of herbicide application to *P. glandulosa* on community plant and vertebrate species richness and diversity. A 1:1 mixture of triclopyr + picloram was applied to three 13 ha plots during 1992 and to 3 additional plots in 1993. Mesquite and forb canopy cover in the zone ≤ 1 m from the soil surface were lower within treated plots than in control plots in both years. Grass canopy cover did not differ between herbicide-treated plots and control plots. Vegetation species richness and evenness, Shannon's index, beta diversity and the proportion of rare plant species did not differ between controls and sites treated during 1992 and 1993. Rodent and avian relative frequency, richness and diversity were not significantly different in 1992 on herbicide treatment plots and untreated controls. It is suggested that the application of triclopyr + picloram in mesquite-mixed grass communities in the Texas Coastal Bend does not significantly reduce plant and vertebrate species richness and diversity within the first 2 years after treatment.

Prostov, Yu.P. and T.A. Farafonova. 1988. Influence of pikloram [herbicide] on some biochemical parameters in broilers. Sbornik Nauchnykh Trudov, Moskovskaya Veterinarnaya Akademiya., No. 159, 62-66. Russian.

Sassman, J., R. Pienta, M. Jacobs, and J. Cioffi. 1984. Pesticide background statements. Volume 1. Herbicides. Agriculture Handbook, United States Department of Agriculture, Forest Service. No.633, 1110pp. This handbook begins with general information including sections on the USDA Forest Service, physical and chemical properties, toxicity, toxicity testing, relative toxicities, the fate and transport of pesticides in organisms, soil and water, assessment of hazards and the assumptions made in the preparation of the data presented. This preliminary section is followed by the background statements on amitrole, atrazine, 2,4-D, 2,4-DP [dichlorprop], dalapon, dicamba, fosamine ammonium, glyphosate, hexazinone, picloram, simazine and triclopyr. Each background statement includes sections on general information such as physical and chemical properties and the normal use patterns, toxicity to various organisms, mutagenicity, fate in the environment and in organisms, use by the USDA Forest Service, exposure and hazard assessment.

Smith, R.A. and D. Lewis. 1988. A potpourri of pesticide poisonings in Alberta in 1987. Veterinary and Human Toxicology. 30: 118-120. Brief case histories are given of poisoning by: carbofuran in dogs, cats, ducks and cattle; lindane, carboxin and thiram in cattle; lindane and carboxin in cattle and a dog; phorate in pigs; chlordane in a dog; picloram in sheep; and 4-aminopyridine in racing pigeons. Simple extraction procedures and a gas chromatography mass spectrometry system were used for diagnosis.

Somers, J.D., E.T. Jr. Moran, and B.S. Reinhart. 1978. Hatching success and early performance of chicks from eggs sprayed with 2,4-D, 2,4,5-T and picloram at various stages of embryonic development. Bulletin of Environmental

Contamination and Toxicology. 20: 289-293. Aqueous solutions of 2,4-D, 2,4,5-T and picloram were sprayed on hens' eggs at 10 times the normal rate (11.2 kg/ha) 0, 4 and 18 days after the onset of embryonic development. The eggs had been stored prior to incubation over a 24-day period. No adverse effects on any parameter used to evaluate either incubation or subsequent live performance could be attributed to either spray treatment or embryonic age when applied. Extended pre-incubation storage significantly reduced hatching success, but no interaction with herbicide treatment was evident. Chicks from eggs stored 1-2 and 23-24 days before incubation performed comparably and were uninfluenced by all treatments during incubation.

NON-TARGET PLANTS AND RECROPPING

Abramova, K.A. T.D. Panasyuk, and E.A. Nikanorova. 1977. The persistence of Tordon 22K [picloram-potassium] in soil and its residual effects on crop plants. Khimiya v Sel'skom Khozyaistve. 15: 55-58. Russian. In trials in Stavropol' and Zaporozh'e provinces, picloram at 1 kg/ha, applied in autumn, gave almost complete control of Russian knapweed [*Centaurea repens*]. Herbicide inactivation was investigated over a period of 46 months after application. Proso millet [*Panicum miliaceum*] and maize were the most resistant cereal crops to picloram residues and crops could be sown in the year following treatments; yields were reduced but were higher than in knapweed-infested fields. Winter wheat could not be sown for 3 years after application of 1 kg/ha. It was found that picloram residues were present in plant tissues at concns. many times greater than those in the soil and both residues in soil and in crop debris could put sensitive crops at risk.

Abramova, K.A., T.D. Panasyuk, E.A. Nikanorova, and V.F. Vasil'chenko. 1975. Picloram behaviour in water, soil and plants. Materialy 10go Mezhdunarodnogo Simpoziuma Stran-Chlenov SEV, Pushchino, SSSR. Vol. 2: 98-100. Russian. Field trials in 1968-73 on a dark-chestnut soil in a region of inadequate rainfall showed that 1 kg picloram/ha persisted in the top 40 cm of soil for 46 months and 2% of the amount originally applied was recovered from the top 80 cm of soil. Picloram residues in plants growing on treated soil amounted to 6 mg/kg found in proso millet straw and 0.2 mg/kg found in the grain. Maize plants growing in pot soil containing 1.5 mg picloram/kg accumulated 83 mg picloram/kg during 6 months. Cereal plants assimilated 1-3% of the applied amount and maize up to 10% with adequate moisture and dense sowing. In trials in 400-g capacity pots, 2 ml picloram/pot completely killed French beans and tomatoes and 4 ml/pot inhibited sunflower growth by 50%.

Agriculture Canada, Research Station, Kentville. 1976. Research Branch Report 1975, pp. 17-30. Picloram residues. The potassium salt of picloram (Tordon 22K) at 4.48 kg/ha (2 p.p.m.) was soil-incorporated to a depth of 15 cm. Analysis of the soil 18, 63, 145, 337, 504, 690 and 843 days later showed the presence of picloram at 1.86, 1.78, 1.32, 0.7, 0.28, 0.12 and 0.02 p.p.m., respectively. Soil containing 1.32 p.p.m. picloram inhibited the growth of carrots, parsnips, potatoes, table beets and rutabagas sown in the glasshouse. One year after the application of picloram, the growth of sweet corn and oats was reduced by about 20% while beans (*Phaseolus* sp.), parsnips and Swiss chard (*Beta vulgaris* var. *cicla*) failed to grow at all. Picloram residues 1055 days after application were 2.5 parts per billion (109) as determined by a bioassay using bean. P. 25. Test for picloram. A rapid, sensitive and specific fluorescence test for picloram was developed. Sulphuric acid 36 N solution was added to the dry residue in quartz tubes or on a white porcelain plate. Under short wavelength UV radiation, yellow fluorescence was observed. The test can also be carried out using glass test tubes and long wavelength UV radiation but this method is not so sensitive.

