Fifteenmile Creek
ECSI #2709

State of Oregon
Department of Environmental Quality — Memorandum

To: Bob Schwarz
ER

Date: 18 October 2000

From: Mike Poulsen
ECD

DRAFT

Subject: Derivation of Emergency Cleanup Levels for Oxyfluorfen in Fifteen-Mile Creek

I have reviewed the Beak International memorandum dated 6 October 2000 regarding target cleanup levels for oxyfluorfen in Fifteen-Mile Creek. The memorandum was prepared following our comments on their 28 September 2000 memorandum. DEQ still disagrees with Beak regarding acceptable values for important parameters. We will continue to evaluate the issues raised by Beak, and may modify some of the values later. We have requested additional details on the supporting fate and transport studies performed by Rohm and Haas. In the interim, I will present a calculation of acceptable oxyfluorfen concentrations in water and sediment for the purpose of making decisions on ending the emergency response actions. Later, we will provide a full response to Beak's 6 October 2000 memorandum.

The primary concerns for DEQ are protection of human health, protection of individuals of threatened or endangered species (such as steelhead trout), and protection of populations of other species. DEQ rules specify the more stringent protection requirements for humans and threatened or endangered species. Emergency cleanup levels will be developed for these two areas.

Threatened or Endangered Species

The threatened species at the site is the steelhead trout (*Oncorhynchus mykiss*). From information provided by the manufacturer, Rohm and Haas, the acute no-observed effect concentration (NOEC) for oxyfluorfen is 0.037 mg/L for *O. mykiss* (also called rainbow trout)[1]. A chronic NOEC should be used for determining the potential for harm. According to DEQ guidance [Attachment 3 to Level III guidance, reference 2], the factor to convert an acute NOEC to a chronic NOEC is 0.03. Therefore, the chronic NOEC for water is calculated as:

$$0.037 \text{ mg/L} \times 0.03 = 0.0011 \text{ mg/L} = 1.1\ \mu\text{g/L (ppb)}$$

To calculate a corresponding acceptable sediment level, DEQ is willing to use the results of a site-specific study that showed a partition/attenuation value of 10,600 for the ratio of sediment concentration to water concentration [3]. The calculated acceptable sediment concentration is therefore:

$$1.1 \text{ ppb} \times 10{,}600 = 12{,}000 \text{ ppb } (\mu\text{g/kg})$$

Human Health

For human health considerations, DEQ's main disagreements with Beak concern the values chosen for the bioconcentration factor (BCF), bioaccumulation factor (BAF), and the degradation half-life ($t_{1/2}$). We also still disagree about the values for the organic-carbon partition coefficient (Koc) and the fraction of organic carbon (foc) that may be present at the site. However, given DEQ's decision to use the site-specific partition/attenuation factor, values for these parameters do not need to be resolved now.

A revision subsequent to the Beak memorandum is the use of a more recent EPA Office of Pesticide Programs' cancer slope factor for oxyfluorfen [4]. Previously, DEQ used the slope factor of 0.128 $(mg/kg/day)^{-1}$ taken from the Federal Register [5]. EPA modified this value based on a policy change revising the interspecies scaling factor from 2/3 to 3/4. The current value is 0.0732 $(mg/kg/day)^{-1}$.

Beak presented the following equation for estimating health risk from exposure to carcinogens:

$$ARL = (CR \times SF \times C_{fish} \times ED / AT) / BW$$

Where (using values acceptable to DEQ):

ARL	=	acceptable risk level (1×10^{-6})
CR	=	consumption rate (0.127 kg/d)
SF	=	cancer slope factor (0.0732 risk per mg/kg/d)
C_{fish}	=	concentration of chemical in fish (mg/kg)
ED	=	exposure duration (30 yr)
AT	=	averaging time (70 yr)
BW	=	body weight (70 kg)

This equation is similar to, but does not exactly correspond to DEQ's guidance equation that uses an age-adjusted food ingestion factor. However, given the use of an upper-bound fish consumption rate for adults, it is acceptable to use this equation applied to adult exposure.

