DETERMINING NEED AND METHODS FOR CHEMICALLY INDUCED DEACTIVATION
SOP:7.1 (revised 9/15/2010)

PROCEDURE TITLE: Determining Need and Methods for Chemically Induced Deactivation

APPLICABILITY: Application of rotenone in waters of the United States

PURPOSE: 1. Mitigate for movement of rotenone and effects to non-target organisms beyond the Treatment Area (see SOP 6)
2. Provide guidance for determining if deactivation is necessary to protect non-target organisms beyond the Treatment Area and a protocol for successful deactivation

LOCATION ON LABEL: "Deactivation" under the heading "Directions for Use"

PROCEDURE:

I.   Need for Deactivation

Rotenone treated water is deactivated to minimize exposure to non-target organisms beyond (e.g. downstream) the Treatment Area, unless determined "unnecessary" by the Certified Applicator. Guidance on the necessity of deactivation is explained below through examples where deactivation is considered "necessary" and "unnecessary." The Project Area includes the Treatment Area and the deactivation zone, if used (see SOP 6).

A.   Necessity and Feasibility of Deactivation

If rotenone-treated discharge affects non-target species beyond the margins of the Treatment Area (see SOP 6.0 for definition), then it is necessary to deactivate the discharge unless:

1. If there is no discharge from the Treatment Area or the discharge goes dry in a distance shorter than 2 miles or 2 hours travel-time (maximum distance/time between drip stations recommended on label) from the lowest drip station or discharge, then it is unnecessary to deactivate the discharge. Examples include ponds or lakes with no discharge or a stream that goes dry (i.e., underground) a short distance (within 2 miles) from the Treatment Area.

2. If there are physical limitations that prohibit the operation of deactivation equipment, then it is unfeasible to deactivate the discharge. Examples include a stream where treated water flows into a canyon or chasm and access to the stream is difficult or safety is an issue. In such situations, the Certified Applicator through bioassay or analytical testing assures that the discharge is no longer toxic at 30 minutes travel time downstream of where the stream emerges at an accessible location and deactivation could be accomplished.

3. If dilution from untreated waters below the Treatment Area renders the discharge with undetectable concentrations of rotenone (defined as active rotenone < 2 ppb; see SOP 16) then it is unnecessary to deactivate the discharge. For example, a stream flowing at 3 ft^3/s and treated at 25 ppb active rotenone flows into a stream flowing at 40 ft^3/s and not treated with rotenone, yields a dilution fraction of 0.075 and an expected active rotenone concentration of 1.9 ppb (0.075 x 25 ppb = 1.875 ppb active rotenone), and it is not necessary to deactivate.

II.   Methods for Chemically-Induced Deactivation

Potassium permanganate ($KMnO_4$) is the only chemical allowed on the label for deactivating rotenone, applied in granular form or as a 2.5% solution (1 pound $KMnO_4$ to 5 gallons (25 g/L) water). A 2.5% solution assures that $KMnO_4$ remains in solution at most water temperatures. The solubility in distilled water is 1.8 pounds $KMnO_4$/5 gallons (43 g/L) water at 10°C and 2.7 pounds $KMnO_4$/5 gallons (65 g/L) water at 20°C.

Deactivation activity increases directly with increase in temperature, and applicators should take in account that chemical reactions slow by 50% for each 10°C reduction in temperature and increase by 2-fold for each 10°C increase (Q10 rule). This is important in determining the stream reach and deactivation lag times at very low temperatures. For example, twice the contact time will be required at a temperature of 5°C than at 15°C with the same level of $KMnO_4$.

$KMnO_4$ is toxic to fish (see SOP 14) at relatively low concentrations and is more toxic in alkaline water than soft water (Marking and Bills 1975). If $KMnO_4$ concentrations are in balance with rotenone concentrations, then toxic levels of $KMnO_4$ are reduced through the oxidation of organic components and rotenone.