Agriculture Canada, Research Station, Regina. 1976. Research Branch Report 1975, pp. 265-272. P. 268. Herbicide behaviour in the environment. Results of investigations into the fate of herbicides in the environment are reported. The persistence of atrazine in Brown soils appeared to be related to Ca content and pH of the soil. The order of leachability of 3 uracil herbicides in a range of soil types was bromacil > terbacil > lenacil. Residue levels of 2,4-D of 0.002 and 0.017 $\mu\text{g}/\text{m}^3$ were detected in the air above Regina in June and July. The rate of volatilization of 2,4-D isooctyl ester from Asquith sandy loam soil was high for the first 24 h, after which time volatilization was negligible. The degradation of C-2242 (chlortoluron) in steam-sterilized soil was negligible, indicating that microbiological processes are important for the breakdown of this herbicide. Residues from spring applications of benazolin, benzoylprop, alachlor, nitrofen, profluralin and picloram were detectable the following October while asulam had disappeared. Benzoylprop-ethyl, alachlor, nitrofen and profluralin were detected only in the top 5 cm of soil whereas residues of benazolin, picloram and the acid derivative of benzoylprop were observed at lower depths. In a study of the persistence of 4 herbicides in irrigation water, simazine was the most persistent, followed by atrazine, monuron and bromacil.

Agriculture Canada, Research Station, Regina. 1979. Research Branch Report, 1976-1978, pp. 325-333. Herbicide behaviour in the environment: herbicide residues in soils. In a 3-year field study several herbicides were applied in early May of each year and the residues remaining in the 0 to 5- and 5 to 10- cm soil depths were measured at 5, 13 and 17 months. Asulam, dicamba, bromoxynil, bromoxynil + MCPA, propanil, 2,4-D and 2,4,5-T were not carried over from one growing season to the next, when applications were made in May. Herbicides applied during the summer or autumn were sometimes carried over, especially if the soil was dry. Slight carry-over (5-15% of the original application) was noted with alachlor, atrazine, benazolin, benzoylprop-ethyl, diclofop-methyl, dichlobenil, dinitramine, EPTC, flamprop-methyl, tri-allate and trifluralin. Moderate carry-over (15-30%) was observed with linuron, nitrofen, picloram, profluralin and simazine. Persistence data with picloram was difficult to assess since the herbicide was leached readily. The rates of degradation of tri-allate and trifluralin were the same when the chemicals were applied alone or together.

Berezovskii, M. Ya. 1974. Residues of herbicides in plants and soil. Doklady Vsesoyuznoi Akademii Sel'skokhozyaistvennykh Nauk imeni V.I Lenina. 6: 16-18. Russian. Picloram at 2-2.5 kg/ha completely kills Russian knapweed [*Centaurea repens*] but residues persist in soil for >3 years. Although proso millet and maize are not sensitive to picloram at 1.5-2 kg/ha, picloram residues were found in these plants 3 years after the soil had been treated. These residues in tolerant crop plants are a potential health hazard to people and animals. Dicamba at 15-20 kg/ha was completely degraded in soil within 1 year but its metabolite 3,6-dichlorosalicylic acid persisted longer in soil and was detected in crop plants 2-3 years after application to soil. Although dicamba and its metabolite have a low

toxicity to animals, the application of high rates of dicamba might lead to the accumulation of metabolites in crop products above the official tolerance level.

Berezovskii, M. Ya. and A.M. Krumzdorov 1974. Picloram residues in soils and plants. Doklady TSKhA. No. 180, II, 151-156. Russian. Trials were carried out in 1969-70 on permanent plots on a pale-chestnut, calcareous-solonchic, heavy loam soil in the low-rainfall area of the Stavropol' District. Picloram-potassium (as Tordon-22K) at 1.5-3 kg/ha was compared with dicamba-dimethylamine (as Banvel D) 10-15 kg/ha for the control of Russian knapweed [*Centaurea repens*] with application at the shooting stage. A little regrowth was noted at 2 years after the application of dicamba at 10-15 kg/ha whereas picloram 1.5-3 kg/ha still showed complete control after 3 years. Dicamba residues were determined by t.l.c. and picloram residues by a bioassay technique; [the herbicide is extracted from plant material by incubating the plant samples in soil and French beans are grown on this soil]. Picloram applications of 1.5-2 kg/ha left residues in the top 40 cm of soil for >4 years whereas dicamba was inactivated within 1 year. Although maize is relatively tolerant to picloram, residues 2 years after soil application accumulated in plants (especially leaves) and were not inactivated before harvest; residues in plants increased with the rate of the initial application. Picloram residues from applications of 1 kg/ha were detected in proso millet leaves 4 years after the application to the soil. The use of picloram is recommended on uncropped land only or on patches of heavy infestation of *C. repens*.

Brooks, J.J., A.S. Johnson, and K.V. Miller. 1993. Effects of chemical site preparation on wildlife habitat and plant species diversity in the Georgia sandhills. Gen-tech-rep-SO. [New Orleans, La.] : Southern Forest Experiment Station. 93: 605-612.

Camargo, L.M.P.C. de A. 1981. Effect of herbicides used on pastures on the entomopathogenic fungus *Metarhizium anisopliae* (Metsch.) Sorokin. [Efeito dos herbicidas utilizados nas pastagens sobre o fungo entomopatogenico *Metarhizium anisopliae* (Metsch.) Sorokin]. Biologico. recd. 1983, 47: 99-102. Portuguese. The results are given of in vitro tests to determine the effects on the entomopathogenic fungus *Metarhizium anisopliae* of herbicides commonly used on pastures in Sao Paulo, Brazil. All 3 herbicide treatments (2,4-D, alone or with picloram or dicamba) were highly toxic to the fungus, totally inhibiting growth and development.

Cessna, A.J., J. Waddington, and S. Bittman. 1989. Residues of 2,4-D and picloram in aspen poplar and soil after application with a roller. Canadian Journal of Plant Science. 69: 205-212. The use of wipers for herbicide application to brush regrowth in pastures was suggested for reducing damage to the forage understory. Estimates of picloram in the soil around the base of aspen poplar (*Populus tremuloides*) regrowth and of picloram and 2,4-D in poplar tissues were made 84 and 39 d, resp., after a roller application of the herbicides in a 7.3:1 w/w 2,4-D: picloram mixture. Bioassay revealed that 11-16% of the picloram applied reached the soil and that, when the herbicide mixture was applied at a high enough concn to

kill the trees, sufficient picloram reached the soil around them to affect legume establishment. Chemical assay revealed that only about 2% or less of the picloram and 2,4-D remained in the poplar tissue and that >80% of this was in the leaves. These residues were unlikely to cause environmental problems because of the small quantities and the slow release from poplar tissue by leaching and decay. The remainder of the applied picloram and 2,4-D was unaccounted for and was assumed lost through metabolism and photochemical degradation.