Ultimately, we want derive an acceptable chemical concentration in water. To accomplish this, the above equation must incorporate additional considerations. The concentration of chemical in fish tissue and water are related by the following equation:

$$C_{fish} = C_{water} \times BAF$$

$$BAF = BCF \times 1.3$$

Where

C_{water}	=	average concentration in water (mg/L)
BAF	=	bioaccumulation factor
BCF	=	bioconcentration factor (5000)

The conversion from BCF to BAF is discussed in the Beak memo. The calculated value of BAF acceptable to DEQ is 6500, based on an assumed BCF of 5,000.

Another consideration that can be included is the degradation of oxyfluorfen over the exposure duration. As presented in the Beak memorandum, the degradation rate constant is defined as:

$$\lambda = \ln 2 / t_{1/2}$$

The degradation should follow an exponential function:

$$C_t = C_0 e^{-\lambda t}$$

The average concentration over a 30-year period is the integral of C_t over 360 months, divided by 360 months:

$$C_{t(avg)} = \frac{C_0 \left\{ \int_0^{360} e^{\lambda t} dt \right\}}{360}$$

Beak calculated the integral using $t_{1/2}$ = 1 month, whereas DEQ would use $t_{1/2}$ = 20 months (600 days). Some of the support provided by Beak for the 1-month half-life is more appropriate to degradation in water, and not in sediment. Our decision to use the longer half-life is based in part on the following conclusions in Rohm and Haas' internal report regarding degradation:

> Laboratory soil metabolism studies with moist metabolically active soils under dark conditions showed little, if any, degradation of oxyfluorfen. These studies were conducted for 30 days under anaerobic conditions, and for one year under aerobic conditions. There were no significant metabolites detected in either the aerobic and anaerobic conditions. [6].

We do not accept the assertion by Beak that the studies using isotopically labeled rings of oxyfluorfen are measuring the removal of the isotope, and not the degradation of oxyfluorfen. We will therefore accept the Rohm and Haas conclusions regarding half-lives on the order of one to two years under dark, wet conditions. However, as stated above, we are pursuing additional details on these studies.

The value that DEQ would use for an average chemical concentration over time is therefore,

$$\int_0^{360} e^{-\lambda t} dt = \frac{1}{\lambda}\left[e^{-360\lambda} - e^{0x\lambda}\right] = \frac{1}{\lambda} = \frac{20}{0.693} = 29$$

$$C_{t(avg)} = C_0 (29/360) = C_0 (0.079)$$

The average water concentration can then be related to the initial water concentration using:

$$C_{water(avg)} = C_{water(initial)}(0.079)$$

Substituting the above equations into the first equation for acceptable risk gives:

$$ARL = (CR \times SF \times C_{water(initial)} \times 0.079 \times BAF \times ED/AT)/BW$$

Solving for $C_{water(initial)}$, we get:

$$C_{water(initial)} = \frac{ARLxATxBW}{CRxSFx0.079xBAFxED}$$

Using the parameter values presented above, the calculated initial acceptable concentration in water is:

$$C_{water(initial)} = 1 \times 10^{-6} \times 70\ yr \times 70\ kg / 0.127\ kg/day / 0.0732\ (mg/kg/day)^{-1} / 0.079 / 6500 / 30\ yr$$

Or,

$$C_{water(initial)} = 0.000034\ mg/L = 0.034\ \mu g/L.$$

As discussed above, the site-specific partition/attenuation factor will be used to convert this acceptable initial water concentration to an acceptable sediment concentration.

$$C_{sediment} = C_{water(initial)} \times 10{,}600 = 0.034\ ppb\ (\mu g/L) \times 10{,}600 = 360\ ppb\ (\mu g/kg)$$

In conclusion, the calculated acceptable concentration of oxyfluorfen is 0.034 μg/L for water, and 360 μg/kg for sediment, based on protection of human health. These values are lower (more conservative) concentrations than those calculated for protection of the threatened steelhead trout.

References

[1] Graves, W.C. and G.J. Smith. 1990. Goal Technical Herbicide: A 96 Hour Static Acute Toxicity Test with Rainbow Trout (*Oncorhynchus mykiss*). Rohm and Haas Report No. 90RC-0098.

[2] DEQ. 1999. Guidance for Ecological Risk Assessment. April 1998 (with Revisions to May 2000).