A.   Application Rates

1. Deactivation of rotenone is a time-dependent reaction; the time the two chemicals are in contact dictates the effectiveness or degree of deactivation. Engstrom-Heg (1972) developed time-lapse curvilinear relationships for deactivating Noxfish® (5% rotenone) concentrations over a range of $KMnO_4$ concentrations in distilled water (Figure SOP 7.1). In distilled water, rotenone is deactivated with KMnO4 at approximately a 1:1 (ppm $KMnO_4$: ppm Noxfish) ratio, when the contact time ("cutoff" in the Figure SOP 7.1) is about 60 minutes. As the contact time is shortened, the ratio of $KMnO_4$: rotenone increases. For example, at 30 minutes contact time the ratio is 1.5–2.0:1.0. The 30-minute contact time is recommended for most stream treatments to assure deactivation. Contact periods shorter than 30 minutes are less efficient and problematic because greater amounts of $KMnO_4$ are required, resulting in higher levels of residual $KMnO_4$ that travel downstream from the Project Area. Contact periods greater than 30 minutes are problematic because it is difficult to maintain $KMnO_4$ residues in the water column without booster stations.

2. Another important consideration is that dissolved electrolytes, aquatic plants, dissolved and suspended organic matter, and streambed materials increase the amount of $KMnO_4$ required. These contribute to the background "oxygen demand" of water that typically ranges from 1–4 ppm for 30 minutes contact time. (e.g., water flowing over granitic bedrock surfaces may have an oxygen demand

of only 1 ppm, while in karst or limestone landscapes, streams with watercress and dissolved organics may have a demand of 4 ppm).

3. The ability to measure $KMnO_4$ in the stream is central to assuring that sufficient material has been applied and that rotenone is deactivated. More $KMnO_4$ than is necessary to deactivate rotenone is applied to yield a measurable $KMnO_4$ residual at the end of the 30-minute contact zone, and this way the Certified Applicator can be sure that all rotenone is gone at the end of the 30-minute contact time. For simplicity, it is recommended that a residual level of 1 ppm $KMnO_4$ be maintained at the end of the contact zone. This is a level not likely toxic to fish during short-term exposures, but can be measured by most commercial devices and is also easily visible to the unaided eye.

4. For example, the application rate of 4 ppm $KMnO_4$ is required for a 30-minute contact zone to deactivate 1 ppm Prenfish® in granitic soils (or equivalent 5% liquid formulation). The calculations are: 2 ppm $KMnO_4$ is needed to deactivate 1 ppm Prenfish® + 1 ppm $KMnO_4$ is needed for background oxygen demand in water + 1 ppm $KMnO_4$ residual is need at the 30-minute travel-time mark.

5. It is only through experience and knowledge of local conditions, soils and rock types that the Certified Applicator will be able to closely predict the oxidizing demand of a stream. In most circumstances, it will be necessary to use professional judgment in selecting an initial concentration.

B.   Application Methods

1. Deactivation is a dynamic operation that presents some difficulties in managing application rates and predicting rotenone concentrations. There is no practical field procedure to determine actual rotenone (i.e., real-time) concentrations at the deactivation station. Certified Applicators should consider using a fully functional, redundant (i.e., backup) deactivation station positioned downstream from the effective reach of the primary deactivation station. The sensitivity of the public, the relative value of the aquatic community downstream of the project, and other issues will determine the need for redundant systems.

2. Some Certified Applicators begin deactivation procedures at the onset of rotenone application to assure that no rotenone passes the deactivation station and to reduce permanganate demand of the streambed immediately downstream from the deactivation station. Other Certified Applicators determine the time (sometimes with dye) when rotenone is expected to arrive at the deactivation station and begin application of $KMnO_4$ at that time. It takes a minimum of 1–2 hours of $KMnO_4$ application for most substances in the streambed to become oxidized and thus, there is less $KMnO_4$ available to reduce rotenone within the first several hours of operation. The deactivation system is operated prior to treatment for several hours during calibration exercises to assist in oxidizing streambed materials.

3. Measurements of residual $KMnO_4$ are taken periodically to assure the residual level of 1 ppm is present at the end of the 30-minute contact zone. Deviations can be addressed by increasing or decreasing the rate of application of $KMnO_4$ to the stream. Measurements every half hour are usually necessary at the beginning of

the treatment, but are scaled back to every 1–2 hours once equilibrium is achieved. Normally, the $KMnO_4$ demand within the deactivation zone decreases over the duration of the treatment as monitored by the residual $KMnO_4$ at the end of the 30-minute contact zone. It is beneficial to have the deactivation station in constant contact (e.g., two-way radios) with the person(s) doing the permanganate monitoring so adjustments can be made instantly, if necessary. The amount of $KMnO_4$ required will decrease as rotenone residues dissipate over time.