Elder, J.H., C.A. Lembi, and D.J. Morre. 1970. Toxicity of 2,4-d and picloram to fresh and salt water algae. N. Cent. Weed Contr. Conf. Proc. 25: 96-98.

Flater, R.L., W. Yarish, and H. Vaartnou. 1974. Effects of picloram on germination and development of six crop species. Canadian Journal of Plant Science. 54: 219-221. In trials in controlled environment, picloram at 1 and 2 ppm significantly reduced germination of alsike clover and lucerne, but had no effect on that of wheat or creeping red fescue. Plant height was reduced in lucerne, alsike clover, wheat and potatoes, and etiolation occurred in potatoes. Picloram at 0.1 ppm caused bending of cotyledons, cupping of trifoliate leaves and elongation of petioles in lucerne and alsike clover, and development was delayed. Red fescue was the most tolerant species.

Gomez, C.A. and R. Riveros. 1975. Picloram residues in the soils of the Rio Sinu valley. Revista Comalfi. 2: 110-128. Spanish. Experiments were carried out in Colombia to study (1) the characteristic symptoms of picloram injury in 2 susceptible species, (2) a method for determining precisely the residues of picloram in soils and (3) the persistence of the compound in the climatic conditions of the Rio Sinu valley. Results showed that cucumber was a better test plant than soybean because not only is it sensitive to concns. in the soil as low as 5×10^{-3} $\mu\text{g}/100 \text{ g}$ of soil but it is not killed by concns. as high as 50 $\mu\text{g}/100\text{g}$. Plant height and leaf growth were found to be adequate parameters for determining picloram residues in these plants. Measurements should be made no later than 15 days after planting and supplemented by visual appraisal of toxicity symptoms. On clay soils in high rainfall conditions in the Rio Sinu valley no residues were detected 150 days after apply picloram at 3.2 kg/ha. From summary.

Grover, R. and G.G. Bowes. 1981. Picloram residue levels for the control of leafy spurge regrowth. Canadian Journal of Plant Science. 61: 661-664. The persistence of picloram in the soil was examined following a single application at 2.24 kg/ha or 4 annual applications at 0.56 kg/ha for the control of *Euphorbia esula*. The concn. of picloram in the upper 7.5 cm of soil decreased from 820 p.p.b. immediately after the application of 2.24 kg/ha to between 17 and 52 p.p.b. 3 years later. Picloram residues ranged from 45 to 165 p.p.b. during the 4 years of annual applications. The critical level of picloram in the soil to prevent *E. esula* re-establishment from seed was approx. 50 p.p.b.

Harrell, B.H. Jr. and T.J. Sheets. 1984. Persistence of low levels of picloram in some North Carolina soils and its effects on flue-cured tobacco. Proceedings, Southern Weed Science Society, 37th annual meeting. 1984, 120. In field studies

at 3 sites in 1980-82, 0.02-25 g picloram/ha was applied before transplanting tobacco. Yield reductions in the 1st year were significant but no reductions occurred in subsequent years, although at one site plant injury from the high rate was visible 3 years after application. Effects on quality showed a similar pattern. In a laboratory experiment, scintillation spectrometry showed that most of the picloram absorbed by tobacco plants grown in a picloram solution accumulated in the leaves and that concn. >50 p.p.b. in leaves of green tobacco would make leaves unmarketable.

Hickman, M.V., C.G. Messersmith, and R.G. Lym. 1989. Picloram Release From Leafy Spurge (*Euphorbia-esula*) Roots In The Field. Weed Sci. 37: 167-174.

Leafy spurge (*E. esula*) was controlled (frequently >85%) by all concn of picloram applied by pipe wick, although control tended to increase as solution concn increased. Picloram release from roots was greater from plants treated in the flowering and seed-filling stages than from plants in the vegetative stage. Picloram release from roots was generally correlated with application rate, averaging 490, 820, and 1420 p.p.b.w. in soil for the 30, 60 and 120 g/litre application rates, resp. Picloram release from roots occurred rapidly with 86% of the picloram detected in the 0- to 13-cm soil depth present by 1 week after treatment. Picloram was detected at all soil depths (0-39 cm) sampled, but >84% was in the upper 13 cm and 8% was in both the 13- to 26- and 26- to 39-cm depths. Leafy spurge shoots emerged through a 7.5- and 15-cm depth of picloram-treated soil at concn up to 1000 p.p.b.w. within 14-21 days after the untreated control. Picloram soil residue had little effect on leafy spurge root growth.

Ismail, B.S. and K. Kalithasan. 1997. Effects of repeated application on persistence and downward movement of four herbicides in soil. Australian Journal of Soil Research. 35: 503-513.

The downward movement and persistence of picloram, terbuthylazine, alachlor, and pendimethalin were studied under field conditions in loamy soil in Malaysia. Picloram and alachlor were applied separately at 0.5 and 2.0 kg a.i./ha, respectively, while terbuthylazine and pendimethalin were each applied at 1.0 kg a.i./ha. Each herbicide was subjected to 2 experimental conditions: (i) the required amount of herbicide applied 2 times, and (ii) the required amount applied 6 times. The presence of these herbicides in soil was assessed by bioassay techniques. Rice seed (*Oryza sativa*) and long bean (*Vigna sinensis* [*V. unguiculata*; cowpeas]) were used to assay pendimethalin and picloram, respectively, while cucumber (*Cucumis sativus*) was used for both alachlor and terbuthylazine. The results showed that both alachlor and picloram moved downward faster than terbuthylazine and pendimethalin. Both alachlor and picloram, but not terbuthylazine or pendimethalin, could be detected in 5-10 cm layer at 1 day after application (DAA). The phytotoxic residues of picloram, pendimethalin, terbuthylazine, and alachlor were detected in the 0-5 cm layer until 84, 56, 49, and 35 DAA (2 applications), respectively. However, after 6 applications, the phytotoxic residue of these herbicides in the top layer was reduced. The results show that pendimethalin was less mobile than the other herbicides. The half-lives of picloram, pendimethalin, terbuthylazine, and alachlor

were 9.7, 6.4, 6.0, and 4.4 days, respectively, after 2 applications, but after 6 applications, the half-lives of these herbicides were shorter.