[3] Polaris Applied Sciences. Information provided by Greg Challenger (Polaris) to Bob Schwarz (DEQ) on 4 October 2000.

[4] EPA. September 24, 1998. Memorandum from Lori Brunsman to William Dykstra. Revised Oxyfluorfen (Goal) Quantitative Risk Assessment (Q_1^*) Based on CD-1 Male Mouse Dietary Study with 3/4's Interspecies Scaling Factor.

[5] Federal Register, Volume 60, Number 187, September 27, 1995.

[6] Qipan Zhang. The Environmental Fate of Oxyfluorfen. Rohm and Haas report. January 1997.

State of Oregon

Department of Environmental Quality — Memorandum

To: Bob Schwarz
ER

Date: 28 September 2000

From: Mike Poulsen
ECD

Subject: Comments on Target Cleanup Levels for Oxyfluorfen in Fifteen Mile Creek
Beak International Memorandum dated 18 September 2000

The following are my comments on the Beak International memorandum dated 18 September 2000 regarding target cleanup levels for oxyfluorfen in Fifteen Mile Creek. This provides follow-up to our conference call on 27 September 2000. The primary concerns for DEQ are protection of human health, protection of individuals of threatened or endangered species (such as steelhead trout), and protection of populations of other species.

With regard to human health, we acknowledge that EPA's integrated risk information system (IRIS) does not provide a determination of oxyfluorfen as a carcinogen. However, EPA's Office of Pesticide Programs (OPP) does consider oxyfluorfen a carcinogen (Class C), and provides a slope factor of 0.128 $(mg/kg/day)^{-1}$. This information has been presented in the Federal Register (see, for example, Volume 60, Number 187, September 27, 1995). Given this determination by EPA OPP, and because of our requirements for considering acceptable toxicity information (OAR 340-122-0084(1)(c)(A)(v)), DEQ considers oxyfluorfen a carcinogen. As such, carcinogenicity should be considered in addition to non-carcinogenic effects in developing an acceptable level of oxyfluorfen in fish tissue. For site cleanups, DEQ uses an acceptable lifetime excess cancer risk level of 10^{-6} for individual chemicals (OAR 340-122-115(2)(a)).

In developing risk calculations under the cleanup program, DEQ conducts the evaluation using reasonable maximum estimates of exposure factors. For this reason, I have comments on some of the parameter values used in developing acceptable sediment levels. The proposed Koc value of 12,600 is based on the average from equations using Kow to calculate Koc. I would prefer to use a measured Koc value. Vince Kramer of Rohm and Haas had previously provided me with an average Koc value of 8100 based on measurements. He just sent me the data (attached) showing four measurements of Koc. The range (2900 to 32,000) is greater than I expected. Because three of the four measurements are at or below the geometric mean of 8100, I am not sure that this value is reasonably conservative. Also, there appears to be a correspondence of Koc with soil type. Because Fifteen Mile Creek can be a high-energy stream, we would expect the sediment to have particle sizes more in the sand range than in the clay range. For this reason, I would suggest using the Koc value of 2900 for sand.

The bioconcentration factor (BCF) is calculated from an equation using Kow. Again I would prefer using a conservative measured value. I have attached the Rohm and Haas report showing a measured BCF of 5000 in fish. The BCF is used with a food chain multiplier to calculate a bioaccumulation factor (BAF). I think this approach is acceptable, although it appears that the multiplier from the referenced table should be 1.3 and not 1.2. Note that there is an equation presented in DEQ guidance for calculating BAF from Kow (logBAF = 0.99logKow - 0.22), but I think the resulting value of 17,000 is inappropriate because logKow is less than 5.

Site-specific data are presented, and used to calculate a Kd value. However, my understanding of this test is that the water measurement was of overlying water, not of pore water. Therefore, I do not think that the ratio of concentration in sediment to concentration in water should be considered a Kd value. The data do not support a modification of the assumed organic carbon fraction in sediment. I acknowledge that using sediment-water partitioning to calculate water concentrations resulting from the presence of oxyfluorfen in sediment is a conservative approach. The site-specific data may provide an indication of the conservatism.