4. The effectiveness of the deactivation is measured by the ability of caged fish to survive in water downstream from the 30-minute contact zone. A 1 ppm residual $KMnO_4$ is not toxic to trout at exposures of less than 96 hours. Mortality of fish at this location is likely attributable to rotenone or other factors such as confinement stress. Replace sentinel fish daily where practical because of confinement stress in flowing water.

5. Continue deactivation until the water directly upstream of the deactivation station can sustain fish in an unstressed state in a bioassay for a minimum of 4 hours. Use caution when using the target fish species in a bioassay at this location unless the end of the deactivation zone is below a fish barrier, especially if this is the last of a series of treatments. Fish that escape cages will not compromise the success of the treatment if it is below a fish barrier.

6. Generally, caged fish are placed above the point of $KMnO_4$ injection and at the end of the 30-minute contact zone. Placing caged fish at the 15-minute contact time point may help with interpreting the progress of deactivation within the deactivation zone. Fish at 30 minutes will survive and those at 15 minutes will show signs of stress but will take many hours to die. Another location for caged fish is below the reach of the redundant (or backup) deactivation stations to provide assurance that total deactivation was achieved. This site is useful for interpretation purposes when fish below the 30-minute contact zone start to die.

7. Continual maintenance of the deactivation stations is required throughout the treatment. On streams, at a minimum expect to run this operation for the duration of the treatment plus the travel time from the most upstream point of project downstream to the deactivation station. For outlets from standing bodies of water, deactivation should continue until water is no longer toxic and may be prolonged by low water temperatures. A supervisor can provide assistance to stations as needed for breaks, errands, and loading and monitoring live fish cages. Each worker maintains a log of activities, application rates, and observations to ensure that prescribed procedures are followed and for future reference.

C.   Application Equipment

1. Dispense $KMnO_4$ in liquid or solid form. Liquid solutions should consist of 1 pound solid $KMnO_4$ mixed into 5 gallons (25 g/L) water. Most liquid applications use a reservoir with a metering device to dispense at a constant measurable rate. However, varying conditions during treatment (changing discharge rates, rotenone concentration, and oxygen demand) may require a change in the dispensing rate of $KMnO_4$, and use of a metering device that can be manually adjusted. A 2.5% $KMnO_4$ solution is dispensed at a constant concentration using the equation:

LF = Y • 70 • Q   where, LF = flow of 2.5% $KMnO_4$ solution (ml/min), Y = desired $KMnO_4$ concentration in stream (ppm) and Q = stream discharge (ft^3/s) or
LF = Y • 2,472 • Q   where, LF = flow of 2.5% $KMnO_4$ solution (ml/min), Y = desired $KMnO_4$ concentration in stream (ppm) and Q = stream discharge (m^3/s). Application of solid $KMnO_4$ is typically done with a device that meters the material out of a reservoir (or hopper) directly into the water. Again, the metering device should be adjustable. $KMnO_4$ crystals can be added to the stream using a mechanical auger of other device using the equation:
SF = Y • 1.7 • Q   where, SF = flow of solid $KMnO_4$ crystals (g/min), Y = desired $KMnO_4$ concentration in stream (ppm) and Q = stream discharge (ft^3/s) or
SF = Y • 60.02 • Q   where, SF = flow of solid $KMnO_4$ crystals (g/min), Y = desired $KMnO_4$ concentration in stream (ppm) and Q = stream discharge (m^3/s).

2. The advantage of liquid formulation application is that the devices require no electricity to run, and are very mobile; thus, these applications are well suited to remote locations with no power or road access. The disadvantage for liquid application is that it requires a large reservoir or making large amounts of liquid for streams with large discharges or if deactivation is extended for many days. The advantage for solid formulation application is that a large reservoir is not needed and the metering device is typically extremely accurate. The disadvantage for solid formulation application is that the equipment is heavy, unwieldy and needs electricity and thus best suited to areas with road access and deactivation of high discharge streams.