Jotcham, J.R., D.W. Smith, and G.R. Stephenson. 1989. Comparative persistence and mobility of pyridine and phenoxy herbicides in soil. Weed Technology 3: 155-161. Bioassays with soyabeans and lentils were used to compare the persistence of 2,4,5-T, triclopyr and picloram in soil after applying 0.038, 0.38 and 3.8 kg/ha under field conditions. Soil samples were collected 1-269 days after spraying and were kept frozen until growth room bioassays were conducted. Triclopyr was slightly less persistent than 2,4,5-T, but neither herbicide was biologically active during the next season. At least 90% of picloram disappeared within 7 months, but its biological activity was more persistent than that of either triclopyr or 2,4,5-T. Nine months after treatment, neither lentils nor soyabeans could be grown in soil treated with picloram at 3.8 kg/ha. Triclopyr and 2,4-D had similar soil TLC mobilities in 4 different soils. Picloram was significantly more mobile than either triclopyr or 2,4,5-T, primarily due to its lower adsorption in the soils examined.

Kirkland, K.J. and C.H. Keys. 1979. The long-term effect of picloram and its residue on grain production and weed control. Weed Science. 27: 493-497. The persistence of picloram applied annually at rates ranging from 0.02 to 0.07 kg/ha was measured each spring over an 8-year period. Picloram residue levels were in proportion to the rate of application. Picloram levels 12 and 24 months after application averaged 45% and 10%, respectively, of the level measured immediately after application. The control of *Polygonum convolvulus* was good, with populations declining significantly over the test period. Wheat growth and yields were not affected by picloram at rates of 0.035 kg/ha or less.

Luken, J.O., S.W. Beiting, S.K. Kareth, R.L. Kumler, J.H. Liu, and C.A. Seither. 1994. Target and nontarget discrimination of herbicides applied to vegetation in a power-line corridor. Environmental Management. 18: 251-255. In field trials conducted in Clermont County, Ohio, during 1990-91, 2 cutting regimens (cut/spray and cut/delay spray) and 4 radiarc-applied herbicides (11.7 litres/ha Garlon (triclopyr) + 18.71 litres Tordon (picloram), 18.71 litres Accord (glyphosate), 18.71 litres Accord + 0.141 litres Escort (metsulfuron), and 28.11 litres Krenite (fosamine)) were tested in a power-line corridor to determine which management combination best eliminated target species (trees) and preserved non-target species (low shrubs, vines, perennial herbs and grasses). When spraying was delayed after cutting, the herbicide with the least impact on non-target species (Krenite) was also least efficient at killing target trees. Spraying soon after cutting improved the tree-killing efficiency of several herbicides, but it also increased the negative impact on non-target species. The herbicide with the most consistent tree-killing ability (Accord + Escort) had the most impact on non-target species. It was concluded that, because none of the herbicide/cutting treatments performed ideally, resource managers must decide the acceptable impact on non-target species when considering herbicide use.

- Marley, J.M.T. 1980. Persistence and leaching of picloram applied to a clay soil on the Darling Downs. Queensland Journal of Agricultural and Animal Science. 37: 15-25.** Picloram (4-amino-3,5,6-trichloropicolinic acid) was applied at six rates (0, 23.3, 70, 210, 630 and 1890 g ha⁻¹) to a montmorillonitic clay soil. Rate of degradation of the herbicide and its vertical movement in the soil profile were determined by bioassays of field samples taken at four times (3.7, 7.4, 16.8 and 28.4 months) after application. Wheat, lucerne and soybeans were sown at various times following application to determine the effect of phytotoxic residues on the growth of these crops. At all four sampling times the zone of highest concentration of picloram was in the surface 15 cm of soil. Picloram was not detected below 30 cm. At selective weed control rates of 23.3 g ha⁻¹ and 70 g ha⁻¹ less than 10% of the applied picloram was present in the soil 7.4 months after application. At the latter rates, the growth of neither wheat nor lucerne was affected when planted 7.4 months after application.
- Meredith, P. 1996. Effects of picloram (Tordon (R)), clopyralid, triclopyr and chlorpyrifos on growth vigor, leaf form, pigmentation, yield specific gravity, tuber shape, and light sensitivity of potatoes. American Potato Journal. 73: 373.**
- Miller, K.V. and Chapman B.R. 1995. Responses of vegetation, birds and small mammals to chemical and mechanical site preparation, In, FRI Bulletin, No 192; Popular Summaries from Second International Conference on Forest Vegetation Management. R.E. Gaskin and J.A. Zabkiewicz (eds). New Zealand Forest Research Institute, Rotorua, New Zealand. p 146-148 1995**
- Nolte, K.R. and T.E. Fulbright. 1997. Plant, small mammal, and avian diversity following control of honey mesquite. Journal of Range Management 50: 205-212.** A field trial was conducted in the Welder Wildlife Foundation Refuge, Texas, on a mesquite-mixed grass community dominated by *Prosopis glandulosa* (honey mesquite), interspersed with chaparral (e.g. *Acacia smallii*, *Celtis pallida* and *Zanthoxylum fagara*) and grasses (*Stipa leucotricha*, *Panicum obtusum* and *Setaria leucopila*), to investigate the effects of herbicide application to *P. glandulosa* on community plant and vertebrate species richness and diversity. A 1:1 mixture of triclopyr + picloram was applied to three 13 ha plots during 1992 and to 3 additional plots in 1993. Mesquite and forb canopy cover in the zone 1 m from the soil surface were lower within treated plots than in control plots in both years. Grass canopy cover did not differ between herbicide-treated plots and control plots. Vegetation species richness and evenness, Shannon's index, beta diversity and the proportion of rare plant species did not differ between controls and sites treated during 1992 and 1993. Rodent and avian relative frequency, richness and diversity were not significantly different in 1992 on herbicide treatment plots and untreated controls. It is suggested that the application of triclopyr + picloram in mesquite-mixed grass communities in the Texas Coastal Bend does not significantly reduce plant and vertebrate species richness and diversity within the first 2 years after treatment.