The fish consumption rate used for exposure calculations was a value of 70 g/day, EPA's median value for subsistence fishers. A more appropriate value can be obtained from a study of Native American fish consumption rates on the Columbia River (*A Fish Consumption Survey of the Umatilla, Nez Perce, Yakama, and Warm Springs Tribes of the Columbia River Basin*, Columbia River Inter-Tribal Fish Commission, Portland, Oregon, Technical Report 94-3, 1994). The upper 90^{th} percentile for consumption is 127 g/day. This study is summarized by EPA in the Exposure Factors Handbook (1997), although they use values such as the 95^{th} percentile, rather than the 90^{th} percentile used in Oregon.

As we discussed in our telephone conversation with Beak International, it is appropriate to consider changes in chemical concentrations over time when calculating risks due to long-term exposure. A key parameter in this case is the half-life of the chemical in the environment. Most of the values reported for oxyfluorfen are relatively low, on the order of a few days or a few months. Vince Kramer had reported some higher half-lives, and has provided us with the supporting data (attached). The measurements were made on flooded soils, which may be representative of conditions in the creek or river. The half-lives varied from 300 days to 600 days. A reasonable maximum value would be 600 days.

The discussion of the elimination of oxyfluorfen from fish concludes that the chemical is rapidly eliminated from to fish exposed via sediment and water. This is a consideration when evaluating bioconcentration and bioaccumulation. However, the results of fish testing in the Columbia River show the presence of oxyfluorfen in the tissue of fish. Apparently, fish rapidly concentrate and/or accumulate quantities of the chemical and are caught before they have time to substantially eliminate oxyfluorfen.

With regard to ecological data, the report summarizes site test data, and concludes that the NOEC level for *Daphnia magna* is 5,500 μg/kg. However, because effects were seen in one of the samples at this level, I would consider the next lowest level (1,470 μg/kg) to be the NOEC.

An important ecological consideration that is difficult to quantify at this time is that, at low concentrations of oxyfluorfen in sediment or water, there may be sub-lethal effects, including avoidance by migrating endangered species.

State of Oregon

Department of Environmental Quality — Memorandum

To: Mike Renz
ER

Date: 24 August 2000

From: Mike Poulsen
ECD

Subject: Cleanup Goals
Goal™ 2XL Herbicide Spill, The Dalles, Oregon

This memorandum presents proposed cleanup goals for sediment and water at the Goal™ 2XL herbicide spill site at The Dalles, Oregon. The active ingredient of Goal™ 2XL is oxyfluorfen. We consider this chemical a persistent, bioaccumulative toxicant (PBT). For PBTs, we consider the only appropriate cleanup goal to be non-detect.

In my discussion with Vince Kramer, Senior Scientist, Environmental Toxicology and Risk Assessment, Rohm and Haas Company (the manufacturer), he stated that the following are the approximate detection limits for analysis of oxyfluorfen:

Soil (sediment)	50 µg/kg (ppb)
Water	0.1 µg/L (ppb)

<u>Environmental Toxicity Information for Oxyfluorfen</u>

The following information was provided in the MSDS for Goal™ 2XL (product code 50495, dated 8/16/99) or was available in the Extension Toxicology Network (EXTOXNET) Pesticide Information Profile.

AQUATIC		
Bluegill sunfish (*Lepomis macrochirus*)	96 hour LC50	0.2 mg/L
Rainbow trout (*Salmo gairdnei*)	96 hour LC50	0.41 mg/L
Channel catfish (*Ictalurus punctatus*)	96 hour LC50	0.4 mg/L
Grass shrimp	96 hour LC50	32 µg/L
Eastern oyster	96 hour LC50	69 µg/L
Fiddler crab (*Uca pugilator*)	96 hour LC50	>1000 mg/L
Freshwater clam	96 hour LC50	9.6 mg/L
OTHER		
Bobwhite quail	21 day dietary LD50	>2150 mg/kg
Bobwhite quail	8 day oral LC50	>5000 mg/kg
Mallard duck	8 day oral LC50	>5000 mg/kg
Honeybee	96 hour LC50	>10,000 ppm
Rat	oral LD50	5000 mg/kg
Dog	oral LD50	5000 mg/kg
Mice	oral LD50	2700 - 5000 mg/kg

Most of these data are based on technical grade material (70-75 percent active ingredient). The spilled formulation contained 21-24 percent active ingredient (a.i.).