D.   Measuring Potassium Permanganate

1. $KMnO_4$ can be measured directly in the field using several analytical techniques. The most accurate method is to make a standard spectrophotometric curve that plots absorbance (at 525 nm) for solutions of known $KMnO_4$ concentration. Samples taken in the field during treatment are measured for absorbance on a portable spectrophotometer, and concentrations can be estimated by reading off the standard curve. See Standard Method 4500-$KMnO_4$ B for details (American Public Health Association 1998).

2. A less accurate estimate of $KMnO_4$, but an easier approach, is the DPD (N, N-diethyl-p-phenylenediamine sulfate) method for measuring total chlorine. Through the introduction of a powder containing DPD, potassium iodine, and a buffer, the oxidizing potential of the solution is measured spectrophotometrically or using a color wheel. The oxidizing potential of permanganate is about 89% of total chlorine, so results from this method can be multiplied by 0.89 to get an approximate measure of $KMnO_4$ concentrations in water (see Hach Chemical Company Method 8167).

III.   Additional Information

American Public Health Association. 1998. Standard Methods for the Examination of Water and Wastewater, 20th edition. American Public Health Association, Washington, D.C.

Engstrom-Heg, R. 1972. Kinetics of rotenone-potassium permanganate reactions as applied to the protection of trout streams. New York Fish and Game Journal 19(1):47–58.

Marking, L.L., and T.D. Bills. 1975. Toxicity of potassium permanganate to fish and its effectiveness for detoxifying antimycin. Transactions of American Fisheries Society 104:579–583.
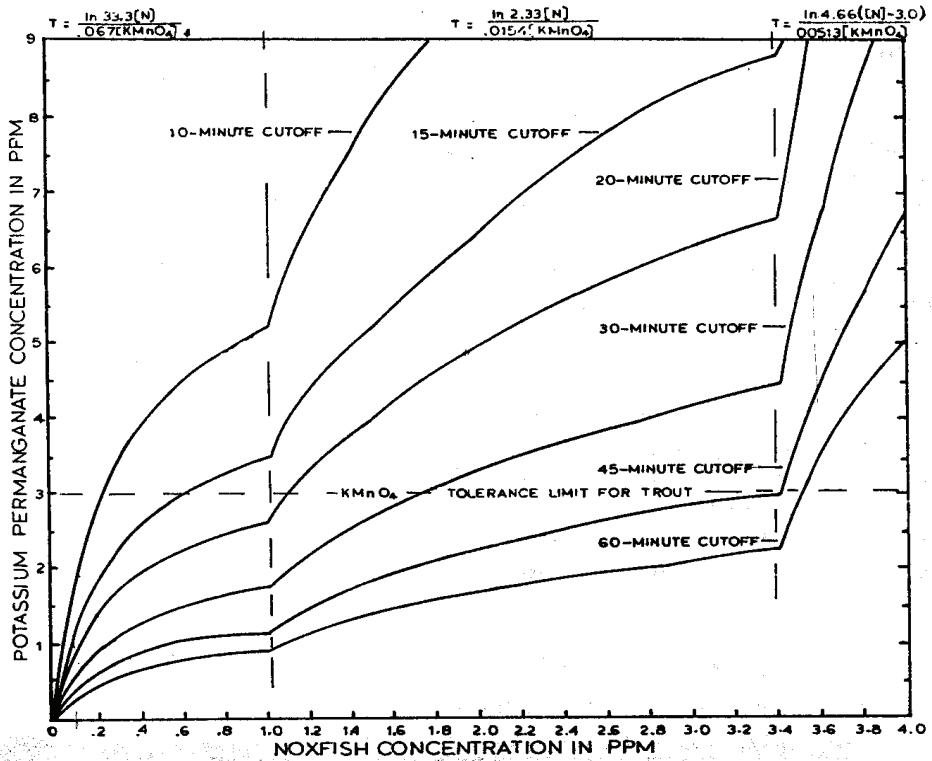
Figure 5. Relationship between Noxfish concentration, potassium permanganate
concentration and contact time required for detoxification.

FIGURE SOP 7.1. Time required (contact-time) for potassium permanganate to deactivate rotenone from Engstrom-Heg (1972).