- Norris, L.A. 1981. The behavior of herbicides in the forest environment and risk assessment. In Weed control in forest management. Proceedings of the 1981 John S. Wright Forestry Conference. H.A. Holt and B.C. Fischer Eds.. 192-215.** US regulations for hazard assessment and the behaviour (movement, persistence and fate) of herbicides in the forest environment are discussed. The specific behaviour of 2,4-D, picloram, atrazine, MSMA, fosamine, glyphosate and hexazinone is reviewed.
- Ogg, A..G Jr. and F.L. Young. 1991. Effects of preplant treatment interval and tillages on herbicide toxicity to winter wheat (*Triticum aestivum*). Weed Technology. 5: 291-296.** Glyphosate + 2,4-D at 0.3 + 0.5 or 0.4 + 0.7 kg/ha applied 31 to 1 d before sowing did not affect wheat yields or grain test wt in field experiments in conventionally tilled and no-till winter wheat. In the conventionally-tilled system in each of 2 years and in the no-till system in a year with 48 mm rain within 7 d before wheat was sown, picloram at 0.14 kg/ha from 31 to 1 d before sowing reduced crop yields by 7-8%. In the conventionally-tilled system in a year with only 2 mm rain within 7 d before wheat was sown, 2,4-D at 3.4 kg/ha and dicamba at 0.14 kg/ha applied 30 to 1 d before sowing reduced wheat yields by 7 and 4%, resp. Grain test wt in both tillage systems were increased slightly by picloram at 0.14 kg/ha, but were decreased slightly by dicamba at 0.14 kg in the year with little rain before sowing. Test weights did not differ among herbicides or tillage systems in the year with significant rain a few days before sowing.
- Perala, D.A. 1971. Controlling Hazel, Aspen suckers, and Mountain Maple with picloram. US Forest Service Research Note, North Central Forest Experiment Station. No. NS-129, 4 pp.** Applications of Tordon 101 (2,4-D + picloram) were made in Minnesota by either (a) mist blowing of 2.5-7.5 lb (a.e.)/acre for control of *Corylus cornuta* on planting sites, or (b) simulated aerial spraying of 0.25-2 lb/acre to release a 2-year-old *Pinus resinosa* plantation from *C. cornuta*, *Populus tremuloides* suckers, and *Acer spicatum*. In both trials, brush control was as good as or better than obtained with 4 lb/acre 2,4-D + 2,4,5-T. With (a), *Pinus resinosa* planted 9 months after treatment was not significantly affected by picloram residues, but suffered from competition by invading grass and sedge. With (b), Tordon dosages of 1-2 lb/acre caused significant Pine mortality; lower dosages were relatively ineffective against *P. tremuloides*.
- Peterson, H.G., C Boutin, P.A. Martin, K.E. Freemark, N.J. Ruecker, and M.J. Moody. 1994. Aquatic phyto-toxicity of 23 pesticides applied at expected environmental concentrations. Aquatic Toxicol. 28: 275-292.** Environment Canada uses an Expected Environmental Concentration (EEC) in evaluating the hazard of pesticides to nontarget aquatic organisms. This concentration is calculated by assuming an overspray of a 15 cm deep waterbody at the label application rate. The EEC of pesticides is then related to the EC50 (concentration causing a 50% reduction in a chosen toxicity endpoint) for a given aquatic test organism. At present, the use of an uncertainty factor is suggested in the literature if only a few species are tested because of important interspecific differences in

pesticide sensitivity. The phytotoxicity of the EEC of 23 different pesticides to ten algae (24 h inhibition of ^{14}C uptake) and one vascular plant (7-day growth inhibition) was determined in an effort to examine the question of interspecific sensitivity and its relation to the development of pesticide registration guidelines. Chemicals included five triazine herbicides (atrazine, cyanazine, hexazinone, metribuzin, and simazine), four sulfonyleurea herbicides (chlorsulfuron, metsulfuron-methyl, ethametsulfuron-methyl, triasulfuron), two phenoxyalkane herbicides (2,4-D and MCPA), two pyridine herbicides (picloram and triclopyr), a substituted urea, an amine derivative, and an imidazolinone herbicide (tebuthiuron, glyphosate and imazethapyr, respectively), a bipyridylum (diquat), a hydroxybenzonitrile (bromoxynil), an aldehyde (acrolein) and an acetanilide (metolachlor) herbicide, as well as two carbamate insecticides (carbofuran and carbaryl) and a triazole derivative fungicide (propiconazole). Test organisms were selected based on ecological relevance and present use in test protocols. Organisms included green algae (*Scenedesmus quadricauda* and *Selenastrum capricornutum*), diatoms (*Nitzschia* sp. and *Cyclotella meneghiniana*), cyanobacteria (*Microcystis aeruginosa*, *Oscillatoria* sp., *Pseudoanabaena* sp., *Anabaena inaequalis* and *Aphanizomenon flos-aquae*) and a floating vascular plant, duckweed (*Lemna minor*). The five triazine herbicides, acrolein and diquat inhibited the carbon uptake of all algae, diatoms and cyanobacteria by more than 50%. Two other pesticides, carbaryl and tebuthiuron, caused more than 50% inhibition in 90% of the algae tested. Nine of the 23 pesticides, five of which were triazine herbicides, were therefore highly phytotoxic to algae. Twelve pesticides inhibited growth of duckweed by more than 50%. Once again, all five of the triazine herbicides were among this group, as well as three sulfonyleurea herbicides and acrolein, diquat, metolachlor and tebuthiuron. Duckweed was the most sensitive organism tested, being equally affected by all pesticides causing algal phytotoxicity (with the exception of carbaryl), as well as being acutely affected by sulfonyleurea herbicides. Green algae were least sensitive to diquat; diatoms and one cyanobacterium were the only organisms that showed sensitivity to glyphosate. Through testing the phytotoxicity of a variety of agricultural pesticides to a wide range of algal taxa, it is evident that there are considerable differences in sensitivity among species and that the use of an uncertainty factor is necessary to provide an acceptable margin of safety in evaluating the hazard presented by these chemicals to the aquatic environment.

Pettit, R.D. 1979. Effects of picloram and tebuthiuron pellets on sand shinnery oak communities. 1979. Journal of Range Management., 32: 196-200. [See FA 40, 2318]. In May 1971, picloram was applied at the recommended dosage of 7 kg/ha a.i. to sandy rangeland in W. Texas dominated by sand shinnery oak (*Quercus havardii*). In 1973, 1975 and 1976 herbage yields on the treated plots were n.s.d. from untreated plots, but the species composition was dramatically changed with better forage plants increasing and most oak being killed. In further tests picloram or tebuthiuron were applied at 1,3,5 and 7 kg/ha in June 1974, and tebuthiuron at 1 kg/ha in Jan. 1975. Tebuthiuron applied in winter or late spring killed most of the

oak at 1 kg/ha, but at higher dosages some of the better forage plants were killed. Picloram killed all the oak at 3,5 or 7 kg/ha, but only partially controlled it at 1 kg/ha. Picloram did not disturb the rest of the plant community as much as tebuthiuron. The herbicides are not recommended for use on poor rangeland, or where there is a shortage of perennial grasses in the ground cover.

Ragab, M.T.H. 1974. Picloram [herbicides] persistence in sandy loam soils and effect of its residue on crops. Minutes, Can. Weed Comm. East Sect., 28th: 37-38.