Vince Kramer provided the following additional information:

Fathead minnow	early development NOEC	0.038 mg a.i./L
Rainbow trout	96 hour LC50	2.8 mg product/L
Rainbow trout	24 hour LC50	6.4 mg product/L
Daphnia magna	48 hour EC50	0.46 mg/L
Algae (*Selenastrum*)	96 hour EC50	1.2 µg/L
Midge (*Chironomus riparius*)	4 day NOEC	7 mg/kg in sediment
Earthworm	14 day EC50	970 mg a.i./kg

For sediment, Vince proposed taking the midge value of 7 mg/kg, and use a safety factor of 100 (10 to account for acute to chronic, and 10 for including sensitive members). This would result in a sediment concentration of 0.070 mg/kg, or 70 µg/kg. This is close to the detection limit, and considering the issue of PBTs and the presence of endangered species, we consider the detection limit to be an appropriate cleanup goal.

For water, Vince proposed using a safety factor of 10 for the flathead (because this is a chronic measure), and safety factors of 100 for the rainbow trout and daphnia. The resulting acceptable levels are all approximately 4 µg/L.

Another potential approach is to see the implication for a water concentration given a cleanup goal of 50 µg/kg in sediment. A simple partitioning approach can be used to relate sediment concentration to interstitial water concentration. The average k_{oc} value for oxyfluorfen is approximately 8,100. An assumed f_{oc} value for Fifteen Mile Creek is 0.005 (0.5 percent organic carbon). Using:

$$Kd = k_{oc} \times f_{oc} = Conc_{sediment} / Conc_{water}$$

$$Conc_{water} = Conc_{sediment} / (K_{oc} \times f_{oc}) = 50 \text{ ppb} / (8100 \times 0.005) = 1 \text{ ppb}$$

The concentration that could be measured in the creek is expected to be less than this value.

Information provided in the EXTOXNET profile for oxyfluorfen, and confirmed by Vince, show a bioconcentration factor of 1300 for bluegill sunfish, and a BCF range of 700 to 5000 for channel catfish. Bioaccumulation factors, which include ingestion in addition to direct contact with water considered in BCFs, would be expected to be greater than these values. Given the BCFs, we consider oxyfluorfen to be of concern with regard to bioaccumulation.

EXTOXNET also reported that oxyfluorfen is moderately persistent in most soil environments, with a representative field half-life of 30 to 40 days. Photolysis may occur, but it is unlikely that oxyfluorfen will undergo biodegradation or hydrolysis.

Because oxyfluorfen has the potential to bioaccumulate and may not readily degrade, a value of 1 µg/L in water may not be protective of fish. We propose the detection limit of 0.1 µg/L as the long-term cleanup goal for surface water.

Other Chemicals

The solvent naphtha in Goal™ 2XL, a mixture of primarily aliphatic hydrocarbons, is most likely a physical hazard to aquatic life. The other individual constituents of Goal™ 2XL that are of interest are naphthalene and N-methyl pyrrolidone.

Naphthalene has an Oregon screening benchmark value (SBV) of 0.62 mg/L for water. Using the partitioning equation presented above, this would result in an acceptable sediment concentration of 25 mg/kg. NOAA presents a threshold effect level for naphthalene for the amphipod *Hyalella azteca* in freshwater sediment of 14.65 ppb (µg/kg). This lower value would be considered our cleanup goal for sediment.

There is little aquatic toxicity information available for N-methyl pyrrolidone. It is not expected to bind substantially to sediment (estimated Koc of 12), it will likely biodegrade, and it has a low BCF (0.23). Because of this, and the fact that the other constituents of Goal™ 2XL are more toxic, it is unlikely that N-methyl pyrrolidone will be of ecological concern once the creek is remediated. Nevertheless, we propose to use the detection limit as a cleanup goal in sediment.

Proposed Cleanup Goals

In summary, the proposed cleanup goals for the primary chemical constituents of Goal™ 2XL are:

Chemical	Sediment (µg/kg)	Water (µg/L)
Oxyfluorfen	DL (50)	DL (0.1)
Naphthalene	15	620
N-Methyl pyrrolidone	DL	DL