Ragab, M.T.H. 1975. Residues of picloram in soil and their effects on crops. Can. J. Soil Sci. 55: 55-9.

Rice, P.M., D.J. Bedunah, and C.E. Carlson. 1992. Plant community diversity after herbicide control of spotted knapweed. Research Paper- Intermountain Research Station USDA Forest Service. INT-460, 6 pp. Herbicides were applied in 1985 to replicated treatment plots at 4 rangeland sites in W.-central Montana with light to moderate spotted knapweed (*Centaurea maculosa*) infestations. Plant community diversity was determined for 2 seasons before the herbicide treatments and for 2 years after spraying. Although knapweed suppression was high, the communities were not converted to grass monocultures. Herbicide-caused depressions in community diversity measurements were small and transitory. Plots treated with Tordon (picloram at 0.25 lb/acre) and Curtail (clopyralid + 2,4-D at 0.19 + 1.0 lb) showed a small 1-year post-spray decline. Diversity in those plots began to increase relative to the untreated plots during the 2nd post-spray growing season. Stinger (clopyralid at 0.25 lb) had the least effect on diversity. No large declines in diversity were caused by these herbicide treatments, and the small depressions observed were probably transitory. Community response data collected from a limited set of pilot study plots suggested that the herbicide treatments increased diversity by 3 years post-spray. Only small amounts of herbicide were leached below 25 cm. Herbicide residues in the soil at 25- to 50-cm depth were generally undetectable and did not exceed 26 ppb at 30 d and trace levels after 1 year. No herbicide residues were detected after 2 years.

Rice, P.M., J.C. Toney, D.J. Bedunah, and C.E. Carlson. 1997. Plant community diversity and growth form responses to herbicide applications for control of *Centaurea maculosa*. Journal of Applied Ecology. 34: 1397-1412. A field experiment conducted from 1988-95 in western Montana, USA, compared the effects of herbicide treatments (picloram, clopyralid and clopyralid + 2,4-D, each at two timings and the recommended rates for control of the exotic forb *Centaurea maculosa*), on the structure and species diversity of native plant communities. The floristic composition of replicated treatment plots was sampled before spraying and for 3 years after the initial herbicide applications at two grassland and two early seral forest sites. Following the third year post-spray measurements, half the treatment plots were randomly selected to be resprayed and community sampling was continued for two more years. Diversity was quantified as species richness and Shannon diversity index. Standing crops by growth form were estimated by double sampling at the conclusion of the experiment. Herbicide treatments had a high

efficacy on the target weed, shifting the plant communities back to a grass-dominated structure. Depressions in plant community diversity were small and transitory. In the third year after the initial applications, there were no significant differences among treatments, and some herbicide-treated plots had begun to surpass the untreated plots in community diversity measures. With most treatments, respraying 3-4 years after the initial applications did not reduce plant diversity compared to untreated levels. Late season applications, made after most herbicide-susceptible forbs had entered summer drought-induced dormancy, minimized impacts on plant community diversity. The behaviour of herbicide residues in the soil is described in relation to community-level effects. Implications of the results for exotic weed management in conservation settings are discussed.

Schroder, G.L. 1982. Herbicides in sugarbeets: spray drift; residues in soil; and chlorophyll fluorescence. Dissertation Abstracts International, B. 42: 10, 3908; 99 pp. In an evaluation of the effects of herbicide drift in sugar-beet, 2,4-D at 0.035-0.28 kg/ha tended to increase yields but reduced % sucrose at late stages. Dicamba at 0.018 kg/ha and picloram at 0.028 kg applied to 12-1f sugar-beet reduced percent sucrose but not the yield. All three herbicides increased storage losses. In a field evaluation, ethofumesate residues, 1 year after applying 1.12 kg/ha overall and 2.24 kg/ha as a banded treatment, reduced the wheat yield in 1977 on a silty clay soil. The yield was not reduced in 1978 on a loam soil, but residues from 4.48 and 8.96 kg/ha overall reduced the yield in 1979 on a clay soil. Crop tolerances of 4 crops to 4 p.p.m.w. in the glasshouse were sunflower > soybean > barley > wheat. In a study of the effects of herbicides on chlorophyll fluorescence, 10-5M diuron and 10-3M desmedipham inhibited uncoupled electron transport in isolated sugar-beet and redroot pigweed [*Amaranthus retroflexus*] chloroplasts. Max. electron transport inhibition was evident 4h after spraying sugar-beet with 1.1 kg diuron/ha. Max. [growth] inhibition occurred 8 and 24 h after spraying with 1.1 kg phenmedipham and desmedipham/ha, respectively. Max. fluorescence occurred within 6 and 8 h after spraying sugar-beet with diuron and phenmedipham, respectively.

Shannon, P.W. and J.M. Leslie. 1982. Chemical control of blackberry in Northland. Proceedings of the thirty-fifth New Zealand weed and pest control conference. M.J. Hartley (Ed.). 166-. The use of 2,4,5-T, 2,4,5-T + picloram, glyphosate, fosamine and triclopyr for blackberry control was investigated. 2,4,5-T, 2,4,5-T + picloram or triclopyr gave near-complete cane knockdown 5-7 months after application in spring or autumn. Glyphosate or triclopyr gave the most regrowth suppression 1 yr after autumn application while 2,4,5-T + picloram gave the most regrowth suppression after spring application. None of the treatments completely killed the blackberry. Picloram residues in soil samples used for bioassay inhibited white clover seedling germination for up to 9 months following spraying. Soil residues of triclopyr caused little inhibition of white clover seedling germination after 3 months.

Shipman, R.D. and T.J. Prunty. 1988. Effects of herbicide residues on germination and early survival of red oak acorns. Proceedings, 42nd annual meeting of the

Northeastern Weed Science Society. 86-91. The response of greenhouse-grown *Quercus rubra* to several herbicides at 1, 2 and 4 times the manufacturer's recommended rate was studied under greenhouse conditions. Dicamba, 2,4-D, picloram, sulfometuron-methyl and triclopyr \pm picloram significantly reduced the percentage of germinating acorns. Picloram, sulfometuron-methyl and triclopyr significantly reduced seedling height. Glyphosate \pm non-ionic wetter, hexazinone and simazine had little or no effect on percentage germination or seedling height. However, hexazinone inhibited photosynthesis and eventually killed the seedlings. Soil type significantly affected herbicide availability and subsequent phytotoxicity.

Thalheim, G. and M. Ahnert. 1982. Phytotoxic side effects on potatoes from the use of Tordon 22K (active ingredient picloram) in the Karl-Marx-Stadt district. [Phytotoxische Nebenwirkungen an Kartoffeln beim Einsatz von Tordon 22K (Wirkstoff Picloram) im Bezirk Karl-Marx-Stadt]. Nachrichtenblatt für den Pflanzenschutz in der DDR. 36: 1-5. German. Instances of potato haulm deformity have occurred in the Karl-Marx-Stadt region of the German Democratic Republic since 1978. The symptoms include leaf epinasty, leaf roll, inhibition of the stem and rudimentary leaves and general growth depression, while in some cases early damage can be so severe that the shoots fail to emerge. The damage is attributed to Tordon 22K (picloram-potassium) contamination of slurry and FYM used to fertilize the fields and produced from cattle which had consumed fodder grown on sites treated with the herbicide. Tordon 22K residues may also accumulate in the daughter tubers in amounts sufficient for symptoms to be displayed by the next generation. The use of Tordon 22K, particularly in connection with the control of *Rumex* sp. in grassland, is discussed and advice is given on how contamination of fodder can be avoided.

Tubea, B., K. Hawxby, and R. Mehta. 1981. The effects of nutrient, pH and herbicide levels on algal growth. Hydrobiologia. 79: 221-228. In trials using stock cultures of *Chlorella pyrenoidosa* and *Lyngbya bergei*, there were no differences in the growth rate of the algae in relation to P or K level but high levels of Ca and Mg increased their growth rate. High levels of N and high pH mostly increased algal growth. Among the herbicides tested at 0.1 to 10 μ M, picloram had no effect on growth, while dinoseb inhibited *L. bergei* but not *C. pyrenoidosa*. In general, growth inhibition increased with increasing herbicide concn., particularly in the case of prometryne and fluometuron. Significant interactions among herbicides and nutrient levels were found for N and pH.

Vallee, J.C., C. Martin, and G. Vansuyt. 1975. Picloram persistence after weed control in crops. Compte Rendu de la 8e Conference du COLUMA. 71-78. French. Serious injury in some tobacco and vegetable (lettuce, pea, tomato etc.) crops in France has been caused by picloram residues both in the soil and in straw. Experiments were, therefore, conducted to investigate picloram persistence. Residues were found in straw from cereals treated with 0.16 to 0.32 kg/ha especially when the straw was decomposing. Every 100 g of straw treated with 0.16 kg/ha contained 5-20 μ g of picloram while 100 g of straw treated with 0.32 kg/ha contained 50-100 μ g. Residues in soil were lower but persistence was prolonged

in soils rich in o.m. Tobacco plants were used as bioassay material, being highly susceptible to picloram at concns. as low as 10-10. Results showed that the use of straw for compost and the ploughing-in of straw before sowing dicotyledonous crops involves considerable risk.

Wells, G.J. 1972. Residual effect of some herbicides on *Medicago* species in the Victorian Mallee. Australian Journal of Experimental Agriculture and Animal Husbandry. 12: 181-184. See also WA 21, 563. Data collected from 1967 to '69 on light soils in the Mallee show that the use of low rates of picloram for controlling skeleton weed (*Chondrilla juncea*) on fallow and in crops severely affected the establishment of pasture medics (*Medicago* spp.) whereas other herbicides studied (an atrazine + aminotriazole mixture, chlorfenac and 2,4-D) had little or no effect even at moderate application rates. Annual medics and lucerne were equally susceptible to picloram, but the variable climate of the Mallee influenced herbicide decomposition and prevented reliable prediction of persistence. Picloram residues had no effect on medic seed viability but were absorbed after seedling germination. Bioassays of picloram residues in a Kattyong sand indicated that the maximum concn. tolerated by germinating medic was 0.0016 ppm.

SOIL MICROBIOTA

- Cadahia, E. 1986. In vitro sensitivity of different strains of *Rhizobium* to herbicides derived from picolinic acid. [Sensibilidad 'in vitro' de cepas de rizobios a herbicidas derivados del ácido picolínico.]. Investigacion Agraria, Produccion y Proteccion Vegetales. 1: 121-130. Spanish/ English.** Sensitivity of *Rhizobium* spp. strains 840, Ve-6, 835 and 914 and *Bradyrhizobium* spp. strains 836 and 717 to picloram and clopyralid at pH 6.8 or 5.5 was studied in liquid and agar culture. Response to both herbicides was similar but there was considerable variation between strains in the level at which growth was inhibited. Minimal inhibitory concn for each strain at both pH are presented. The herbicides were more toxic at pH 5.5.
- Ebbersten, S. 1972. Picloram (4-amino-3,5,6-trichloropicolinic acid). Studies concerning persistence in soil and plants and biological methods for determining picloram residues. [Pikloram (4-amino-3,5,6-trikloropikolinsyra). Studier av persistens i jord och växter samt metodstudier rörande biologisk bestämning av pikloramrester]. Uppsala, Institutionen för Vaxtödling, Lantbrukshögskolan 175 pp. Swedish English** This publication is divided into 2 main sections: 1. A literature survey including sections on (a) the effects of picloram on higher plants, soil micro-organisms and higher animals (mammals, birds and fish), (b) the persistence of picloram in plant tissue, soil and water and (c) methods for determining picloram residues. 2. Results of investigations carried out in Sweden during 1966-70 to study persistence and movement in the soil, determination of residues and the effects on following crops of wheat and potatoes.
- Schuytema, G.S., A.V. Nebeker, and W.L. Griffis. 1994. Effects of dietary exposure to forest pesticides on the brown garden snail *Helix aspersa* Mueller. Archives of Environmental Contamination and Toxicology 26: 23-28.** Brown garden snails, *Helix aspersa*, were fed prepared diets with 12 pesticides used in forest spraying practices where endangered arboreal and terrestrial snails may be at risk. Acephate, atrazine, glyphosate, hexazinone, and picloram were not lethal at concentrations of 5,000 mg/kg in 14-day screening tests. The remaining seven pesticides, lethal to 13-100% of the tested snails at 5,000 mg/kg, were evaluated in 10-day definitive feeding sites. Azinphosmethyl (Guthion) and aminocarb were the most, with 10-day LC50s of 188 and 313 mg/kg, respectively. Paraquat, trichlorfon and fenitrothion had 10-day LC50s of 659, 664, and 7,058 mg/kg, respectively. Avoidance of pesticide-containing foods occurred, e.g., 10-day LC50s of gt 10,000 mg/kg for carbaryl and methyl parathion. Significant decreases ($p < 0.05$) in snail weight (total, shell-only, body-only) or shell diameter were accompanied by a significant decrease in the amount of food consumed/snail/day. Concentrations

of pesticide in tissues were measured in snails exposed to atrazine and azinphosmethyl; there was no bioaccumulation.

- Sims, G.K., J.D. Wolt, R.G. Lehmann, J.P.E. Anderson (ed.), D.J. Arnold (ed.), F. Lewis (ed.), and L. Torstensson. 1992. Bioavailability of sorbed pesticides and other xenobiotic molecules. Proceedings of the international symposium on environmental aspects of pesticide microbiology, 17-21 August 1992, Sigtuna, Sweden. 159-164.** The relevance of degradation processes and sorption mechanisms in soil to bioavailability, and the effects of sorption on the degradation of weakly and strongly sorbed compounds are discussed. The results of many studies indicated that sorbed phase materials were not directly available to microorganisms in soil. Sorption effects on biodegradation were observed with strongly sorbed compounds that interacted with soil by either partitioning (naphthalene) or ionic interactions (diquat). Even weakly sorbed materials (pyridine, flumetsulam [N-(2,6-difluorophenyl)-5- methyl [1,2,4]triazolo[1,5a]pyrimidine-2-sulfonamide] and picloram) persisted longer when sorbed. It was concluded that interactions between sorption and biodegradation should be considered in modelling pesticide fate, and that the half-life of a compound in soil may best be treated as a variable (dependent upon sorption and possibly other factors), rather than a constant.
- Spiridonov, Yu.Ya., A.N. Samokhvalov, V.O. Rudakov. 1981. Sensitivity of several soil microorganisms to picloram. Pochvovedenie 12: 62-8. Russian.**
- Tu, C.M. 1994. Effects of herbicides and fumigants on microbial activities in soil. Bulletin of Environmental Contamination and Toxicology. 53: 12-17.** A study was conducted to examine the effects of 6 herbicides (2,4-D, dicamba, glyphosate, paraquat, picloram and simazine) and 3 fumigants (DD (1,3-dichloropropene and 1,2-dichloropropene), dichloropropene (1,3-dichloropropene) and Vorlex (80% 1,3-dichloropropene and 20% methyl isothiocyanate)) on microbial activities in sandy loam soil. Soil samples (with no history of pesticide treatment) were collected from southwestern Ontario from a depth of up to 15 cm. Herbicides and fumigants at 10 and 100 µg/g, resp., were applied to the soil. The effects of pesticides on the denitrification of nitrate and nitrite were studied. The results showed that the pesticide effects had no consistent pattern with length of time of incubation. Dichloropropene was the only pesticide to affect microbial ammonification of organic N indigenous to soil. With the exception of paraquat and Vorlex, all pesticide treatments affected nitrification of ammonium from soil organic N during 2 weeks incubation. No inhibition was observed after 3 weeks incubation in all treatments. It is suggested that the nitrifying organisms (mainly *Nitrosomonas* spp. and *Nitrobacter* spp.) recover after 3 weeks and nitrification proceeds as normal. The process of microbial denitrification (active species are mainly *Pseudomonas* spp., *Achromobacter* spp., *Bacillus* spp. and *Micrococcus* spp.) was found to be influenced by soil aeration, moisture, organic matter, acidity and temp. It is concluded that the N₂O evolution from the soil anaerobic assay

system indicates that the pesticides used in this experiment are non-toxic to denitrifying microorganisms.

Wardle, D.A. 1989. The influence of environmental variables and herbicide application on the soil microbial biomass (microbial biomass, moisture level). University of Calgary, 243 p.p. Equations for predicting the total soil microbial biomass were evaluated from a statistical viewpoint, and, where necessary, re-determined after correcting for dependency and non-normality of the data used. The fumigation-incubation method of microbial biomass determination depends on values of the k_c -factor which is the fraction of microbial biomass carbon released within 10 days of fumigation. The three k_c - values currently in use, i.e. 0.41, 0.45, and 0.50, all have a high degree of associated variability, which is influenced by variability between microbial species and estimates of bacterial:fungal ratios in soil samples. Four methods have been directly or indirectly calibrated against the fumigation-incubation technique, i.e. substrate-induced respiration (S.I.R.), ATP analysis, ninhydrin-extractable nitrogen, and fumigation-extraction. However, when problems associated with dependency and non-normality are corrected for it is uncertain as to whether or not these methods provide a realistic estimate of soil microbial biomass carbon. Evaluation of methods used for predicting total microbial biomass carbon were performed on soil samples maintained at five different moisture levels for 4 incubation periods. These were amended with C^{14} -labelled microbial tissue, and fumigation k_c values determined. Values of k_c were significantly affected by soil moisture content, time of preincubation, and sampling strategy (blocking effects). Microbial biomass for these samples was predicted using fumigation-incubation ($k_c = 0.41$), fumigation-incubation (different k_c value for each sample and treatment), S.I.R. with and without remoistening, and oxygen uptake curves (with fumigation). Little agreement was found between any of the five approaches used, with r^2 values between pairs of methods always being below 0.50. The different approaches also often predicted different responses of the microbial biomass to the soil moisture gradient. The S.I.R. method agreed reasonably well with techniques used to measure only the active microbial biomass, and it is concluded that S.I.R. and related techniques (including selective inhibition) can be used for assessing the dynamics of the active biomass. In a field study examining the effects of temperature and moisture on S.I.R. and basal respiration determinations, soil moisture was the principal factor involved, especially in conditions of rapid soil moisture fluctuation. Soil temperature was important only when soil moisture content was relatively constant, or when variations of soil moisture were removed using partial correlation analysis. The response of S.I.R., basal respiration, and inhibition by selective inhibitors in soil to various herbicide applications were determined in laboratory studies and in field plots. In the laboratory study response of biotic variables occurred only at concentrations of 200 ppm glyphosate, 2,4-D, or picloram, which is probably two orders of magnitude higher than what probably occurs in field situations. In field

experiments, glyphosate and 2,4-D had little effect on the biotic variables tested compared with the natural dynamics of these variables.

Welp, G. and G.W. Brummer. 1999. Effects of organic pollutants on soil microbial activity: the influence of sorption, solubility, and speciation. *Ecotoxicology and Environmental Safety, Environmental Research*, 43: 83-90.

Investigations were conducted on 12 organic chemicals (2,4-D, 2,4,5-T, atrazine, picloram, 4-chlorbenzeamine, pentachlorophenol (PCP), hexachlorobenzene, DDT, trichloroethene, benzene, phenol, and linear alkylbenzenesulfonate) and up to 18 soil samples from A horizons of different soils in Germany. Seven of the 12 chemicals tested revealed distinct microbial toxicity in soils at doses up to 5 mmol/kg, PCP being the most toxic. Three chemicals were toxic only in some soils, and 21 chemicals were generally not toxic to soil microorganisms even at high doses.